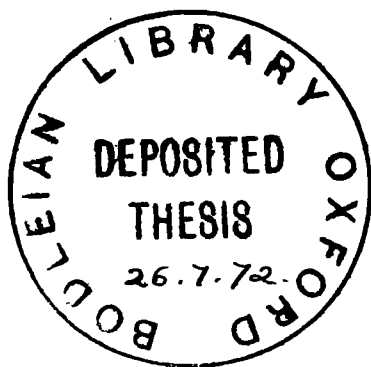


The Electron Microscopy of Alkali Halides



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Thesis submitted for the degree Doctor of Philosophy
in the University of Oxford

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In memory of my father.

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PREFACE

This thesis is an account of work carried out since October 1966 in the Department of Metallurgy, University of Oxford, at the instigation of Professor P. B. Hirsch, F.R.S., and under the supervision of Dr M. J. Goringe. It describes techniques for systematic assault on obstacles previously impeding the successful transmission electron microscopy of lattice defects in alkali halides, and their application to a fundamental study of irradiation damage aggregates in irradiated alkali halide crystals.

§1 provides a brief introduction to relevant physical, chemical and electrical properties of the alkali halides. A survey of radiation damage in alkali halide crystals follows in §2, in particular summarising and interpreting very recent work not previously reviewed, of crucial importance to implementation and subsequent interpretation of alkali halide microscopical investigations. §3 describes a series of techniques for preparation of suitable thin foil specimens from bulk crystals, and establishes minimum acceptable irradiation conditions under which electron microscopy of alkali halides can proceed. A fundamental consideration of the theory and practice of liquid helium electron microscopy appears in §4, together with its specific application to alkali halide microscopy. §5 details electron microscopical observation and analysis of irradiation defects in alkali halide crystals introduced under a wide range of irradiation conditions, and indicates probable models for their interpretation.

Portions of this study have appeared in abbreviated form in the following publications:

- §3 (Proc. 4th Eur. Cong. Elect. Microsc. (Rome 1970) 1, 265.
(J. Phys. E 3, 81 (1970).
- §4, §5 (Proc. Sept. Cong. Inst. Microsc. Elect. (Grenoble 1970),
(2, 239, 289.
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- §5 (International Conference on Colour Centres in Ionic
(Crystals (Reading 1971), G 139.
(A.E.R.E. Research Report R 6953 (1971).
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The author wishes to express his particular gratitude to those individuals who have made this study possible:

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support in the latter stages of this study. Finally, to my wife Dianne, without whose herculean efforts this study and accompanying thesis would never have been accomplished; her considerable patience, forbearance and unhesitating assistance were continually offered under conditions which would have proved intolerable to a less resilient marriage.

A large number of individuals contributed their expertise to portions of this study. Dr P. S. Turner adapted his electron scattering factor computer program to the Oxford 1906A for calculating the scattering parameters in alkali halides described in §3.6. Mrs Elizabeth Hewat contributed her modification of Dr C. J. Humphreys' many-beam diffraction program for the author's use. Dr Goringe computed Bethe loss and Rutherford scattering expressions for all twenty alkali halides, applied in §2.4. Dr D. T. Grubb conducted measurements of phosphor screen efficiency utilised in §3.7. Mr R. W. Ditchfield willingly conducted the energy loss experiments described in §5.3.3.3. Dr Pooley, Dr Hughes and Mr R. K. Dawson performed irradiations and spectroscopical measurements and supplied a majority of crystals examined.

Numerous useful ideas emerged from discussions with Dr G. S. Baker, Dr R. Bullough, Dr D. J. H. Cockayne, Dr R. C. Crawford, Mr S. M. Davidson, Dr B. L. Eyre, Dr G. W. Groves, Dr C. J. Humphreys, Dr A. Pogany, Dr M. Stoneham, Dr J. P. Stott, Dr J. M. Titchmarsh, Dr J. Vander Sande, Dr J. A. Venables, Dr V. Vitek and Dr M. J. Whelan.

Messrs R. H. Donaghay, A. Davis, G. Dixon-Brown and S. L. Strange assisted in maintenance of the vintage 18 year-old Siemens microscope employed for this study. Mr D. W. Tansley contributed his considerable expertise in design and construction of the eminently successful liquid helium stage described in §4.10; his advice on design and construction of apparatus described in §3.4 were similarly invaluable. Miss Susanne Lythell performed the unenviable task of typing the final manuscript, relieved at the point of exhaustion by Mrs Janet Caldwell.

The work described in this thesis is that of the author alone, except where an alternative source is cited and in the discussion of models in §5.7, which emerged jointly from discussions involving the author, Dr Pooley, Dr Hughes and Professor Hirsch.

A handwritten signature in black ink, appearing to read 'L. W. Hobbs', written in a cursive style.

L. W. Hobbs

Hilary Term, 1972.

ABSTRACT

An electron microscopical study has been made of lattice defects introduced into alkali halide single crystals by ionizing radiation and mechanical deformation. Detailed observations have not been possible previously because of severe irradiation damage introduced by the investigating electron beam and the difficulty of preparing suitable thin foil specimens, particularly from the more hygroscopic alkali halides. This thesis concerns itself with the detailed solution of these two chief problems, as well as of a number of other minor difficulties, and the subsequent identification and characterisation of defects and defect aggregates of sufficient size to be resolved in the electron microscope. In particular, the eventual fate of point defects produced by an ionization mechanism at temperatures between 5 K and 800 K is investigated, and two observable point defect sinks are studied and identified as point defect aggregates, one definitely interstitial, the other involving at least one vacancy species. The interaction of point defects and point defect aggregates induced by irradiation with mechanically introduced dislocations is also studied.

The importance of this work lies in the solution of at least one long-standing problem in the study of irradiation defects and colour centres in ionic crystals. It has long been known that

ionizing radiation induces efficient Frenkel defect production in alkali halides initially in the form of F and H centres. The F centres are easily detected because of their strong optical absorption in the visible region and because they are stable in isolated form up to ~ 400 K. The fate of the complementary halogen interstitial defects is far less clear, since the H centre is unstable above the 30-50 K bulk diffusion threshold and at temperatures as low as 5 K for large irradiation doses.

Considerable indirect evidence is reviewed which suggests the presence of large interstitial clusters whose size depends on the temperature of irradiation and irradiation dose. In particular the behaviour of the broad trapped-hole V absorption bands suggests some form of halogen molecule species. By implication, then, the eventual fate of the interstitial defects complementary to the F centre is probably in the form of halogen molecular aggregates which serve as efficient intrinsic sinks for interstitial defects produced during irradiation. However, the form of such a sink has remained a mystery, and its existence has not previously been conclusively established. An allied problem is the fate of irradiation damage products at temperatures above room temperature where the normally isolated halogen vacancy species becomes mobile. Controversial evidence is shown to suggest presence of both alkali metal colloids and microcavities involving large scale aggregation of vacancies in the anion sublattice. However, the form of interstitial halogen stabilisation in this temperature range has remained particularly obscure.

Direct transmission electron microscopy is an obvious technique by which to study suspected defect aggregates of dimensions appreciably in excess of those of simple point defects. However, in comparison with other radiation sources typically employed for alkali halide damage studies, the electron microscope also represents a radiation source of vastly greater intensity. The most probable energy loss modes are investigated for the case of an energetic (100 keV) electron beam in a thin foil (<1000 nm thick), and a typical energy deposition rate is calculated at $\sim 10^{23} - 10^{24}$ eV $\text{cm}^{-3} \text{sec}^{-1}$. This corresponds to an ionization damage rate $\sim 10^{19}$ F $\text{cm}^{-3} \text{sec}^{-1}$ for most commonly studied alkali halides, or what corresponds to a saturation defect dose each second. Clearly, only limited information about existing radiation damage products can be derived under such observation conditions, and ascriptions are by no means safe. In addition it is shown that dense, large-scale defect aggregation accompanies defect production in the electron microscope, and this is of sufficient scale and density to obscure previously existing lattice defect images; in most cases the continued rate of defect production is also of sufficient magnitude to destroy any previously existing defects.

A second difficulty in the transmission electron microscopy of these crystals is the preparation of suitable thin foil specimens. Sufficient transmitted intensity and resolution require that a thickness <500 nm is utilized, while observations indicate that foil regions thinner than 100 nm are unrepresentative of the bulk.

Preparation of such a foil first requires initial sectioning of a bulk crystal to dimensions ~ 1 mm. In the alkali halides cleavage is a convenient sectioning technique, but an analysis of cleavage mechanisms and observation of foils prepared from cleaved sections indicate that cleavage to such dimensions introduces unacceptable plastic bending deformation. Sectioning by this method is also limited to the principal $\{100\}$ cleavage planes. An alternative chemical sectioning technique is described, by which it is possible to section uniformly to <0.5 mm dimensions and to any orientation with little incidental deformation.

A technique for thickness reduction to foil dimensions is next required. Two existing techniques, viz. electron beam flashing and ion beam thinning are shown to introduce either unacceptable mechanical deformation or intolerable radiation damage. Chemical thinning is a suitable alternative, and a precision chemical jetting method is described for producing consistently good quality foil regions for sections of arbitrary orientation in a large number of alkali halides. A survey is made of common solvents suitable for use as polishing and washing reagents; for all but the most or least reactive of the alkali halides, these consist of an alcohol and an ether. An additional difficulty found with the alkali halides is susceptibility to atmospheric (or dissolved) moisture. The evaporation in atmosphere of polishing or washing solvents

sufficiently cools a foil to condense atmospheric moisture and impair foil quality through dissolution and etching. In more hygroscopic alkali halides, simple exposure of a dry thinned foil to atmosphere is sufficient to induce these effects. Therefore a technique is devised for performing all polishing operations and foil transfer to the electron microscope in dry inert atmosphere or vacuum to preclude atmospheric contact. With this procedure foils of even the more sensitive alkali halides can be preserved for observation.

One further difficulty remains. Alkali halide crystals are insulator materials, and, particularly at low temperatures, ionic conduction is insufficient to preclude a static charge accumulating at the surface of a thin foil exposed to energetic electron bombardment. Charge acquisition arises from secondary electron emission, leaving a net positive charge on the foil surfaces, whose necessarily non-symmetrical electric field inconveniently deflects the investigating electron beam. A theory is developed to estimate the magnitude of charge, field and beam deflection and to minimise these effects. It is found that at room temperature a close-mesh copper grid or evaporated carbon layer is sufficient to permit microscopy; below 200 K only an evaporated aluminium layer deposited on one surface is sufficient to alleviate charging effects. The way these measures, applied only to a single surface, minimise beam deflection is by confining the electric field to primarily within

the specimen; over the small distances represented by foil thickness, deflection of a 100 keV electron beam is unobservable.

In order to minimise radiation damage occurring during observation, the irradiation beam current density must be reduced to the absolute minimum level consistent with statistical image quality and adequate focussing. The latter limits are established in a consideration of photographic emulsion sensitivity, phosphor screen response, and electron statistics. Extinction and absorption parameters are calculated for the alkali halides studied, and many-beam rocking curves are computed to ascertain optimum operating conditions. In the absence of image intensification, a beam current density $\sim 1 \text{ mA cm}^{-2}$ represents the coincidental limit for both adequate resolution and focussing of meaningful detail. Image intensification cannot improve on image statistics in recording, and so it is useful only for improving focussing and area selection procedures.

In alkali halides easily damaged at room temperature (LiF, KCl, KI, etc.) the statistical electron limit for resolution on a scale of 5 nm necessarily implies production of many times a saturation density of defects. A very few alkali halides have defect production efficiencies sufficiently reduced at room temperature to enable brief examination at room temperature with an identifiable separation of internally- and externally-produced defects.

However, in these crystals it is the coincidental low mobility of point defects which in large part contributes to their usefulness at room temperature.

A drastic alternative approach to the irradiation damage problem is to dope with a large electron-trapping impurity concentration; this has the two-fold effect of depressing defect production via the electron-hole recombination mechanism and inhibiting defect mobility. The limited success of previous investigations in NaCl-CaCl₂ is shown to be attributable to these effects. However, both mechanical and (of course) irradiation behaviour are drastically altered from pure crystal behaviour. In pure alkali halides, which alone retain important intrinsic mechanical and coloration properties, the only way to reduce the production of point defects is to reduce the temperature of observation below all defect mobility thresholds; this threshold is < 30 K in most alkali halides.

It is shown that the effect of irradiation at such temperatures is not simply one of preventing defect aggregation and thus observable defect cluster formation; in the alkali halides the extent of the replacement collision sequence is sufficient to induce rather large interstitial transport such that saturation defect density at any temperature (below room temperature) precludes successful observation because of dense observable defect aggregations. At

saturation only the aggregate distribution is affected, a lower density of larger clusters obtaining at room temperature and a higher density of smaller clusters at low temperature. Instead, retardation of aggregation in the earlier stages of defect production brought about by reduction of bulk defect mobility increases interstitial-vacancy defect recombination kinetics in the absence of efficient defect aggregate sinks. Thus, in the early stages of irradiation defect saturation is approached at first considerably more slowly at low temperatures than at room temperature, until a certain critical defect density leads to the start of aggregation and a faster rate of approach. This alteration in kinetics enables ~20 sec observation at absolute minimum irradiating beam current below 30 K in all alkali halides before low temperature defect aggregation becomes apparent.

Additionally, in some alkali halides, notably KI, the initial defect production efficiency (as measured by F centre density) reduces by as much as three orders of magnitude at low temperatures. This is because of the quenching of the non-radiative electron-hole recombination process as evidenced by an increase in the alternative radiative recombination (luminescence). The increased observation time afforded, relative to efficiently damaged crystals (for example KCl) is not however found to be in proportion to the relative decrease in initial F centre production efficiency, and this

discrepancy is explained in terms of differing interstitial-vacancy recombination volumes in different alkali halides and the possibility of luminescence quenching in the presence of a strong ionisation or electric field.

The design of a low temperature electron microscope stage suitable for such low temperature investigations is discussed at some length from a fundamental consideration of heat transfer. The flow properties of various cryogenic fluids are analysed, and procedures are derived for their most stable application. Suitable methods for temperature measurement are described and their limitations established. Likewise, techniques for reducing specimen contamination and obtaining adequate specimen tilt at low temperatures are discussed. A working cold stage design is presented which has been used with great success in this study, and this is compared with other designs appearing in the literature. Finally, problems of cryomicroscopy specific to the alkali halides are discussed, viz. quenching stresses and differential thermal contractions, and appropriate solutions are indicated.

Using this low temperature facility, a definitive electron microscopical study is made of radiation defect aggregations in alkali halides both internally irradiated in the microscope and irradiated externally in bulk with high energy electrons and γ radiation. The particular advantage accruing from the new possibility

of studying externally irradiated crystals is that optical and other spectroscopic measurements can be made in irradiated crystals prior to examination, and the point defect populations inferred from these measurements compared with microscopical observations. In particular, it is possible to overlap the regime of defect concentrations ($\sim 10^{17} - 10^{18} \text{ F cm}^{-3}$) normally studied in other alkali halide experiments, and to compare the state of defect aggregation with other crystal properties. Nevertheless, it is established that defect aggregations occurring at the saturation level during internal irradiation of thin foils in the microscope are in many ways similar to those produced by external radiation in bulk, at least for low microscope beam currents. Only at higher beam currents is a definite post-saturation/thin foil behaviour obtained, differing markedly from saturation behaviour in bulk crystals irradiated at lower radiation intensities.

The principal defect aggregation present in all alkali halides examined when irradiated at or below room temperature is a planar interstitial aggregate with a displacement vector near $a/2 \langle 101 \rangle$ and giving rise to contrast resembling a simple dislocation loop. The morphology of these aggregates differs widely among different alkali halides. In KCl, for example, the aggregates are long dipole defects elongating in one direction along $\langle 100 \rangle$ and growing to $\sim 100 \text{ nm}$ in length. In NaBr the aggregates resemble those occurring in KCl but are an order of magnitude smaller in size.

In KBr and KI, following initial elongation along $\langle 100 \rangle$, the aggregates become round planar loops of diameter exceeding 100 nm; in KI the habit plane of these loops has been determined to be between (001) and (101) for a $|101|$ displacement vector, the loop normal $\sim 10^\circ$ from $|101|$ for externally irradiated crystals but much closer to $|001|$ for aggregates produced by in situ foil irradiation. From observation of externally irradiated crystals it has been ascertained that these interstitial clusters grow in size rather than in number with increasing irradiation, and can be followed from a defect concentration as low as $10^{17} \text{ F cm}^{-3}$. The number of lattice sites associated with these clusters is always found to be very close to the total number of defects produced by irradiation, as inferred by F centre density measurements; these clusters therefore account for the fate of nearly all interstitials produced during irradiation at temperatures appreciably in excess of the interstitial mobility threshold.

The temperature dependence of interstitial aggregation is also investigated. Aggregates exceeding dimensions $\sim 10 \text{ nm}$ and in density $\sim 10^{17} \text{ cm}^{-3}$ are formed for saturation radiation doses at temperatures as low as 5 K. Increasing irradiation temperature above 30 K results in a marked increase in the rate of aggregation, and above $\sim 50 \text{ K}$ aggregation is nearly as rapid as at room temperature, although cluster size remains considerably smaller. During low

temperature irradiation existing interstitial aggregates formed at higher temperatures are seen to grow, and annealing low temperature damage clusters to room temperature results in nucleation of new clusters and appreciable growth of any existing interstitial aggregates. The addition of 200 ppm Na^+ to KI completely inhibits observable clustering below 30 K and measurably impedes aggregation up to above liquid nitrogen temperature, in agreement with what is known of the effect of smaller monovalent impurities in stabilizing halogen interstitials as H_Λ centres.

Several possible models for these interstitial aggregates are explored. The principal difficulty is explaining the magnitude of the observed strain, where the only apparently available defect is the nearly strain-less H centre. The most probable model involves some form of precipitation of an $|\text{X}_2^0|$ molecular halogen species produced by H centre interactions. One possible configuration is a $\langle 110 \rangle$ planar alignment of halogen molecules introducing a displacement which is a sizeable fraction of $a/2 \langle 110 \rangle$. Such a configuration could be stabilized by hole delocalisation onto neighbouring halogen ions in the $\langle 110 \rangle$ row to form a $|\text{X}_4^{2-}|$ molecular species. On this model elastic dipole interactions between molecules can be made to explain many features of loop morphology but not the initial elongation along $\langle 100 \rangle$ or the differences between round loop and dipole configurations. A principal objection to this model is the decided absence of displacement fault contrast in those

alkali halides exhibiting large round loops, which would be expected if the displacements introduced were non-integer fractions of $a/2$ $\langle 110 \rangle$.

An alternative configuration can be envisaged to obviate the fault problem, in which a perfect interstitial dislocation loop is constructed of anion and cation interstitials derived essentially from secondary creation of Schottky vacancy pairs induced by the strains associated with halogen molecule formation in the vicinity of the loop core. The interstitial halogen molecules responsible subsequently stabilise in the induced divacancies, leaving a perfect dislocation loop surrounded by a diffuse cloud of halogen molecule-divacancy centres, denoted $|H_V^+|$. The latter could constitute the dipolar defects recently detected by ionic thermal current measurements. A consideration of H centre stabilization kinetics indicates that the mechanism must initiate by H centre precipitation and subsequent $|X_2^0|$ halogen molecular formation at the loop core, followed by crowdion rearrangement in both anion and cation sublattices. Provided the resulting $|H_V^+|$ centres remain randomly distributed, no fault contrast results, yet the molecular species aggregate in close proximity to the perfect dislocation loop they induce.

This form of clustered halogen molecular precipitation best explains the complexity of V band absorptions in alkali halides. At

very low temperatures or for very low doses, only isolated molecules form and give rise to V_4 band absorption. As temperature or dose increases, V_2 band absorption arises from small molecular aggregations, and saturates as clusters begin to grow via the induced crowdion mechanism. V_3 band absorption arises from halogen molecules subsequently stabilised in divacancies resembling $|X_3^-|$ molecular ions. The random distribution of these centres explains the breadth of the eventual V_3 band, and for larger clusters, the observed proportionality of the V_3 band with F centre density.

Interstitial aggregates are not the only sinks for halogen interstitials. It is found that dislocations, introduced into a crystal before irradiation, climb during irradiation. Analysis of the helical climb of screw dislocations and comparison with F centre measurements indicate that the capture radius of a dislocation for the point defect inducing climb is ~ 150 nm, which is consistent with interstitial halogen diffusion. A halogen molecular precipitation at or near the dislocation core may then be again invoked to explain climb by the same mechanism as loop formation and also the V_x band found associated with irradiation of deformed crystals.

- It is also observed that glide dislocations interact with interstitial aggregates during plastic deformation of irradiated crystals. A simple hardening theory based on planar precipitate, dipole or dislocation hardening is derived to explain the magnitude

of observed hardening based on dislocation/cluster interactions for known cluster dimensions. In particular, considerable differences in both the magnitude of hardening and its relationship to F centre density are predicted between crystals containing large loop clusters (KI) and those with dipole-like aggregates (KCl); these differences are observed.

A second defect aggregate species is found to form during intense thin foil irradiations, at room temperature in KCl and above ~ 400 K in NaCl. This defect can exceed dimensions ~ 100 nm diameter and has a spherically symmetrical strain field. An analysis of the observed lattice strain induced by these aggregates in KCl indicates an outward strain (dilatation) $\sim 5\%$. The direction of the strain in KCl is consistent with potassium colloid formation, but inconsistent with a previous ascription to voids; these aggregates also anneal out at temperatures consistent with colloid break-up. Energy loss analysis indicates an unknown loss peak at 3.4 eV which could conceivably relate to the bulk plasmon loss in potassium metal. However, attempts to observe similar defects in crystals externally treated to produce colloids were unsuccessful, and examination of thin foil irradiation conditions indicates their size, at least, could be a thin foil anomaly. Furthermore, the magnitude of strain observed is found to be larger than that likely to be induced by alkali colloid formation. On the other hand, it is shown that both magnitude and direction of strain can be accounted for

by aggregation of $|H_V^+|$ halogen-divacancy centres, produced by the induced crowdion mechanism, to form halogen-filled cavities. Analysis of the expected lattice strain induced by such an aggregation indicates that the occluded molecular halogen must be liquid under considerable pressure. Further experiments are indicated to confirm this interpretation.

§1. General Properties of the Alkali Halides

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1.1 Introduction

The alkali halides (from Arabic alqili, ashes of the saltwort plant; and Greek halos, sea) are ionic salts composed of the alkali metals and the halogen gases. They are historically some of the most widely studied crystalline materials, chiefly because they were available in natural or easily prepared artificial crystals in relative purity long before modern sophisticated crystal growth and refining procedures had produced virtually pure semiconductors, and because the crystalline bond was relatively well understood from ionic chemistry.

A variety of techniques has been used to study the alkali halides, two of the most powerful being ionic conductivity (reviewed by Lidiard 1957) and, because they are spectrally transparent from the infrared to the ultraviolet, optical spectroscopy. The latter has revealed the presence of a large number of lattice defects known as colour centres after their optical spectra (see Schulman and Compton 1962); these have subsequently been studied with a wide range of spectographic techniques (EPR, ENDOR, laser spectroscopy). Transparency has also been put to advantage in observing plastic flow and internal stress states by stress birefringence (first used by Obreimov and Schubnikoff, 1927) and in decorating dislocations with colloidal metal particles (Amelinckx 1958). The smooth cleaved surfaces of alkali halide crystals have lent themselves to discovery and development of etch pitting (Johnston 1961), surface decoration (Bethge 1962; Serna and Bru 1968) and slip band replication

(Matucha 1968) techniques for revealing defects near the surface. Also, epitaxial growth has been widely performed on cleaved alkali halide substrates (e.g. Matthews 1966). Of course, the crystal structure of NaCl was the first to be elucidated by x-ray diffraction by the Braggs in 1913. Subsequently, x-ray techniques have been extended to include x-ray topography (Ikeno, Maruyama and Kato 1968) and diffuse scattering (Trinkaus, Spalt and Peisl 1970) methods for revealing lattice defects. Recently, even proton scattering is being applied to defect studies in the alkali halides (Morita et al. 1971).

Electron microscopy has not been much applied (see §5.1) because of the difficulties of chemical reactivity (§3.4) and electron irradiation damage (§2.5) inherent in preparing and examining suitable thin foils in this way. Potentially, electron microscopy is a powerful technique because it nicely spans the gulf between the single defect resolution of spectroscopic methods and the much larger scale of optical and x-ray microscopy. This range (~ 2 nm to $1 \mu\text{m}$) embraces most defect aggregates which cannot be characterised spectroscopically, as well as linear lattice defects (dislocations).

Since the application of electron microscopy, as well as the interpretation of radiation damage and other lattice defects, requires some knowledge of the physical, chemical and electrical properties of alkali halide crystals, we briefly outline in this Chapter the most important of these before discussing in detail the formation and observation of lattice defects. Special properties of relevance to

some specific considerations are discussed individually in the appropriate sections (e.g. electrical conductivity to charge acquisition, §3.5; chemical reactivity to thin foil preparation, §3.3 and §3.4; surface energy to cleavage, §3.2; thermal expansion to differential contraction stresses, §5.11).

1.2 Crystal Structure

The alkali halides crystallise in two crystal structures, the f.c.c. NaCl and the primitive cubic CsCl structures, illustrated in fig. 1.1a, b. Other possible arrangements, the ZnS (wurtzite or zincblende) structures of fig. 1.1c, are possible but are found only for the related halides NH_4F and AgI and Tl halides. The alkali halides which crystallise in each structure have been listed in Table 1.1. The choice between eight-fold (CsCl), six-fold (NaCl) or four-fold (ZnS) coordination rests primarily on ion size ratio and secondarily on ionic polarisability and the degree of ionic bonding. Ionic radii for alkali and halide ions are listed in Table 1.2 for all twenty alkali halides. The stability limits for each structure on a purely hard sphere model are

$$\begin{array}{lll} \text{CsCl} & 0.73 < r_1/r_2 < 1.0 &) \\ & &) \\ \text{NaCl} & 0.41 < r_1/r_2 < 0.73 &) \text{ (1.1)} \\ & &) \\ \text{ZnS} & 0.22 < r_1/r_2 < 0.41 &) \end{array}$$

where r_1/r_2 is the radius ratio for r_2 the larger ion. These ratios are listed parenthetically for each alkali halide in

Table 1.1 It is clear from Table 1.1 that hard sphere predictions are not strictly obeyed; this is because polarisation and the nature of the lattice bond can alter the expected geometric constraints. Since, in fact, so few alkali halides actually occur in the CsCl structure, we shall concern ourselves in the remainder of this thesis primarily with alkali halides crystallising in the NaCl structure.

The degree of ionic character depends on the difference in electronegativity of the ions concerned; LiI, then, is the least ionic, while CsF is the most ionic, ionic character decreasing along the diagonal in Table 1.1. Cohesion in strictly ionic lattices can be treated on the Born model (see Tosi 1964; Fumi and Tosi 1964); in a simple treatment the lattice energy U is given by

$$U \approx \frac{-Ae^2}{r_0} (1 - \rho/r_0) \quad (1.2)$$

where A is the Madelung constant (1.763 for CsCl structures, 1.748 for NaCl structure, 1.641 for the Wurtzite structure), r_0 is the equilibrium ion separation and ρ/r_0 is deduced experimentally from compressibility ($\sim 0.9-0.12$). The first term reflects the long range Coulombic ion attractions, the second the close range ion repulsions. Resulting lattice energies for the alkali halides are typically in the range 5-10 eV ion⁻¹.

Lattice parameters appearing in the literature are often older values; we have collected in Table 1.3 the latest available (100) lattice parameter values listed in the ASTM powder file (1968). It

will be noted that lattice parameters in alkali halides are rather large in comparison to metals. This has implications for electron microscopy; see §3.6. Mass density, molecular weight and corresponding ion site density are listed in Table 1.4. The ion site density is particularly important when comparing defect saturation density levels in various alkali halides. This is often better expressed as a fraction of the available sites, e.g. 10^{-3} .

1.3 Crystal Growth and Purity

Large crystals of alkali halides may be grown by either the Bridgman-Stockbarger method or the Kyropoulos method. Table 1.4 lists also melting and boiling points for the alkali halides, indicating that melt temperatures are easily obtained. Commercial producers (Harshaw, Korth, Hilger-Watts) tend to use the Bridgman-Stockbarger method because large ingots can be produced. On the other hand some of the purest crystals come from small boules produced by the Kyropoulos method.

Purity is a very important quantity in alkali halides, since various impurities radically affect both mechanical and irradiation properties. For example, 50 ppm Ca^{2+} in NaCl can raise the flow stress by an order of magnitude (e.g. Johnston 1962). Very small impurity additions sensitise early stage coloration by irradiation, and a number of the optical absorption centres once thought to be intrinsic defects have recently been shown to be impurity-related. Crystals produced ten years ago were of considerably poorer quality than those produced more recently, and purity still varies widely

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among manufacturers, primarily because these crystals are produced for their optical properties for use as windows or prisms, where dispersed impurities are of little concern.

Table 1.5 lists spectrographic analyses of a number of alkali halides used in this study and derived from various sources. One should note that it is still difficult to obtain some alkali halides in very pure form. On the other hand, modern Harshaw NaCl is quite clean and considerably better than Hilger and Watts NaCl, particularly as regards divalent impurities. Alkali impurities of smaller size than the host ions they replace (e.g. Na^+ in KI, K^+ in RbCl) are particularly important to low temperature irradiation properties. Available Rb halides are very poor in this respect. Early Harshaw KI was also suspect for this reason. A fortunate accident in utilising one of these impure crystals (with 200 ppm Na^+) led to the discovery of a remarkable effect in low temperature irradiation behaviour as seen in the electron microscope (see §5.4). Crystals are very often grown in air, and this can lead to high O^{2-} and OH^- impurity levels, which are known to sensitise alkali colloid production during irradiation (see §2.6).

1.4 Mechanical Properties

Huntington (1958) has collated various experimental and theoretical data for the elastic constants of the alkali halides. The relevant stiffness constants C_{ij} are C_{11} , C_{12} and C_{44} , and their related compliances S_{11} , S_{12} and S_{44} ; the former are listed

in Table 1.6. From these may be derived the shear modulus

$G = C_{44} = 1/S_{44}$. Poisson's ratio ν is not well defined for cubic crystals; usually the Voigt average

$$\nu_V = \frac{1}{2} \frac{4 C_{12} - 2 C_{44} + C_{11}}{3 C_{12} + C_{44} + 2 C_{11}} \quad (1.3)$$

is used. Most alkali halides obey the Cauchy relation

$$C_{12} = C_{44} \quad (1.4)$$

relatively well. The isotropic criterion

$$2 C_{44} = C_{11} - C_{12}$$

however is not; consequently the alkali halides must be reckoned relatively anisotropic materials. In general, $(C_{11} - C_{12}) > 2 C_{44}$; this is attributed to the action of the closed shell repulsive potential between adjacent alkali and halide ions. The exception is LiF for which $(C_{11} - C_{12}) < 2 C_{44}$; this result derives from the small size of the Li^+ ion, most intimate contact occurring between the halide ions along the $\langle 110 \rangle$ directions which reverses the inequality. It is customary to define an anisotropy ratio A

$$A = 2 C_{44} / (C_{11} - C_{12}) , \quad (1.6)$$

although the anisotropy factor

$$H = 2 C_{44} + C_{12} - C_{11} \quad (1.7)$$

is also used (Hirth and Lothe 1968). Most alkali halides have $A < 1$ (or $H < 0$) with A generally in the region 0.3 - 0.7 (see Table 1.6).

This makes some alkali halides about as anisotropic (but in the opposite sense) as copper. Defect image contrast obtaining in the electron microscope is intimately related to crystalline anisotropy, since the degree and sense of anisotropy affects defect strain fields

(see Humble 1967). Detailed contrast simulations (e.g. Bullough, Maher and Perrin 1970) have, in general, been performed only for the isotropic case.

The glide direction in the rock salt structure is $\langle 110 \rangle$, which is the shortest lattice vector connecting ions of the same kind; the slip vector is thus $a/2 \langle 110 \rangle$. The $\langle 100 \rangle$ glide direction is electrostatically impossible because ions of opposite sign alternate along this direction, and $\langle 100 \rangle$ slip brings rows of like ions in apposition. The corresponding slip vector in the CsCl chloride structure is $a \langle 100 \rangle$. The preferred glide plane in the rocksalt structure is $\{110\}$. This is not the closest-packed plane which contains a $\langle 110 \rangle$ slip vector (the close-packed planes are $\{100\}$, $\{110\}$, and $\{111\}$ in that order), but is the plane on which lattice resistance to $\langle 110 \rangle$ slip is least. Glide of $a/2 \langle 110 \rangle \{110\}$ edge dislocation is illustrated in fig. 1.2. When slip occurs in $\langle 110 \rangle$ over $\{110\}$, it can be seen from fig. 1.2 that the larger (except in the Rb halides) anions ride up over one another, increasing the interplanar spacing, but the electrostatic bonding across the plane is not seriously disturbed. For $\{100\}$ slip the increase in interplanar spacing is small (actually zero for an ion radius ratio > 0.63) but at an intermediate position a cation on one side of the slip plane is equally distant from two cations and two anions on the opposite side of the slip plane. Cohesion is then destroyed if the ions act as unpolarizable charges; if the ions are polarizable, cohesion is restored by induced dipole interactions. Thus ion core repulsions favour $\{100\}$ slip and Coulomb forces $\{110\}$ slip if

apparently a facile process. The unique correspondence of Burgers vector and slip plane also considerably simplifies possible dislocation interactions (see §5.6.2). Gilman and Johnston (1960) have determined that the gross yield stress corresponds to the stress required to move a dislocation through freshly annealed crystal at some uniform velocity. This is generally a very small stress, e.g. $\{110\}$ yield stresses in most alkali halides (see §5.6.1.1) are $\sim 20\text{--}30 \text{ g mm}^{-2}$, and very sensitive to prior incidental damage (Shlichta 1966). Fontaine (1968) has suggested that $\frac{a}{2} \langle 110 \rangle$ dislocations in the NaCl alkali halides are dissociated on $\{110\}$ by $\sim 8 \text{ b}$ (i.e. have an extended core structure) and calculates a stacking fault energy $\gamma_{110} \sim Gb/30 \approx 200 \text{ ergs cm}^{-2}$ on a simple electrostatic model. Such dissociation is expected to determine the pressure dependence of cross slip.

1.5 Chemical Properties

Being ionic materials composed of polarizable ions, the alkali halides are generally soluble in polar solvents. In fact, an extensive attempt has been made (Miravittles Mille 1945) to relate polarizabilities to solubility. Table 1.7 lists the solubility of most alkali halides in common polar solvents. In addition, specific nucleophilic reactions exist, particularly for the iodides, some of which react readily with ethers and ketones.

Of particular import to preparation of thin foils suitable for electron microscopy (§3.3, §3.4) is that almost all alkali halides are hygroscopic and a good many are seriously deliquescent. Therefore, contact with atmospheric moisture is often deleterious and to be avoided in the thin film stage. Appropriate measures are discussed in §3.4. Contact with moist atmosphere is also responsible for atmospheric embrittlement during mechanical testing. On the other hand, immersion in solvents leads to remarkable increase in plastic properties, first noted by Joffé et al. (1924) and subsequently coined the Joffé effect. Joffé's original explanation was that dissolution removed surface imperfections which nucleated microcracks leading to cleavage: this explanation seems to have been vindicated by the work of Stokes, Johnston and Li (1959) who showed that chemically polished and carefully dried NaCl crystals retained their remarkable plasticity if subsequently protected from atmospheric moisture attack.

1.6 Electrical Properties

Alkali halides are insulators (band gap ~ 10 eV), and so they do not exhibit the electronic conduction characteristics of metals and semiconductors. Accordingly, bulk resistivity is high, $\rho \sim 10^8$ ohm cm at room temperature. What electrical conductivity there is in the alkali halides is governed almost entirely by the movement of cation vacancies under an applied electric field strength E

(see Etzel and Maurer 1950; Lidiard 1957). The activation energy for conduction therefore consists of the formation energy $\phi/2$ of cation vacancies (which are thermally created), where ϕ is the vacancy pair production energy, and the activation energy for diffusion ξ_j . It can be shown (e.g. Dekker 1965) that in an ionic solid at temperature T the current density j under an applied electric field E is given by

$$j = \frac{veC}{6a^2} \exp(-\phi/2kT) \left\{ \exp\{-(\xi_j - aeE/2)/kT\} - \exp\{-(\xi_j + aeE/2)/kT\} \right\} \quad (1.8)$$

where v is the cation vacancy jump frequency, e the electronic charge, a the jump distance (shortest interionic distance = $a_0/\sqrt{2}$ in rock salt structure) and C an entropy constant.

For $E < 2kT/ae \sim 3 \times 10^6 \text{ V cm}^{-1}$,

$$j = \frac{ve^2 C E}{6 akT} \exp\{-(\xi_j + \phi/2)/kT\}; \quad (1.9)$$

i.e. Ohm's law is obeyed so that

$$j = \sigma_c^i E, \quad (1.10)$$

with the intrinsic conductivity σ_c^i given by

$$\sigma_c^i = \frac{ve^2 C}{6 akT} \exp\{-(\xi_j + \phi/2)/kT\}. \quad (1.11)$$

Alkali halide crystals normally contain a small divalent impurity concentration which establishes a constant concentration level for cation vacancies (which are created to maintain electrical neutrality) at temperatures below the intrinsic conductivity region

(i.e. for $T < 800$ K). In this region, called the extrinsic conductivity range, thermal vacancy concentration is $\ll$ divalent impurity content, and we have

$$\sigma_c^e = \frac{ve^2 N_d}{6akT} \exp(-\xi_j/kT), \quad (1.12)$$

where N_d is the divalent impurity concentration. We note that in either case to a first approximation

$$-\ln \sigma_c \propto 1/T; \quad (1.13)$$

i.e. the slope of the $\ln \sigma_c$ vs $1/T$ curve is approximately constant in each region, which is experimentally observed, and from which ξ_j and ϕ can be determined.

For large electric fields, viz. $E > 2kT/ae \sim 3 \times 10^6$ V cm⁻¹ in the extrinsic region,

$$\begin{aligned} j &= \frac{ve^2 N_d}{6a^2} \exp(-\xi_j/kT) \exp(aeE/2kT) \\ &= \sigma_c^e \frac{kT}{ae} \exp(aeE/2kT); \end{aligned} \quad (1.14)$$

or at constant T ,

$$j \propto \sigma_c^e \exp E, \quad (1.15)$$

in distinction to the linear relation for small fields. In either case, we note conductivity diminishes exponentially with temperature.

Table 1.1

Alkali Halide Crystal Structures(bracketed values are radius ratios r^+/r^-)

Cs Cl (8 : 8) Na Cl (6 : 6) ZnS (4 : 4)

LiF LiCl LiBr LiI

(0.44) (0.33) (0.31) (0.28)

NaF NaCl NaBr NaI

(0.70) (0.52) (0.49) (0.44)

KF KCl KBr KI

(0.98) (0.74) (0.68) (0.62)

RbCl† RbBr† RbI† RbF RbCl RbBr RbI

(0.92*) (0.82) (0.76) (0.69)

CsCl CsBr CsI CsF CsCl†

(0.93) (0.87) (0.78) (0.80*)

(NH₄Cl) (NH₄Br) (NH₄I†) (NH₄Cl†) (NH₄Br†) (NH₄I) (NH₄F)

(0.82) (0.76) (0.69) (0.92*)

† high temperature or high pressure forms

* r^-/r^+ ratio

Table 1.2
Ionic Radii
 (radii in Ångstrom units)

Li^+	0.60	F^-	1.36
NH_4^+	1.48	Cl^-	1.81
Na^+	0.95	Br^-	1.95
K^+	1.33	I^-	2.16
Rb^+	1.48	H^+	1.54
Cs^+	1.69		

Table 1.3

Lattice Parameters

(values are in Ångstrom units at room temperature)

Alkali halide	Structure	ion pairs/ unit cell	a_0	ASTM reference
LiF	NaCl	4	4.0270	4-0857
NaF	NaCl	4	4.64	4-0793
KF	NaCl	4	5.347	4-0726
RbF	NaCl	4	(5.63)	-
CsF	NaCl	4	6.01	15-759
LiCl	NaCl	4	5.1396	4-0664
NaCl	NaCl	4	5.6402	5-0628
KCl	NaCl	4	6.2931	4-0587
RbCl	NaCl	4	6.5810	6-0289
CsCl	CsCl	1	4.1230	5-0607
LiBr	NaCl	4	5.5013	6-0319
NaBr	NaCl	4	5.9772	5-0591
KBr	NaCl	4	6.5966	4-0531
RbBr	NaCl	4	6.889	8-480
CsBr	CsCl	1	4.287	5-0588
LiI	NaCl	4	6.00	1-0592
NaI	NaCl	4	6.473	6-0302
KI	NaCl	4	7.0655	4-0471
RbI	NaCl	4	7.342	6-0218
CsI	CsCl	1	4.5679	6-0311

Table 1.4

Physical Properties

Alkali halide	MW	ρ (298K)	ion density ($\times 10^{22} \text{ cm}^{-3}$)	m.p. (K)	b.p. (K)
LiF	25.94	2.601	6.04	1143	1899
NaF	42.00	2.79	4.00	1253-1270	1973
KF	58.10	2.48	2.57	1153	1773
RbF	104.48	-	-	1033	1683
CsF	151.91	3.586	1.42	957	1523
LiCl	42.40	2.068	2.94	886	1626
NaCl	58.45	2.165	2.23	1074	1686
KCl	74.55	1.984	1.60	1049	subl. 1773
RbCl	120.94	2.76	1.37	988	1663
CsCl	168.37	3.97	1.42	tr. to β 718	-
LiBr	86.86	3.464	2.40	820	1538
NaBr	102.91	3.203	1.87	1028	1663
KBr	119.01	2.75	1.39	1003	1653
RbBr	165.40	3.35	1.22	955	1613
CsBr	212.83	4.44	4.44	909	1573
LiI	133.86	4.061	1.83	719	1463
NaI	149.92	3.667	1.47	924	1573
KI	166.02	3.13	1.13	996	1693
RbI	212.40	3.55	1.01	915	1573
CsI	259.83	4.510	1.04	894	1553

Table 1.5

Analysis of Principal Impurity Content

	(in ppm)										
	Li	Na	K	Rb	Cs	Ba	Ca	Mg	Cd	Fe	Pb
LiF (H)		100					<30	300	<10		
NaCl (H)							<10		<10	<10	
NaCl (H&W)			100			30		50		5	10
NaBr (H)	10		300	3			<10		<10		
KCl (H)				3			<10		<30		
KBr ₂ (H)				10		10	<10		<30		
KI (H)				5	<5		2		<10		
KI (H)		200		5	10		2		<10		
RbCl (H&W)		<10	1000				<10		<10		

H = Harshaw

H & W = Hilger and Watts

Impurity levels not otherwise listed are <3 ppm

Table 1.6

Elastic Constants[†] $(C_{ij} \times 10^{11} \text{ dynes cm}^{-2})$

	C_{11}	C_{44}	C_{12}	$\frac{1}{2}(C_{11}-C_{12})$	A	H	ν_V
LiF	11.12	6.28	4.20	3.46	1.82	+5.64	0.187
NaCl	4.87	1.26	1.24	1.82	0.694	-1.11	0.248
NaBr	3.87	0.97	0.97	1.5	0.647	-1.06	0.250
KCl	3.98	0.625	0.62	1.68	0.372	-2.11	0.252
KBr	3.46	0.505	0.58	1.44	0.351	-1.87	0.260
KI	2.67	0.42	0.43	1.12	0.375	-1.40	0.252

[†] Huntington (1958)

Table 1.7

Alkali Halide Solubility in Polar Solvents

	(in g/100g solvent)					
	H ₂ O	MeOH	EtOH	PrOH	BuOH	Acetone
LiF	0.26(0.13)					3.3x10 ⁻⁷
LiCl	45.4	29.8(43.8)	20.4	14.0(n)	11.5(n)	7.7
LiBr	60.4	140	41.8			21.5
LiI	62.9	77.4(171)	71.5	59.7(n)	53.0(i)	36.3
NaF	4.22	0.41	0.095		0.003(n)	2.4x10 ⁻⁷
NaCl	26.5(35.8)	1.3	0.065	0.012(n)	0.014(n)	4.1x10 ⁻⁶
NaBr	48.2	15.6	3.6	0.47(n)	0.20(i)	0.072
NaI	64.9	47.5(72.0)	32.9(42.6)	22.1(n)	4.0(i)	27.6

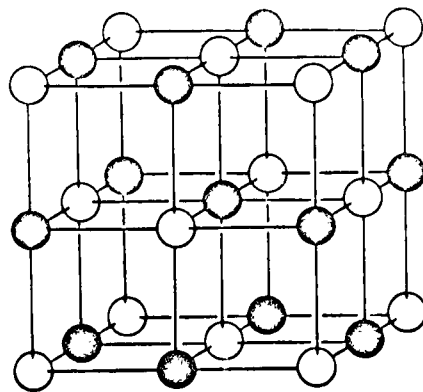
n normal } solubility chosen for listing is the higher of the two forms
i iso
() values are solubilities determined by another investigator
where they differ markedly from the value chosen for listing.

Table 1.7 (contd)

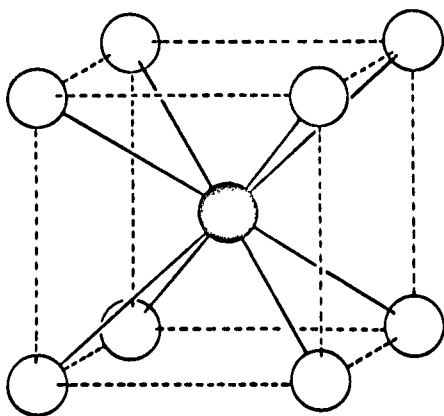
	H ₂ O	MeOH	EtOH	PrOH	BuOH	AmOH	Acetone
KF	48.0	0.192	0.106				2.2×10^{-5}
KCl	26.5	0.59	0.022	0.004(n)	0.006(n)	8.0×10^{-4} (n)	0.9×10^{-5}
KBr	40.5	2.17	0.142	0.035(n)		0.003(i)	0.011
KI	60.4(114.5)	15.3	2.16	0.43(n)		0.098(i)	1.78
RbF	75.1						3.6×10^{-4}
RbCl	48.6	1.41	0.078	0.015(n)		0.09(i)	2.5×10^{-4}
RbBr	53.7	10.1					0.032
RbI	62.1	10.1		0.212(n)	0.062(i)	0.043(i)	0.634
CsF	85.4						0.0036(0.077)
CsCl	66.1	3.4	0.032			0.09(n)	0.004
CsBr	55.2(124.3)	2.2					0.043
CsI	46.9	3.7					1.59

Fig. 1.1. Cubic crystal structures for alkali halides.

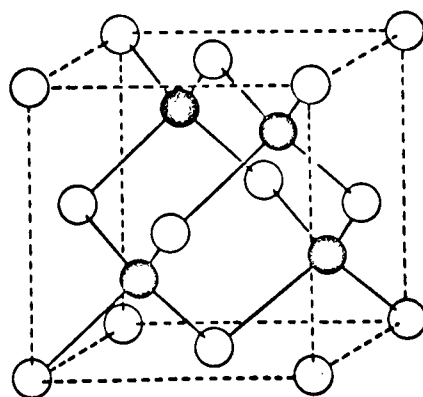
- (a) Clinographic projection of the cubic NaCl unit cell, sixfold coordination.
- (b) Clinographic projection of the cubic CsCl unit cell, eightfold coordination.
- (c) Clinographic projection of the cubic ZnS (zincblende) unit cell, fourfold coordination. A related hexagonal structure (wurzite) is also possible which differs only in the next-nearest-neighbour configurations.



(a)
NaCl

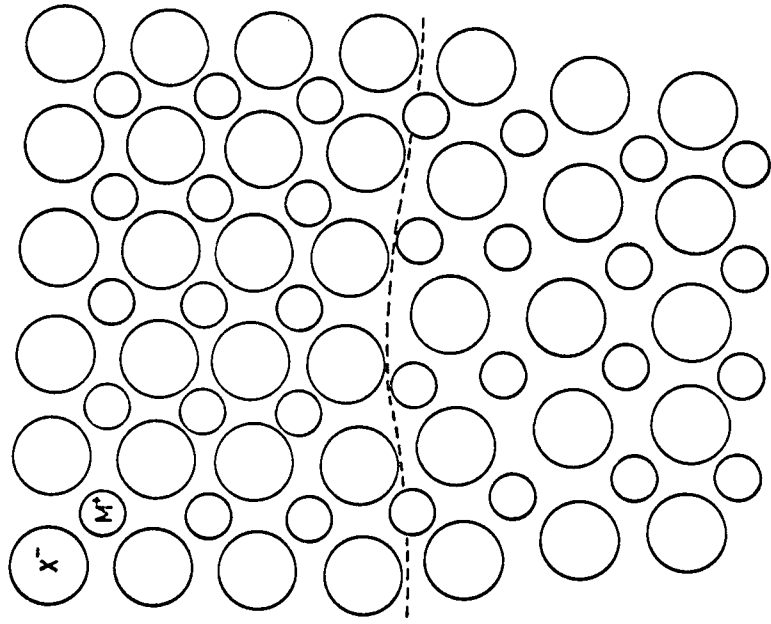


(b)
CsCl

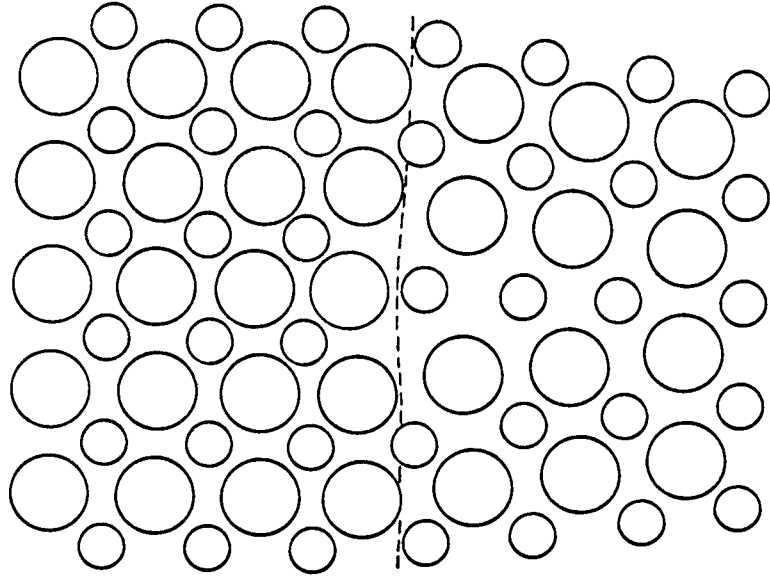


(c)
ZnS

Fig. 1.2. Glide of an edge dislocation with Burgers vector $a/2 \langle 1\bar{1}0 \rangle$ over a $\{110\}$ slip plane in the NaCl structure. The two symmetrical configurations (a) and (b) alternately obtain as the dislocation glides along the slip plane. For the $\{110\}$ slip illustrated, the larger anions ride up over each other, but the electrostatic binding across the slip plane is not seriously disturbed. The latter is not true for $\{100\}$ slip.



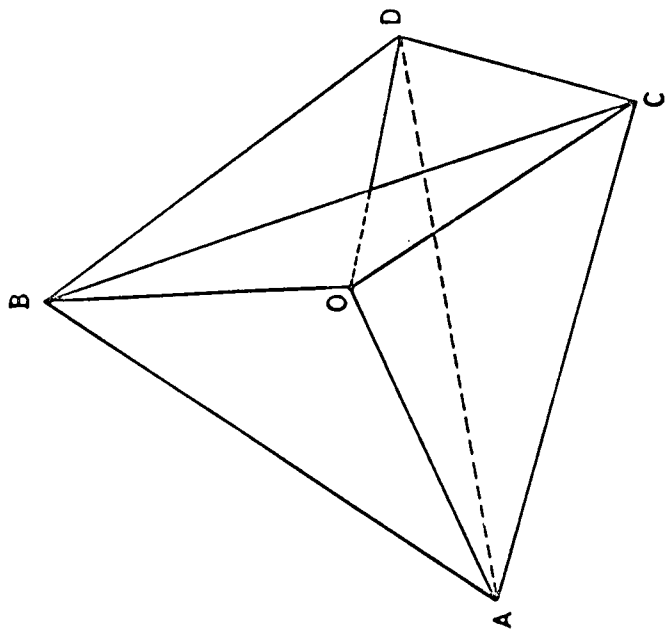
(a)



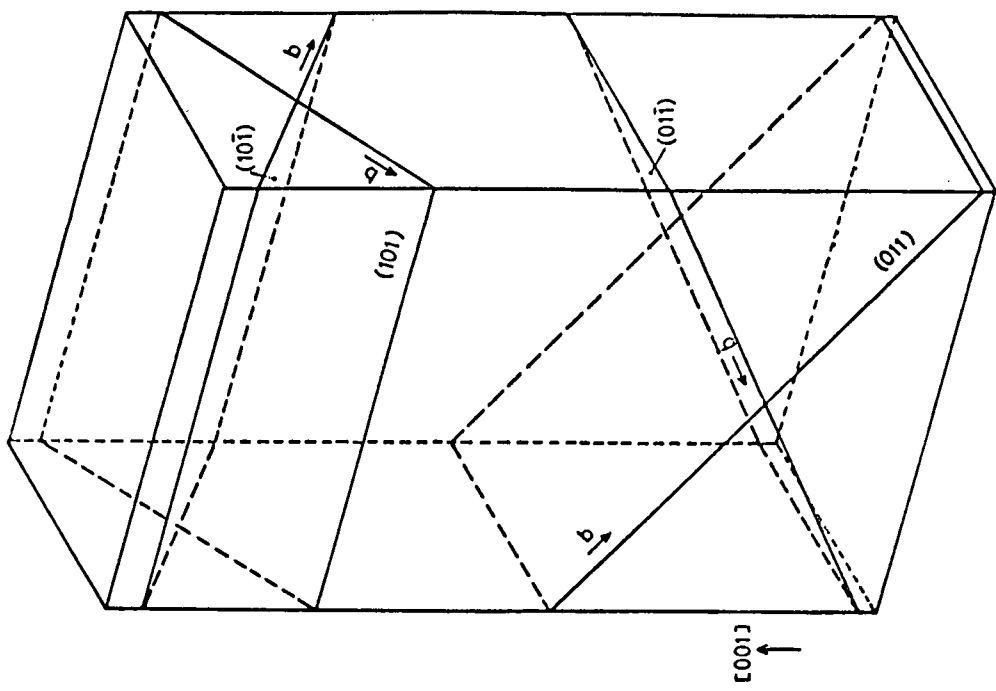
(b)

Fig. 1.3. The six $\langle 1\bar{1}0 \rangle \{110\}$ principal glide systems in the NaCl structure.

- (a) Variant of the Thompson tetrahedron due to Groves and Kelly (1970) for use in the NaCl structure. O lies in the centre of the tetrahedron. The planes OAB, OAC, OAD, OBC, OBD, OCD are $\{110\}$. The directions AB, AC, AD, BC, BD, CD are $\langle 110 \rangle$, and each lies uniquely in only one $\{110\}$ plane.
- (b) The four equally stressed $\langle 1\bar{1}0 \rangle \{110\}$ slip systems for a NaCl structure crystal in $[001]$ compression. Slip generally nucleates on only one system, usually one with shortest slip distance across the crystal, and slip on other systems is strongly excluded.



(a)



(b)

52. Radiation Damage in Alkali Halide Crystals

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2.1 Introduction

The term radiation damage is a phenomenological appraisal of what happens when an ordered arrangement of atoms becomes disordered or transformed by the passage of radiation during its interaction with matter. The stress on damage arises because of an initial preoccupation of radiation studies with the progressive deterioration of nuclear reactor materials during service. For the present discipline, as it has since developed to encompass a wider range of materials and increasingly fundamental studies of specific defects, a more appropriate term would undoubtedly be radiation effects (Chadderton 1967). Since many of the radiation effects in the alkali halides, specifically, are not only physical but also radiochemical in nature, the term radiolysis has also been suggested (Crawford 1968). However, precisely because radiation defects are created so efficiently and on such a vast scale in alkali halides, in comparison with most other materials, we prefer to retain the more emotive epithet damage, implying as it does serious and inconvenient (for the purposes of electron microscopy) disruption of the crystal lattice. It is hoped that this choice will serve as a constant reminder of the magnitude of difficulty confronting the electron microscopist intending study of these materials.

It is an inescapable fact that copious radiation damage accompanies the passage of energetic electrons through alkali halides, and therefore must inevitably result during their electron microscopical examination. Indeed, it is not hyperbole to state that catastrophic damage accompanies electron microscopy of these materials (the physical

Processes underlying efficient defect creation in the alkali halides will be discussed later in this chapter). Such damage is not entirely disadvantageous, since the electron microscope at least provides a convenient in situ radiation source for production of radiation defects, at energy levels far lower than those required to effect even simple atomic displacements in other materials, and at intensities vastly in excess of those attainable in conventional alkali halide damage studies. It is, in fact, a central (and unique) feature of alkali halide irradiation that ionic displacements occur at very low cost in terms of expended energy; this property arises from the ionic (and thus electronic) structure of these crystals. Nonetheless, the scale of radiation damage accompanying intense irradiation effectively prevents conventional electron microscopical characterisation of the resulting irradiation defects, or indeed of any defects previously residing in the lattice; special conditions of examination must be applied if any desired feature is to survive. Successful application of these conditions requires a thorough understanding of the radiation damage process occurring in the alkali halides, and of the sorts and properties of the radiation defects produced.

In this chapter, therefore, we review in detail all aspects of the production of defects in alkali halide crystals which are likely to affect potential electron microscopy of this class of materials. We also indicate those aspects of radiolysis studies which can be significantly advanced by application of electron microscopical techniques. Finally, we specify the rather special conditions under which electron microscopy of alkali halide crystals is likely to be successful, and

specifically exploit certain properties of alkali halide defects which can prolong the time available for meaningful electron microscopical analysis. In this connection, we offer some new conclusions about the role of various irradiation defects, arising from a critical examination of recent irradiation data, which have direct relevance to the electron microscopical results detailed in §5.

These discussions are, of course, inextricably bound up with the subject of colour centres in ionic crystals, for which so vast a literature now exists as to almost defy cataloguing (however, see an attempt by Jain et al. 1971). Therefore, some considerable space will be devoted to elaboration of those specific colour centre properties which have enabled an extraordinarily comprehensive picture of radiation damage in alkali halides to emerge over the last productive decade. These properties also underscore the subtle electronic character of defects and of the radiation damage process itself in alkali halides, which serves to distinguish these crystals from most other inorganic substances. This basic distinction will be continually invoked to explain differences in irradiation behaviour between alkali halides and other polar, as well as non-polar, materials.

2.2 Point Defects in Ionic Crystals

Whenever some form of lattice disorder is localised in a small region of atomic dimensions in an otherwise ordered lattice, we speak of the resulting lattice perturbation as characteristic of a point defect. Typical examples are an atom (or ion) missing from its lattice -

site, an atom (or ion) accommodated interstitially in the lattice, a foreign atom (or ion) species substituted for a normal lattice species, etc. Point defects are to be distinguished from line defects, such as dislocations, and planar defects, such as stacking faults. All these defects have associated with them some form of accommodating lattice strain, and it is often this perturbation which enables their presence to be detected, e.g. from changes in density, lattice parameter, internal friction, etc. In simple materials such as metals, point defects are essentially atomic defects and can be to a first approximation treated on a simple hard sphere model. Point defects in ionic crystals, on the other hand, have another dimension associated with them, the electronic one, introducing not only local lattice strain but local charge distribution as well which can alter the effective size of the defect. In fact, some point defects in ionic crystals (the self-trapped hole is a good example) are purely electronic in aspect, involving no real atomic or ionic defect. Moreover, it is precisely these electronic aspects which enable a far subtler study to be made of defects in ionic crystals than in non-polar materials. Ionic crystals are, additionally, compounds of two or more ionic species; as in ordered metallic alloys, this introduces a further order of complexity. In ionic crystals, particularly, occurrences in one ionic sublattice can have profound influence not only elsewhere in the same sublattice, but also in the other sublattice(s), because of the Coulombic lattice potential.

In this section we briefly summarise the basic sorts of point defects arising in ionic crystals in general (with of course specific

reference to the alkali halides). In the following section we shall go on to investigate specifically those point defects likely to be introduced in alkali halides by irradiation.

2.2.1 Equilibrium thermal defects

(a) Schottky defect

A Schottky defect comprises a vacant anion site and a vacant cation site, formed by removal of an interior anion and cation to the crystal surface. The pair of oppositely charged vacancies produced satisfies charge neutrality and also increases the configurational entropy of the crystal. At any temperature T there will be a thermodynamic equilibrium concentration of Schottky defects formed spontaneously so as to minimise the free energy of the crystal. The equilibrium relation between the concentration N_v^+ of cation vacancies and N_v^- of anion vacancies is then given by (Lidiard 1957)

$$N_v^+ N_v^- = \exp (S_s/k) \exp (-\phi_s/kT), \quad (2.1)$$

where $S_s = S_v^+ + S_v^-$ is the total change in vibrational entropy in the neighbourhood of a Schottky pair and $\phi_s = \phi_v^+ + \phi_v^-$ is the formation energy for a pair of vacancies.

On the Einstein model, if each of the n perturbed nearest neighbour ions surrounding the vacancy changes its vibration frequency from ν to ν_v , the change in vibrational entropy per vacancy summed over the three vibrational modes of each perturbed ion is

$$S_v = 3 n k \ln (\nu/\nu_v). \quad (2.2)$$

The vacancy coordination number in the Na Cl structure is 6, so that

$$N_V^+ N_V^- = (v/v_V)^{18} \exp (-\phi_s/kT). \quad (2.3)$$

Typically $v/v_V \sim 2$, so that the contribution of vibrational entropy can be large.

The formation energy ϕ_s will be a function of volume, and thus of temperature; but so too will the vibrational entropy, since (at zero pressure)

$$\frac{dS_s}{dT} = \frac{1}{T} \frac{d\phi_s}{dT} ; \quad (2.4)$$

and from (2.1)

$$\ln (N_V^+ N_V^-) = S_s/k - \phi_s/kT, \quad (2.5)$$

we find that

$$\frac{d}{dT} (S_s/k - \phi_s/kT) = 0. \quad (2.6)$$

Therefore, the slope of a $\ln (N_V^+ N_V^-)$ vs $1/T$ plot yields ϕ directly regardless of T . The vacancy product $N_V^+ N_V^-$ can be obtained from ionic conductivity measurements in the high temperature intrinsic conductivity region, yielding a Schottky pair formation energy $\phi_s \sim 2$ eV, or about 1 eV per vacancy.

ϕ_s may also be obtained by theoretical calculations of lattice energies at absolute zero temperature. These must take account of both the lattice energy and the polarisation induced by the vacancy. For example, Mott and Littleton (1938) have shown that on the Born model

$$\phi_s = A \frac{e^2}{a'} (1 - 1/b) - \frac{1}{2} e^2 (1 - 1/\epsilon) (1/r_V^+ + 1/r_V^-) \quad (2.7)$$

where A is the Madelung constant, a' the shortest interionic distance,

b the Born exponent, ϵ the static dielectric constant, and r_v^+ and r_v^- the effective vacancy radii.

(b) Frenkel defect

A Frenkel defect consists of a vacant cation or anion lattice site and its respective ion in an interstitial position. If we denote by N_i the concentration of interstitial ions of one species, and by N_v the number of vacancies of that species, we can show by similar reasoning to (2.1) that

$$N_i N_v = \exp (S_f/k) \exp (-\phi_f/kT).$$

We let ν_i be the vibration frequency of the interstitial, ν_i' that of its n' nearest neighbours, and ν_v that of the n nearest neighbours surrounding the vacant site. It can then be shown (Mott and Gurney 1948) that

$$S_f = k \ln \left\{ \left(\frac{\nu}{\nu_i} \right)^3 \left(\frac{\nu}{\nu_v} \right)^{3n} \left(\frac{\nu}{\nu_i} \right)^{3n'} \right\}. \quad (2.8)$$

Since $\nu_i > \nu$, we expect that the vibrational entropy contribution will be smaller than for Schottky defects.

The formation energy will depend on the interstitial accommodation volume and the interstitial ion size. For Frenkel defects of purely thermodynamic origin, the larger anion radii in most alkali halides imply that cation interstitials will be more easily accommodated and will predominate over anion interstitials. A typical Frenkel cation pair formation energy is $\phi_f \sim 2.9$ eV (Na^+ in Na Cl); and since $\phi_f > \phi_s$, Schottky defects are expected to predominate over Frenkel defects in alkali halides in thermal equilibrium.

Table 2.1 indicates the magnitude of thermal defect concentration in sodium chloride at a variety of temperatures. Except near the

melting point, the concentration is negligible compared with defects arising from incidental impurity levels in the crystal.

2.2.2 Impurity defects

(a) Divalent cation impurities

For every substitutional positive divalent impurity ion incorporated into an alkali halide lattice there must be a compensating cation vacancy (since this is far easier to accommodate than a compensatory anion incorporated interstitially) to maintain overall charge neutrality. The divalent impurity concentration is typically in the ppm range (see Table 1.5) and sets the cation vacancy level for ionic conductivity in the extrinsic conductivity region. Not all cation vacancies are free, however, because of the expected binding energy between cation vacancies (negatively charged) and divalent cations (positively charged), resulting in the formation of divalent cation-cation vacancy complexes. Binding energies have been calculated by Bassani and Fumi (1954) and measured, e.g., by Ikeya et al (1965) in the region 0.3 - 0.4 eV, although recent measurements (Kumano and Hanabusa, 1968) find binding energies as high as 0.6 eV. The activation energy for migration of these complexes is ~1 eV (Crawford 1970). These defects are, therefore, relatively stable at room temperature (at room temperature nearly all vacancies form complexes with divalent ions) and do not constitute an appreciable source of cation vacancies. The importance of such a source will be considered in §5.7.

Divalent cation impurities themselves are important because they act as electron trapping centres. The effect of divalent ion concentration

on radiation defect production is discussed in §2.8. There is also considerable evidence (Bassani and Thomson 1956; Brown and Pratt, 1963; Chang and Graham 1964; Newey 1963) that the divalent impurity-cation vacancy complex segregates at dislocation cores and provides an effective pinning mechanism with an activation energy ~ 1 eV. These complexes can also trap mobile interstitial defects (Itoh and Ikeya 1967).

(b) Monovalent cation impurities

Commercial alkali halide crystals invariably contain rather larger amounts of monovalent impurity, usually foreign alkali metal ions, in concentrations often exceeding 10^{18} cm^{-3} . These ions introduce no gross electrical imbalance, but there is considerable evidence recently (Itoh and Saidoh 1969; Saidoh and Itoh 1970) that the strain fields around substitutional monovalent cation impurities can trap one or more anion interstitials at low temperatures. This effect has considerable import for the electron microscopy of alkali halide crystals and is discussed in §2.8 and §5.4. Otherwise, the monovalent impurity concentration has little effect on properties such as flow stress or room temperature radiation damage behaviour, and so is generally ignored.

(c) Anion impurities

Halogen anions can be rather freely substituted in alkali halides to provide a continuous range of mixed halide solid solutions. Since it will be shown later that the radiation damage process occurs primarily on the halogen sublattice, it is to be expected that halogen

substitution will have a decided influence on the efficiency of this process (Still and Pooley 1969). There is also evidence (Itoh, Royce and Smoluchowski 1965b) that larger halogen interstitials created by irradiation are readily replaced with smaller halogen interstitials in crystals containing additions of smaller halogen ion impurity.

Other anion impurities can influence point defect distribution. The $|\text{OH}^-|$ hydroxyl ion is often present in synthetic crystals grown in air or in crystals containing occluded water. Lütty (1962) has shown that this molecule can be converted to $|\text{H}^0|$ neutral hydrogen under irradiation, which produces a characteristic colour centre of its own (see §2.3). The $|\text{OH}^-|$ ion and several other oxygen-bearing anion complexes (CO_2^- , SO_2^- , O_3^- , NO_3^-) have also been shown to catalyse halogen vacancy aggregation (see §2.6.5.2).

(d) Non-stoichiometric additions

Non-stoichiometric additions of either cation or anion species can be introduced into a crystal, for example by heating in the vapour of the appropriate constituent alkali or halogen, with the simultaneous incorporation of a corresponding number of electrons or holes to maintain charge balance. The latter may be trapped at an interstitial site if the excess ions are accommodated interstitially, forming neutral interstitial atoms, or they may be trapped at vacancy sites if the excess ions are accommodated substitutionally with the simultaneous formation of ion vacancies of the opposite species. Colour centres may thus be formed additively in this way (see van Doorn 1962). Alternatively, either ion species may be made to leave the crystal during electrolysis

at elevated temperatures with the same result.

2.2.3 Electronic defects

Ionic defects are not initially neutral with respect to the ionic lattice and have a charge associated with them at the moment of their creation. An electron or hole may become trapped in the resulting Coulombic potential well (often nearly instantaneously; see Ueta 1967); the resulting defect is called a colour centre, because electronic transitions of the electron or hole correspond to absorption of specific wavelengths often in the visible region, and may be neutral or even reverse their charge if more than one electron or hole is trapped. Emission may occur from excited states of the trapped electron or hole, corresponding to luminescence. Trapping energies can be quite high, often >2 eV, though a trapped electron centre may easily be annihilated by absorption of a hole and vice versa. Electrons and holes may also be trapped at impurity ions exhibiting the wrong valence, and the hole may even be self-trapped in the perfect lattice.

Trapping an electron or hole radically alters the properties of the trapping centre; its stability and configuration in the lattice are affected, as well as its mobility. These aspects are discussed in §2.3 and §2.6 where the properties of simple and aggregate colour centres are delineated. Since free electrons and holes are released into the lattice by ionizing radiations, colour centres are a major product of alkali halide irradiations. Many of the differences in irradiation behaviour between alkali halides and other materials can be explained on the basis of electronic defect properties.

2.2.4 Point defects introduced by plastic deformation

If a dislocation in an alkali halide crystal is forced to move non-conservatively in the lattice, it will leave behind trails of charged point defects. One mechanism by which this most frequently happens is the creation of single or double jogs on dislocations by dislocation intersections, which when forced to move on planes on which they cannot glide trail behind them rows of neutral or charged point defects. Possible intersections in the NaCl structure are discussed in §5.6.1. A second jog-producing mechanism is the multiple cross-glide mechanism responsible for dislocation multiplication and slip band broadening in the NaCl structure (Johnston and Gilman, 1960; Mendelson 1962). Dislocation dipoles alternatively left behind immobile jogs, as well as single dislocations themselves, serve as important sinks for point defects.

There is also optical absorption evidence that trapped hole defects, not necessarily vacancy or interstitial defects (e.g. V_k centres; see §2.3.3.1) are formed during plastic deformation of alkali halides (Hersh 1959; Hersh and Hadley 1963; Butler 1966; Clark and Newman 1971). This is a rather interesting confirmation of electronic activity associated with dislocations and their movement in alkali halides.

2.3 Colour Centres in Alkali Halides

2.3.1 Band structure and nomenclature

When alkali and halogen ions are brought together from infinity to form an ionic crystal the unoccupied 3s alkali ion level and the

occupied 3p halogen ion level, each initially located below the zero energy level by the respective alkali and halogen ionization energies, separate and broaden into bands which subsequently form the conduction and valence bands of the resulting solid. At the equilibrium ion separation the energy gap between them (ignoring the electron wave vector direction) is ~ 10 eV, and it is this large band gap which accounts for the insulator properties of the alkali halides and gives rise to the wide "window" in the absorption spectra between the infrared and the ultraviolet which is responsible for their transparency.

Attempts have been made to understand the resulting band structure in more detail. The most sophisticated band structure calculations available are those performed recently by Kunz (1971).

It has long been known that alkali halides exposed to irradiation or heated in alkali vapour develop characteristic colours (NaCl, yellow; KCl, purple; KI, green) which arise from absorption of specific light wavelengths and are attributable to optical transitions to excited electron states in the band gap. The defects responsible for introducing these intermediate states (i.e. colour centres) now include a wide range of electronic, ionic and impurity defects, various aspects of which have been reviewed successively in the literature (Pohl 1937; Mott and Gurney 1948; Seitz 1946; 1954; Przibram 1956; Pick 1958; Dexter 1958; Schulman and Compton 1962; Compton and Rabin 1964; Markham 1966; Royce 1967; Fowler 1968; Crawford 1968; Sonder and Sibley 1972). Many of these defects have no proper optical absorption bands, but are widely studied by other techniques, such as electron paramagnetic (spin) resonance

(EPR), electron nuclear double resonance (ENDOR), laser spectroscopy, thermal conductivity, small angle and diffuse x-ray scattering, and most recently electron microscopy and particle channelling.

The most characteristic and exhaustively studied of all colour centres is the F centre (from German Farbe, colour) comprising a single anion vacancy and trapped electron which exhibits hydrogen-like transitions at energies a few eV above the valence band. Optical excitation to the first excited state gives rise to a broad, bell-shaped absorption band in the middle of the visible spectrum which is chiefly responsible for the characteristic hue of coloured alkali halide crystals. In addition to the F centre levels, there is a series of bound electron-hole exciton levels, still below the conduction band; these can be excited by radiation into the near uv and are responsible for a series of absorption peaks on the long wavelength tail of the first fundamental absorption. There is also a set of trapped hole centres with optical transitions in the violet region corresponding principally to anion interstitial defects. As well as absorption spectra, there are emission spectra which correspond to transitions from excited states and also to electron-hole recombinations.

Colour centres can be introduced into alkali halide crystals in a variety of ways. Crystals may be irradiated; this will be shown to give rise principally to Frenkel pair production in the anion sublattice. Crystals may be additively coloured with a non-stoichiometric excess of either ion species introduced by heating the crystal together with alkali or halogen vapour; in this way vacancies of the opposite species are created to maintain charge neutrality. Crystals may be coloured

electrolytically at elevated temperatures by application of a strong electric field to induce ionic motion and thus depletion of either species near an electrode. In this section we shall concentrate on those centres likely to be induced by irradiation, investigating the mechanisms by which they are created and their subsequent fate in the lattice.

Nomenclature for the vast catalogue of colour centres now extant is currently irregular and often inconsistent because defect centres have invariably been called after the property they manifest, usually various absorption bands which historically have been named in a rather haphazard manner. Often an assignment has been made on the basis of speculation before definitive evidence for a presumed defect structure had been established; this procedure has resulted in a host of anomalies. For example, the absorption bands lying to shorter wavelengths of the F band were called V bands (for violet) and first ascribed to cation vacancy trapped hole centres which were then called V centres; however, recent work has shown that almost without exception the V bands are associated with anion interstitial centres and have nothing to do with the cation vacancy centres now referred to as V centres. Understandable confusion results.

In this chapter and throughout this thesis we shall try to utilise a self-consistent notation for colour centres, Table 2.2, part of which is to be shortly introduced by Sonder and Sibley (1972) in an attempt to standardise references to those centres which are reasonably well characterised and to discourage premature assignment to those that are not. An attempt will be made, wherever possible, to separate the identity

of centres from any experimental manifestation attributed to them, such as absorption bands, and vice versa. In this way it is hoped that unnecessary confusion will be avoided. Names of centres will appear as upper case letters F, M, R, H, I, H_A, etc., and they are not to be confused with chemical species, such as hydrogen or iodine, which will always appear in square brackets, e.g. $|I_2^-|$, $|H^O|$. $|X|$ will be used to denote a halogen species and $|M|$ an alkali one. The sign appearing within the brackets denotes only the electronic charge of the defect configuration and not the net charge with respect to the perfect lattice. The latter will, for clarity, appear outside the brackets if necessary or as a superscript to the colour centre notation. For example, an F centre is a neutral species in the lattice, F^O , while an empty halogen vacancy is positively charged, F^+ ; $|X_2^-|$ is usually a self-trapped hole, $|X_2^-| + h = |X_2^-|$, and has a net positive charge associated with it $|X_2^-|^+$. However, $|X_2^-|$ can also represent a halogen atom incorporated interstitially into the lattice and bound to a neighbouring halogen ion sharing a single lattice site; in this case the defect is perfectly neutral, i.e. $|X_2^-|^O$.

2.3.2 Trapped electron centres

Historically the first group of colour centres to be investigated were the trapped electron centres, associated with halogen ion vacancies and their aggregates. The potential well introduced by absence of a lattice anion is particularly deep and represents an efficient trap for electrons, capable even of trapping more than one electron. Fig 2.1 illustrates principal absorption bands arising from electron excess

centres whose configurations are depicted in fig 2.3.

2.3.2.1 F centres

The F centre comprises an electron bound to an isolated halogen vacancy, with the electron spending most of its time in the vicinity of the six neighbouring cations. Unlike the empty vacancy, the F centre is electrically neutral, and this affects its mobility. The F centre ground state lies about three-quarters of the way from the valence to the conduction band, below the bound exciton states. The centre is stable (in the dark) at or below room temperature with a thermal dissociation energy ~ 2.3 eV (KCl).

Since the F centre is isoelectronic with the hydrogen atom, the excited states have been treated with hydrogen-like wave functions (Huang and Rhys 1950; Pekar 1953); but since the true wave functions are rather more compact than these, predictions on the hydrogen model are not entirely adequate. However, the assumptions of a single square well potential and a single lattice vibrational mode about the centre yield fairly accurate predictions of many F centre properties (Klick, Patterson and Knox 1964).

The optical absorption band associated with the F centre lies in the middle of the optical range, 2-5 eV, in most alkali halides (see Fig 2.1), and corresponds to excitation of the F centre electron from the ground state to a first excited state still lying below the conduction band. The most comprehensive data on the absorption spectra of the F centre are those of Dawson and Pooley (1969) who have expressed the temperature dependence of the absorption peak for all twenty alkali

halides in the form

$$E_p(T) = E_1 + E_2 \coth (E_3/2 kT) \quad (2.9)$$

The $\coth (1/T)$ term expresses the dependence of F band absorption on the lattice vibrational modes interacting with the defect electrons for the two electronic states. The form of (2.9) has the advantage that all absorption peaks can be extrapolated to zero temperature, where the absorption can be accurately described by a Mollwo-Ivey relation of the form

$$(E_1 + E_2) = 60.5 \pm 9.8 a^{-1.81 \pm 0.10} \text{ eV} \quad (2.10a)$$

for NaCl structure;

$$(E_1 + E_2) = 190 \pm 41 b^{-2.28 \pm 0.10} \text{ eV} \quad (2.10b)$$

for CsCl structure,

where a is the face centred cubic $\langle 100 \rangle$ lattice spacing in $\text{\AA}$ and b is the body centred cubic $\langle 100 \rangle$ lattice spacing multiplied by $\sqrt{3}$ to give an equivalent f.c.c. unit cell size.

The halfwidth H is related to the vibrational modes interacting with the ground and excited electronic states and has the general form (Markham 1959)

$$H(T)^2 = \sum_j \frac{\epsilon_j^2}{2 \omega_j} \coth \left(\frac{\hbar \omega_j}{2kT} \right), \quad (2.11)$$

where ω_j is the frequency of the j 'th vibrational mode associated with normal coordinate q_j for the ground state and ϵ_j is the variation of transition energy with q_j . Assuming only one interacting mode gives a reasonable fit to experimental data, i.e.

$$H(T)^2 = H(0)^2 \coth (E_4/2 kT), \quad (2.12)$$

with $H(0) = 0.169 \text{ eV}$ and $E_4 = 0.012 \text{ eV}$ (KCl).

The density of F centres can be related to the optical density of

coloration by Dexter's (1956, 1958) variation of Smakula's (1930)

formula

$$Ff = \frac{n m^* c}{2 \pi e^2 \hbar} \left(\frac{\epsilon_c}{\epsilon_{\text{eff}}} \right)^2 \int \mu(E) dE, \quad (2.13)$$

where F is the density of F centres in cm^{-3} , f is the so-called oscillator strength which relates to the probability of an optical transition, n is the index of refraction, m^* is the effective electron mass, ϵ_c is the average electric field in the crystal, ϵ_{eff} the field effective in inducing the transition, and $\mu(E)$ the absorption coefficient in cm^{-1} . For a sufficiently localised centre, such as the F centre, a Lorentz field is applicable, given by

$$\epsilon_{\text{eff}}/\epsilon_c = 1 + \left(\frac{n^2 - 1}{3} \right), \quad (2.14)$$

and for a Gaussian peak shape

$$\int \mu(E) dE = (\pi/4 \ln 2)^{1/2} \mu H. \quad (2.15)$$

If the absorption is expressed as the peak optical density (absorbance)

$$\mu' = \log_{10} (I_0/I), \quad (2.16)$$

where I_0 and I are respectively the incident and transmitted intensities, (2.13) becomes

$$F = 2.01 \times 10^{17} \frac{n}{(n + 2)^2} \frac{\mu H}{f z}, \quad (2.17)$$

where z is the depth of coloration in cm.

There is also associated with the optically-excited F centre an emission due to radiative decay of the first excited state of the F centre. The emission peak occurs with an energy considerably less than the optical excitation, in the infrared ~ 1 eV (KCl). The disparity, known as Stokes' shift, is essentially a consequence of the Frank-Condon principle. The

lifetime of the excited state is found to be $\sim 10^{-6}$ sec (Swank and Brown 1962, 1963). Emission is more efficient at low temperatures, since at higher temperatures the F centre electron may be thermally excited into the conduction band, with little thermal activation energy (~ 0.11 eV in KCl). For the same reason, F centres can be bleached at room temperature in the presence of light.

The β band, discovered by Delbecq, Pringsheim and Yuster (1951, 1952) appears superimposed on the low energy tail of the first fundamental absorption band and is also associated with the F centre. It corresponds to preferential production of perturbed exciton states in the vicinity of the F centre vacancy, i.e. optical excitation of a valence electron into an exciton level perturbed (localised) by the F centre (Fuchs 1958), producing a configuration similar to an F centre with an extra electron (F^- centre) and an associated hole shared by neighbouring halogen ions.

2.3.2.2 F^+ centre

The F^+ centre is an empty isolated halogen vacancy, i.e. an F centre without its electron or fully ionized F centre, which thus has a net positive charge. Its manifestation is the α band, first noted also by Delbecq, Pringsheim and Yuster (1951, 1952) and thought to be similar in origin to the β band viz. excitation of a valence electron into the unoccupied F centre state, introducing a configuration similar to an F centre with associated hole shared by neighbouring halogen ions (Dexter 1951). Bassani and Inchauspé (1957) investigated

an alternative model in which the excited state involved an excited electron situated on an alkali ion adjoining the vacancy. Timusk (1965), however, has produced good experimental agreement with the original Dexter model, and it is accepted that the absorption places an electron in the unoccupied F centre levels of the empty halogen vacancy.

Empty vacancies can be generated by irradiation at low temperatures (Rüchardt 1955; Chiarotti, Giuliani and Lynch 1960; Bauser and Lüty 1961; Kurz and Gebhardt 1964), but above 150 K the α band bleaches, presumably due to onset of vacancy diffusion and formation of divacancies or release of trapped interstitials (see §2.6). There is evidence that considerably more than half of the vacancies produced by irradiation below 50 K are empty (Klick and Patterson 1963; Ritz 1966), but most of these are unstable at higher temperatures (Itoh, Royce and Smoluchowski 1965a, b; Giuliani and Reguzzoni 1968). Lüty (1961a) has proposed the explanation that the presence of nearby halogen interstitials lowers the electron trapping cross section of anion vacancies; at low temperatures isolated interstitials are stable (see H centre below), but at temperatures above ~50 K these diffuse away to sinks and the higher electron trapping cross section returns, converting F^+ to $\dot{F}$ centres. There is evidence that production of at least some of the F^+ centres at low temperatures is structure sensitive and depends on divalent (electron trapping) impurities (Behr and Waidelich 1966; Giuliani et al. 1965); however, subsequent studies (Giuliani and Reguzzoni 1968) have shown that F^+ centre production is an intrinsic process as well.

2.3.2.3 F⁻ centre

The F⁻ centre results from an F centre trapping a second electron, thus bleaching the F band and producing a very broad F' band peaking at lower energies. The cross section for trapping has been measured ($7.5 \times 10^{-15} \text{ cm}^2$ in KCl: Glaser and Lehfeldt 1956). The second electron may be trapped in either the F⁻ ground state or an F⁻ excited state (Crandall 1965). Since the binding energy for this second electron is smaller, the F⁻ centre is unstable somewhat below room temperature; e.g. Pick (1958) found a half life on the order of seconds (in KCl) at 230 K. Although Pick did not find a unique activation energy for dissociation, analysis of Pick's data with this assumption yields thermal dissociation energies ~ 0.5 eV. Illumination into the F⁻ band ($\sim 2-3$ eV in KCl) produces a photocurrent due to electronic and not ionic conduction, which gives an indication of the optical ionization energy. The F⁻ band is unstable optically even at low temperatures, suggesting that the electron is excited directly into the conduction band. A point to emerge from study of the reconstruction of F centres from F⁻ centres is that one F⁻ centre can produce two F centres: one from the F⁻ centre ionized and the other from trapping of the electron released into the conduction band by a negative ion vacancy; the electron so released is trapped in the excited state, F* (Markham 1952).

2.3.2.4 F aggregate centres

The M, $\dot{R}_1$, R₂, N₁ and N₂ bands, all lying to the low energy side of the F band, correspond on the proposal of Pick (1960) and the evidence of van Doorn and Haven (1956) and van Doorn (1957, 1960, 1962) to F

aggregate centres; the M centre (for Molnar) corresponding to F_2 , R to F_3 , N to F_4 . These centres have been reviewed by Compton and Rabin (1964).

The M centre in f.c.c. alkali halides lies along $\langle 011 \rangle$ (Neubert and Susman 1965); in b.c.c. alkali halides along $\langle 100 \rangle$ (Lynch, Brothers and Robinson 1965). The two R bands apparently correspond to two transitions in the same centre, an equilateral triangle F_3 configuration (Silsbee 1965). The F_3 model for an R centre appears largely confirmed (Krupka and Silsbee 1966; Seidel, Shwoerer and Schmid 1965; Hughes and Runciman 1965; Pierce 1966). Recent theoretical (Stoneham 1966) and experimental (Schneider and Kabler 1966) work on the N bands indicate that the F_4 model is inconsistent, and that the N band may arise from an F_3 configuration different from an R centre, though Silsbee (1965) has shown that the R centre does have transitions in the N band.

At low temperatures the formation of aggregate centres appears a purely statistical production phenomenon (Rabin 1963; Wallis and Faraday 1964). F aggregate centres are in general stable in the dark at or below room temperature. At higher temperatures they become unstable, dissociating into F centres or other aggregate centres.

2.3.2.5 F impurity centres

The A band, discovered by Petroff (1950), appears on the low energy side of the F band and appears associated with it. Lütty (1961b) and Kojima, Nishimaki and Kojima (1961) have shown that the centre responsible, now designated an F_A centre, is an F centre with a foreign

alkali metal ion as a nearest neighbour, the F_A band corresponding to a perturbed transition along the line between the F centre and the impurity ion. A second manifestation, the B band, very nearly underlies the A band and corresponds to a perturbed transition of the F centre normal to the line between the F centre and the impurity ion.

F_A centres have been extensively reviewed by Lütty (1968); they are of interest to studies of F centre properties because they remove the annoying high symmetry of the F centre, introducing a permanent internal perturbation far stronger than applied external perturbations. In similar manner, an F centre similarly associated with a divalent metal impurity ion is denoted an F_2 centre.

2.3.2.6 U centres

Four types of impurity are associated with the hydrogen impurity in alkali halides which are the analogues of the halogen ion defects: the U centre which is an $|H^-|$ ion substituted for a halogen ion (alternatively, an F centre plus a hydrogen atom; Hilsen and Pohl 1933, 1938); the U_1 centre which is an interstitial $|H^-|$ ion; the U_2 centre which is an interstitial $|H^0|$ atom (Delbecq, Smaller and Yuster 1956); and the U_3 centre which is a substitutional $|H^0|$ atom (Virmani, Zimbrick and Zeller 1970). The absorption of the U band is similar to that of the F band but shifted to considerably higher energies (Lüpke 1934) (in KCl $\sim$ 5.85 eV). A further excited state appears to exist (Timusk and Martienssen 1963; Smith and Spinola 1965) as well as photoconductivity (Ueta, Hirai and Ikezawa 1961; Goto, Ishii and Ueta 1963). No luminescence is observed, the excited centre appearing to dissociate

instead (Delbecq, Smaller and Yuster 1956). There is evidence (Pooley 1966c; Hughes and Pooley 1971) that U centres are formed by capture of protons by F centres in proton-irradiated alkali halides, and that U centres can form from irradiation of alkali halides containing hydroxyl $|OH|$ impurities acquired through exposure to atmospheric moisture.

2.3.3 Trapped hole centres

It is reasonable to assume that a trapped hole centre represents the antimorph of the F centre, i.e. a hole trapped at a cation vacancy; in fact, early speculation (Seitz 1954) assigned just such a configuration to the trapped hole bands. These bands occur on the high energy side of the F band (towards the violet) and are thus termed V bands. Subsequent studies showed, however, that the V bands were associated primarily with halogen chemical ("molecular") species (Herish 1957a, b); two particularly well understood hole centres, the V_k centre and the H centre, have confirmed this notion. The V bands, first catalogued by Dorendorf (1951) and more recently by Ishii (1966) are illustrated in fig 2.2, and the hole excess centres responsible depicted in fig 2.4.

2.3.3.1 V_k centre

The V_k centre, first analysed by Castner and Känzig (1957) and Delbecq, Smaller and Yuster (1958) using EPR, is an $|X_2^-|^+$ molecular ion oriented along $\langle 110 \rangle$. No real imperfection is involved: a hole is self-trapped in the halogen valence band, the physical approach of the two halogen ions stabilising the centre. Two optical absorptions

are observed: one in the uv and one in the red.

It is of interest to know why a hole can be self-trapped in the lattice while an electron is not. Gilbert (1966) has analysed three major contributions to the trapping energy: (i) the localisation energy required to localise the hole or electron in the region of the lattice site; this energy is respectively $\frac{1}{2}$ the valence band or conduction band width, viz. -0.3 eV for a hole in KCl, -1.9 eV for an electron; (ii) lattice polarisation energy, gained by lattice relaxation around the trapping centre, +0.5 eV for a hole, +0.3 eV for an electron; (iii) bonding energy, +1.5 eV for $|\text{Cl}_2^-|$ because of strong molecular bonding, -0.3 eV for $|\text{K}_2^+|$ where molecular bonding is weak. The trapping energy is thus the sum of (i), (ii), and (iii) or, +1.5 eV for holes, -1.3 eV for electrons. Consequently, hole trapping at $|\text{Cl}_2^-|^+$ is reasonable, whereas electron trapping at $|\text{K}_2^+|^-$ is not. An alternative way of looking at the trapping is by use of the "polaron" concept (e.g. Lee, Low and Pines 1953) which assigns to an electron in the conduction band (or to a hole in the valence band) a "polaron mass" (Toyozawa 1954), which takes into account both the lattice and the electronic polarisations it introduces. The hole polaron has an essentially infinite effective mass, and its trapping state is of low symmetry (Knox and Teegarden 1968).

There is also associated with the V_k centre a recombination luminescence (Kabl α 1964; Murray and Keller 1965; Keller and Murray 1966; Delbecq, Ghosh and Yuster 1966; Hadley et al 1966) which implies destruction of the V_k centre by an electron and subsequent radiative decay of the resulting exciton state (Pooley and Runciman 1970).

Ramamurti and Teegarden (1966) have demonstrated that the V_k or $|X_2^-|^+$ centre may be converted to an excited $|X_2^{2-}|^*$ molecule directly by an exciton without release of a free electron. The alternative radiationless transition of this excited state is fundamental to the production of radiation damages in alkali halides by ionizing radiations and will be discussed in §2.4.

2.3.3.2 Interstitial halogen centres

The H centre, discovered by Duerig and Markham (1952) has been shown to be an $|X_2^-|^0$ halogen molecule ion located at a single halogen lattice site along $\langle 110 \rangle$ (Compton and Klick 1958). Since this is a crowdion configuration, the H centre may be viewed as four halogen nuclei distributed over three anion sites, i.e. $|X_4^{3-}|$, with the hole spending at most 10% of its time away from the central $|X_2^-|$ molecule, providing quantum mechanical bonding via the two outside collinear halogen ions (Känzig and Woodruff 1958). It is the form taken by the halogen interstitial in alkali halides (a halogen interstitial atom), and one of two primary complementary products of radiation damage (the F centre is the other) in alkali halide crystals (Faraday and Compton 1965).

Dienes, Hatcher and Smoluchowski (1967) have calculated the elastic distortions and lattice relaxations around the $|Cl_2^-|^0$ molecular ion in NaCl and KCl, and shown that, neglecting the third and fourth collinear halogen ions, the $\langle 111 \rangle$ orientation should be preferred to $\langle 110 \rangle$ by 0.2 eV; however, they conclude that it is necessary to take into account the spread of the holes onto the two outside collinear halogen ions, and this would explain the observed $\langle 110 \rangle$ axis. A $\langle 111 \rangle$ oriented

$|F_2^-|$ centre also has been detected in LiF (Chu and Mieher 1968).

Bachmann and Peisl (1970) have calculated the elastic distortions around a $\langle 110 \rangle$ oriented H centre in KBr and also the elastic interaction between two H centres and between an H centre and an F centre. These calculations will be discussed in §2.6 and §5.6 where H centre aggregation is considered.

The F^+ centre is also created, often preferentially, by very low temperature irradiation and appears to have its complement too, the I^- centre or interstitial halogen ion (Gebhardt 1962), thought to occupy a $(1/4, 1/4, 1/4)$ interstitial site (Klick and Patterson 1963; Kurz and Gebhardt 1964; Itoh, Royce and Smoluchowski 1965a). The I^- absorption band lies on the lower energy side of the α band and in KCl decreases commensurately with that band in the temperature range 11-30 K (Behr, Peisl and Waidelich 1967a, b; Giuliani and Reguzzoni 1968), suggesting that above 11 K the interstitial ion is increasingly mobile and annihilates F^+ centres via a $\langle 111 \rangle$ interstitialcy mechanism (Tharmalingam 1964). The presence of impurities stabilises the interstitial ion, preserving F^+ centres to higher temperatures and accounting for the apparent extrinsic dependence of F^+ centre production. If the suggestion of Lüty (1961a) is correct that F^+ centre electron trapping is reduced in the presence of a nearby interstitial ion, it is reasonable to assume that F^+ centres will be annihilated with even marginal interstitial ion mobility. The H centre becomes similarly unstable somewhere between 20 and 77K (Behr, Peisl and Waidelich 1967a, b; Giuliani and Reguzzoni 1968), and either annihilates F centres or is stabilised by clustering or at impurities.

2.3.3.3 II-impurity centres

The V_1 band was one of the first optical absorption bands attributed to trapped-hole centres, but has only recently been identified with any certainty. Delbecq et al. (1969) and Patten and Keller (1969) present strong evidence that the V_1 band arises from an II_A centre, i.e. an II centre associated with a monovalent alkali cation impurity. This configuration assumes importance in the inhibition of interstitial aggregation which is discussed in §2.8 and subsequently in §5.4 with particular reference to low temperature electron microscopical observations. Konitzer and Hersh (1967) have noted that the II_A centre forms as the H centre absorption band disappears (in KI ~ 55 K) indicating that mobile II centres can be trapped at monovalent impurity sites to form a stable defect configuration. There is now considerable evidence (Itoh and Saidoh 1969) that interstitials are indeed effectively trapped at monovalent cation impurities.

There is likewise experimental evidence that interstitials can be trapped at divalent cation impurities (Sonder and Sibley 1965; Itoh and Ikeya 1967; Ikeya and Itoh 1969). The resulting defects (divalent cation + anion interstitial) have been denoted H_2 centres by Itoh. Accompanying the divalent cation impurity is a corresponding cation vacancy (to maintain overall charge neutrality), and there is also evidence that anion interstitials may be trapped in these cation vacancies; this defect gives rise to the so-called Hayes-Nichols band (Hayes and Nichols 1960) and for uniformity has been denoted an H_V centre in the discussion of §2.8.3.

2.3.3.4 Interstitial aggregate centres

While the initial products of irradiation at very low temperatures are the F or F^+ centres and the H or I^- centres, prolonged irradiation produces the H' band (Faraday and Compton 1965); in addition the V_2 and V_3 bands are eventually produced at all temperatures (Konitzer and Hersh 1966). The V_4 band is also created by irradiation at low temperatures where the H centre becomes unstable (Kingsley 1962; Itoh 1966). Itoh et al. (1967) claim that, in fact, the H' band comprises several bands, one of which is the V_4 band. Since the H' band becomes predominant at heavy irradiation doses or with appreciable interstitial mobility, Itoh et al. conclude that the H' band arises from aggregated H centres, which is consistent with the suggestion of Itoh (1966) that the V_4 band arises from a neutral di-interstitial halogen molecule $|X_2^0|$ centre with a $\langle 100 \rangle$ symmetry axis.

White and Greene (1969) have estimated the binding energy of the molecule relative to two isolated H centres in NaCl at 1.5 eV and have shown that the $\langle 100 \rangle$ molecular axis orientation is at least stable. Dienes, Hatcher and Smoluchowski (1970) calculate rather less difference, but conclude the molecule is still more stable than two isolated H centres. Presumably several orientations of the neutral molecule are stable at liquid helium temperature, which accounts for the multiplicity of H' band structure; but at liquid nitrogen temperatures only the most stable is present to account for the V_4 band.

Konitzer and Hersh (1966) conclude from radiation and annealing experiments in KI that the V_2 and V_3 bands, which are produced proportionately with the F centre at all temperatures, are both associated with an

$|X_3^-|$ interstitial molecule. Herrmann and Pinard (1970b) have observed that the V_2 band in KCl saturates quickly and is replaced by the V_3 band which grows in proportion to the F centre all the way to F centre saturation. The present electron microscopical studies of interstitial clusters (§5.7) suggest a model (Hobbs, Pooley and Hughes 1972) for interstitial clusters starting with an $|X_4^{2-}|$ configuration along $\langle 110 \rangle$ stabilised by quantum mechanical binding.

2.4 Irradiation Energy Loss Rates

Ritz (1964) and Hughes et al. (1967) have conclusively shown that what is important for the production of defects in alkali halide crystals is really the amount of energy absorbed by the lattice and not the mechanism of the absorption. Efficient damage production has been demonstrated with x, γ , electron and proton radiations, and surprisingly even uv (Hall et al. 1964; Pooley and Runciman 1966).

The two requisites for displacement damage (resulting in vacancies, interstitials) are momentum and energy transfer; leaving aside the momentum requirement, we shall first consider the energy transfer. The fact that many forms of radiation are rather equally effective in producing damage contingent only on the amount of deposited energy suggests that the various operative inelastic scattering modes, from the higher order excitons through the high energy x-ray losses, eventually decay with sufficient frequency to a common excitation mode to produce damage by some singular displacement mechanism. Therefore, the individual

operative transfer modes are less important than the total integrated energy loss effected by them. Accordingly, rather simple isotropic theories can provide a reasonable estimate of the energy available for damage production.

We shall consider energy deposition for four commonly employed radiation types, including considerations of energy loss modes, energy deposition rate per quanta, range and practically attainable dose rates.

2.4.1 Energy loss modes

The response of a dielectric medium to external electromagnetic fields can be described by a dielectric function $\epsilon(k, \omega)$ whose real and imaginary parts are functionally related respectively to the index of refraction and absorption coefficients. If the dielectric function ϵ is of the form

$$\epsilon = \epsilon_1 + i \epsilon_2, \quad (2.18)$$

energy will be absorbed from radiation passing through the medium in proportion to an energy loss function described by the imaginary part of the dielectric function

$$-(\text{Im } \epsilon)^{-1} = \epsilon_2 / (\epsilon_1^2 + \epsilon_2^2) \quad (2.19)$$

The energy loss spectrum provides particularly revealing information about which energy loss processes are responsible for transfer of energy to the medium. Such information may be obtained directly from a measured absorption spectrum; or indirectly by reflection, making use of the Kramers-Kronig relations (Kramers 1947; Jahoda 1957; Pines 1963) to ascertain the real and imaginary parts of the dielectric constant.

Optical reflectivity spectra have been obtained by Ehrenreich and Philipp (1962) and Philipp and Ehrenreich (1963b) in the region 5-25 eV at room temperature. Further reflectivity determinations have been carried out more recently at low temperatures (e.g. Tomiki 1966; Roessler and Walker 1967).

Optical absorption spectra have been measured by Ely, Teegarden and Dutton (1959), Onaka (1961), Milgram and Givens (1962), and a comprehensive study at 10 K has been made by Teegarden and Baldini (1967). X-ray absorption measurements have been made by Best and Robins (1961). Electron energy loss measurements have been made by Best (1962), Pradal and Gout (1964), Creuzberg and Raether (1964a, b, 1965), Creuzberg (1965, 1966a), Keil (1966) and most comprehensively by Creuzberg (1966b), in the range 0-30 eV, the range of most probable energy loss corresponding to a transition from closed p orbital of the halide ion in the upper valence band to an electron orbital of s-like symmetry.

All these spectra exhibit first a primary exciton line at low energy, followed by a succession of strong exciton lines at progressively higher energies corresponding to exciton states degenerate with continuum states. The electron energy loss spectra show also broad peaks attributable to longitudinal plasma excitations (this appears to have been finally rather conclusively demonstrated by Creuzberg 1966b), although plasma excitations appear to be less probable than in for example aluminium, because of the competing single electron excitations. Excitonic excitations are particularly probable because the smaller dielectric constant of alkali halides ($\sim 1/10$ that in semiconductors) and the large lattice parameters imply large Coulomb forces between electron and hole and high

probability of tightly bound localised states. The classical model for plasma oscillations in a conductor may be extended to an insulator by regarding the (valence) electrons as bound to equilibrium sites by elastic forces exhibiting a natural frequency ω_o . The plasmon oscillation frequency Ω is then given by

$$\Omega = (\omega_o^2 + \omega_p^2)^{\frac{1}{2}} \quad (2.20)$$

where ω_p is the free electron plasmon frequency calculated on the basis of the effective valence electron density (Philipp and Ehrenreich 1963a). Direct measurements of the mean free path length λ for inelastic scattering processes (Creuzberg and Raether 1964a) yield $\lambda_p \sim 500-1000$ nm for the plasma loss, in agreement with dielectric theory (Creuzberg and Raether 1964b). This is, of course, $\sim$ the thickness of useful films in electron microscopy. Therefore, all electrons will have suffered on average at least one plasmon loss in passing through such a thin film.

Previous electron energy loss spectra have been measured with polycrystalline powder or evaporated films of grain size comparable to or smaller than the inelastic scattering mean free path, presumably contributing large surface effects. It was possible in the course of this study to obtain the spectra of fig 2.5 from single crystal films, with of course, only two continuous surfaces. A Siemens Elmiskop I electron microscope fitted with a Mollenstedt velocity analyser (Cundy 1967) was used to obtain the spectra and adapted to take the special specimen chamber and loading lock facilities described in §3.4. These experiments are discussed in §5.3.3.3.

2.4.2 Energy loss rates from ionizing radiations

2.4.2.1 Electron irradiation

We consider both a 100 keV electron beam as obtained in a transmission electron microscope and the 400 keV electron beam of a Van de Graff generator.

(a) Ionization processes

A relativistic energy loss expression for ionization processes has been derived from Bethe (1933) based on the electron-electron scattering cross section of Möller (1932) and the assumption that velocity of the electron is large compared to the orbital electron velocities,

$$-\frac{dE}{dz} (E)_i = \frac{2\pi e^4}{m_e v^2} N_i Z_i \left\{ \ln \frac{m_e v^2 E}{2\bar{I}^2 (1-\beta^2)} - (2/(1-\beta^2) - 1 + \beta^2) \ln 2 + (1-\beta^2) + \frac{1}{8} \{1 - \sqrt{(1-\beta^2)}\}^2 \right\}. \quad (2.21)$$

dE is the energy lost per electron in traversing thickness dz of a crystal containing density N_i ions each with Z_i electrons, E is the kinetic energy of an incoming electron of velocity v , $\beta = v/c$, and m_e is the electron rest mass. $\bar{I}$ is a mean ionization potential averaged over all ionization processes; a reasonable choice for $\bar{I}$ is that determined by Bakker and Segrè (1951) from stopping power measurements,

$$\bar{I} = kZ, \text{ where } 9.1 < k < 12.7 \text{ for } Z > 6. \quad (2.22)$$

In any event, (2.21) is relatively insensitive to choice of $\bar{I}$ because $\bar{I}$ enters logarithmically.

For non-relativistic electrons, $E \ll mc^2$, (2.21) reduces to

$$-\frac{dE}{dz} (E)_i = \frac{2\pi e^4}{E} N_i Z_i \ln \frac{E}{\bar{I}} \sqrt{\frac{e}{2}} \quad (2.23)$$

which is the result from Mott's (1930) non-relativistic electron scattering cross section. In the limit of high energy, $E \gg mc^2$,

$$-\frac{dE}{dz} (E)_i = \frac{2\pi e^4}{m_e c^2} N_i Z_i \left\{ \ln \frac{E^3}{2 m_e c^2 I} + \frac{1}{8} \right\}. \quad (2.24)$$

The total stopping power for a crystal containing more than one species is

$$-\frac{dE}{dz} (E) = - \sum_i \frac{dE}{dz} (E)_i. \quad (2.25)$$

This stopping power has been plotted in fig 2.6 for several alkali halides for incident electron energies from 40 keV to 4 MeV.

It is often more convenient to determine $dE/dz(z)$ to provide information about the uniformity of energy loss and incident electron range; $dE/dz(z)$ for KCl is plotted in fig. 2.8 for both 100 keV and 400 keV electrons.

If the efficiency of defect production with energy deposited $\partial N / \partial E$ is known, the rate of defect production $\dot{N}$ per unit volume can be obtained from

$$\dot{N} = \phi \left| \frac{dE}{dz} \right| \left| \frac{\partial N}{\partial E} \right| \quad (2.26)$$

where ϕ is the electron incidence rate.

Determinations of $\partial N / \partial E$ will be discussed later in §2.5.3.

(b) Knock-on displacements

If the incident electron energy is high enough to transfer to the ion nuclei the energy $E' > E_d$, the isotropic displacement threshold for ionic displacements (~ 25 eV), we must consider also the cross section per ion for scattering from the nucleus, which for each ion species is given by (Dugdale and Green 1954)

$$\sigma_{N,i} = 4\pi a_H^2 \frac{E_R^2}{m_e^2 c^4} Z_i^2 \left(\frac{1-\beta^2}{\beta^4} \right) \left\{ \frac{E'_i}{E_d} - 1 - (\beta^2 + \pi\alpha\beta) \ln \frac{E'_i}{E_d} - 2\pi\alpha\beta \left(\sqrt{E_m/E_d} - 1 \right) \right\} \quad (2.27)$$

where a_H is the Bohr radius (0.053 nm), E_R the Rydberg energy (13.6 eV), $\alpha = Z_i/137$, and $E'_i = 2E(E+2mc^2)/M_i c^2$ is the maximum energy that can be imparted to the ion nucleus. The primary knock-on ions may have sufficient energy imparted to them to displace further ions, and if we sum over all displacements and all ions, we have, using the approach of Kinchin and Pease (1955)

$$\dot{N} = \sum_i N_i \sigma_i \phi \left(1 + \ln \frac{E'_i}{E_d} \right). \quad (2.28)$$

It is often convenient to compare the damage rates of the two processes in terms of displacement cross sections. For this comparison we define a mean pseudo-cross section (per ion) for displacement by ionization

$$\bar{\sigma}_I = \frac{1}{N_o} \frac{\partial N}{\partial E} \sum_i \frac{dE}{dz_i}, \quad (2.29)$$

for comparison with the average nuclear displacement cross section (per ion)

$$\bar{\sigma}_N = \frac{1}{2} \sum_i \sigma_{N,i} \left(1 + \ln \frac{E'_i}{E_d} \right). \quad (2.30)$$

$\bar{\sigma}_I$ is typically $\sim 10^{-20} \text{ cm}^2$, whereas $\bar{\sigma}_N$ scarcely exceeds 10^{-23} cm^2 even at 4 MeV. In fact, incident energy damage thresholds are generally $> 350 \text{ keV}$. Therefore, it is reasonable to expect that electron irradiation damage in alkali halides arises almost exclusively from ionization processes even at high energies.

So far as range is concerned, we can evaluate (2.27) for the smallest energy transfers appropriate to, say, phonon modes and find that the resultant energy loss is still negligible compared to the ionization loss of (2.21). It is, in fact, a general property of energetic radiation (e.g. Bethe and Ashkin 1953) that principal determinants of rates of energy loss and thus range are interactions with electrons and not nuclei.

It will be seen from fig 2.8 that energy loss rate is rather uniform over the total range ($\sim 10^7$ eV cm⁻¹); this is a consequence of the long range Coulomb interaction applicable to charged particle collisions, which renders most probable low energy loss events. This uniformity of energy deposition is an important property, since it implies a uniform damage density for representative electron microscope observations and uniform coloration for optical accurate density measurements. However, because of their small size electrons are subject to considerable straggling at the very end of their range, resulting in a rather uncertain energy loss and range in this region. An attempt to depict this effect has been made in fig. 2.8. One way to minimise the effects of straggling is to use a crystal of thickness either slightly less than the maximum range indicated or to irradiate a crystal of thickness $\sim$ twice the range indicated from either side.

2.4.2.2 Proton irradiation.

We shall consider here 400 keV protons which can be as conveniently produced in the Van de Graff generator as 400 keV electrons.

(a) Ionization losses

The stopping power formula analogous to (2.21) is derived from Bethe's (1932) expression for incident light nuclei

$$-\frac{dE}{dz} (E)_i = \frac{4\pi e^4}{m_e v^2} \sum_i N_i Z_i \left\{ \ln \frac{2m_e v^2}{\bar{I}} - \ln(1-\beta^2) - \beta^2 \right\} \quad (2.31)$$

Protons of 400 keV are non-relativistic, so (2.31) reduces to

$$-\frac{dE}{dz} (E) = \frac{2\pi e^4}{E} \sum_i N_i Z_i \frac{m_p}{m_e} \ln \left(\frac{4E}{\bar{I}} \frac{m_e}{m_p} \right), \quad (2.32)$$

where m_p is the proton mass and m_e the electron mass. Evaluated for 400 keV protons, this loss rate is as expected larger than for electrons ($\sim 5 \times 10^8$ eV cm⁻¹) and extends over rather shorter range, fig. 2.8.

The corresponding ionization mean pseudo-cross section (per ion) given by the same expression as (2.29) is $\sim 8 \times 10^{-18}$ cm².

(b) Knock-on displacements

The cross section for primary knock-on displacements is given by Nielsen (1956) for each ion

$$\sigma_{N,i} = 4\pi a_H^2 Z_i^2 \left(\frac{m_p}{M_i} \right) \left(\frac{E_R}{E E_d} \right)^2 (1 - E_d/E'_i) \quad (2.33)$$

where M_i is the ion mass. The total displacement production is then

$$\dot{N} = \sum_i N_i \sigma_i \phi \ln(E'_i/E_d), \quad (2.34)$$

and the average total displacement cross section per ion

$$\bar{\sigma}_N = \frac{1}{2} \sum_i \sigma_i \ln(E'_i/E_d). \quad (2.35)$$

For 400 keV protons, $\bar{\sigma}_N \sim 3 \times 10^{-19}$ cm² or 25 times smaller than that for ionization. This 4% contribution may be dismissed, except at high doses.

Then, the trapped proton itself introduces U centres upon being trapped at

F centres and must be taken into account.

2.4.2.3 X rays

X rays have long been popular as a readily available source of radiation for production of colour centres in alkali halides. However, because of uncertainty in energy distribution in an x-ray beam, the non-uniform energy loss rate and the presence of absorption edges, energy deposition cannot be accurately characterised without dosimeter measurements (Ritz 1964) and spectral analysis.

Fig 2.7 illustrates the energy distribution of the continuous x-ray spectrum of tungsten bombarded by 50 keV electrons, plotted against quantum energy rather than the more usual wavelength which can give a distorted impression of the energy contribution by low energy quanta. The energy distribution function for total x-ray production can be derived analytically for thick targets by applying the Thomas-Whiddington law, and has the form (Kramers 1923)

$$I(E) dE = \frac{4 \pi e^2}{9\sqrt{3} m_e c^3} Z (E_0 - E) dE \quad (2.36)$$

where E_0 is the energy at the short wavelength limit, i.e. the incident electron energy. The efficiency of x-ray production for thick targets is

$$\text{eff} = \frac{2\pi}{9\sqrt{3}} \frac{e^3}{m_e h c^3} Z V \sim 9.2 \times 10^{-10} ZV \quad (2.37)$$

where V is the accelerating potential in volts and Z the target atomic number. Efficiencies for x-ray production are very low, typically below 1%, and this is spread over the solid angle 2π above the target.

The absorption of x rays is attributable to three mechanisms:

the photoelectric effect (ionization of innermost electron shell, for which the cross section is largest); the Compton effect (a quantum mechanical scattering of x rays by electrons); and electron-positron pair production. Pair production is strictly a high energy process and will not be considered here. The photoelectric effect is the primary mechanism of energy loss at low x-ray energies (<50 keV). The Compton scattering is about comparable to the photoelectric production for the very lightest alkali halides for 50 keV quanta, but only a small contribution for heavier ions or slightly less energetic quanta. In photoelectron production an x-ray quantum loses its entire energy in the event. Intensity and energy are thus statistical quantities (there being a unique energy associated with each quantum); both can be represented in the form

$$\begin{aligned} I &= I_0 \exp(-\mu z) \\ E &= E_x \exp(-\mu z) \end{aligned} \quad (2.38)$$

where E_x is the integrated incident beam energy and E is understood to mean energy available in the beam; μ is an absorption coefficient representing all absorption processes. The energy loss rate is thus a function of penetration only, and can be obtained from (2.38) by differentiation,

$$\frac{dE}{dz}(z) = -\mu E_x \exp(-\mu z). \quad (2.39)$$

In a crystal of more than one atomic species the absorption coefficient may be obtained from

$$\mu = \frac{1}{V_c} \sum_i N_i \mu(a)_i, \quad (2.40)$$

where V_c is the volume of the unit cell containing N_i atoms (ions) of

each kind, $\mu(a)_i$ are the atomic absorption coefficients appropriate to each atom (ion), and the summation is carried out over the unit cell.

The largest contribution to μ will be from ionization of K shell electrons in light elements. For non-relativistic quanta the cross section for K shell ionization is (Heitler 1936)

$$\sigma_{K,i} = \left\{ \frac{8\pi e^4}{3m_e^2 c^4} \right\}^{4/2} \frac{Z_i^5}{137^4} \left(\frac{1}{\gamma} \right)^n \quad (2.41)$$

where $\gamma = E/m_e c^2$, $n \sim 3$ (8/3 for low energies and 7/2 for high energies) and the absorption coefficient $\mu = \sum_i \mu_i \sigma_{K,i}$. Alternatively, μ can be expressed empirically in the form

$$\mu = \rho \sum_i (C_i \lambda^3 - D_i \lambda^4 + \sigma_c N_i Z_i) \quad (2.42)$$

where λ is the x-ray wavelength, C_i and D_i are constants for each element catalogued in the International Tables for X-Ray Crystallography (1962), and σ_c is the cross section for Compton scattering (see §2.4.2.4).

The total rate of energy loss $\frac{dE}{dz}(z)$ for a beam of energy distribution $I(E)$ is then given by

$$\frac{dE}{dz}(z) = \int_0^E I(E) \mu(E) E \exp(-\mu Z) dE. \quad (2.43)$$

The integral (2.43) was evaluated numerically using the energy distribution in fig. 2.7 for tungsten at 50 kV with $\mu(E)$ evaluated from (2.42) for KCl. The total energy loss rate, plotted on fig. 2.8, is expressed as loss rate per most probable quantum (25 keV) so that it can be directly compared with particle energy losses. The "range" (for 1% of initial loss rate) is about 5 times larger than the 100 keV electron range (approximately 0.5 mm), but the loss rate falls off rather quickly after about 10μ . Ideally the loss rate should be corrected slightly to exclude

the contribution of fluorescent radiation and photoelectrons which leave the crystal. Strongly absorbed quanta with energies just above the K absorption edges of each ion, in this case K and Cl (3.5 and 2.7 KeV), contribute a disproportionate share of damage production within their very limited range ($\sim 1 \mu\text{m}$). These energies are easily removed from the spectrum by a sufficiently thick x ray tube window (Hall, Pooley and Wedepohl 1964); an attempt has been made to depict their contribution for the case of unfiltered x rays in fig. 2.8.

2.4.2.4 γ radiation

A typical γ quantum is that of ^{60}Co $\sim 1 \text{ MeV}$ (in fact, the AERE Harwell " γ pond" has an average γ quantum $\sim 0.8 \text{ MeV}$). For these high energies, energy loss from the photoelectric process becomes negligible compared to that from Compton scattering. Pair production is appreciable only well above 1 MeV . The maximum energy that can be transferred from the γ quantum is

$$E' = \frac{2 E_{\gamma}}{m_e c^2 + 2 E_{\gamma}} \quad (2.44)$$

which approaches the incident γ energy for $E_{\gamma} \gg m_e c^2$.

The differential cross section for Compton scattering is given by the Klein-Nishina formula (Klein and Nishina 1929)

$$\frac{d \sigma_c}{d \Omega} = \frac{e^4}{2 m_e^2 c^4} \frac{(1 + \cos^2 \theta)}{\{1 + \gamma(1 - \cos \theta)\}^2} \left\{ 1 + \frac{\gamma^2 (1 - \cos \theta)^2}{(1 + \cos^2 \theta) \{1 + \gamma(1 - \cos \theta)\}} \right\} \quad (2.45)$$

where $\gamma = E_{\gamma}/m_e c^2$. Transforming (2.44) to energy coordinates,

$$\frac{d\sigma_c}{dE} = \frac{\pi e^4}{m_e^2 c^4 E E_\gamma} \left\{ 1 + \left(\frac{E}{E_\gamma}\right)^2 - \frac{2(\gamma+1)}{\gamma^2} + \frac{1+2\gamma}{\gamma^2} \left(\frac{E}{E_\gamma}\right) + \frac{1}{\gamma^2} \left(\frac{E}{E_\gamma}\right)^2 \right\} \quad (2.46)$$

which is valid for $\frac{1}{1+2\gamma} \leq \frac{E}{E_\gamma} \leq 1$. The total cross section per electron scattering centre is then

$$\sigma_c = \frac{\pi e^4}{m_e^2 c^4 \gamma} \left\{ \left(1 - \frac{2(\gamma+1)}{\gamma^2}\right) \ln(2\gamma+1) + \frac{1}{2} + \frac{4}{\gamma} - \frac{1}{2(2\gamma+1)^2} \right\} \quad (2.47)$$

which reduces to

$$\begin{aligned} \sigma_c &= \frac{8\pi e^4}{3m_e^2 c^4} (1 - 2\gamma + \frac{26}{5} \gamma^2 + \dots) \text{ for } \gamma \ll 1 \\ \sigma_c &= \frac{8\pi e^4}{3m_e^2 c^4} \left(\frac{3}{8\gamma}\right) (\ln 2\gamma + \frac{1}{2}) \text{ for } \gamma \gg 1. \end{aligned} \quad (2.48)$$

Comparison with (2.41) shows why Compton scattering is not significant at low energies ($\gamma \ll 1$), and likewise the photoelectric process at high energies ($\gamma \gg 1$).

The absorption coefficient is simply the total cross section for all electrons,

$$\mu = \sum_i N_i Z_i \sigma_c. \quad (2.49)$$

By reasoning similar to (2.39), we have for the energy loss rate

$$\frac{dE}{dz}(E, Z) = -\mu E_\gamma \exp(-\mu z) \quad (2.50)$$

which differs from (2.39) in that the energy E of the γ quantum can range over all values up to E' , whereas the x ray quantum had a unique energy. If we restrict ourselves to the range over which (2.47) is valid, i.e. $E > E_\gamma / (1+2\gamma)$, (2.50) is nearly independent of energy for this region, and we calculate for a 1 MeV quantum $\sigma_c \sim 2 \times 10^{-25} \text{ cm}^2$, $\mu = 0.13$ and $\frac{dE}{dz}(\text{o}) \sim 10^5 \text{ eV cm}^{-1}$.

Furthermore, dE/dz is uniform (to within a factor of 2) over the 6 cm range of applicability for which $E > E_\gamma/5$, and is virtually flat over the first 1 cm, fig. 2.8. However, the energy loss rate is considerably smaller than for other forms of radiation, and since γ flux is also small, one pays for the penetration/uniformity with vastly increased irradiation times.

2.4.2.5 Radiation efficiencies

A comparison of the time rate of energy deposition (eV sec^{-1}) is also meaningful, since the practical flux limits attainable for these radiations vary enormously. A commonly used unit of energy deposition is the Rad.

$$1 \text{ Rad} \equiv 10^2 \text{ erg g}^{-1},$$

and typical energy deposition rates are $\sim \text{MRad h}^{-1}$. Table 2.3 compares typically attainable time rates of deposition under various irradiating conditions. It must be emphatically noted that the energy deposition rates for typical operating conditions on the electron microscope are orders of magnitude above those commonly attained in other irradiation arrangements. This has important consequences for electron microscopy since, as can be seen from Table 2.3, saturation damage normally occurs in alkali halides like KCl at $\sim 1000 \text{ MRad}$; this level is attained in a fraction of a second in the electron microscope beam and is consequently unavoidable. The severity of this condition is discussed further in §2.5.3.

The 400 keV electron and proton irradiations as produced in a Van de Graff generator are convenient for producing useful damage con-

centrations in reasonable times. Proton irradiation is rather more useful for optical density measurements because its short range keeps the optical density within reasonable limits (Pooley 1966c) and absence of straggling keeps coloration uniform. Electron irradiation is more convenient for external irradiation of crystals intended for electron microscopy, because the increased range permits relatively uniform irradiation of crystals ~1 mm thick, a convenient starting size for foil preparation, (see §3.2). Also the energy loss rate is sufficiently high and the dose rate so easily adjustable that a wide range of dose rates (10^{16} - 10^{20} eV cm⁻³ sec⁻¹) is available for dose rate dependence experiments.

γ irradiation involves long exposure times, but is comparatively inexpensive and suitable for providing the large irradiated specimens necessary for irradiation hardening experiments. X rays do not exhibit sufficiently uniform energy loss rates over this size specimen and are in any event slow compared with 400 keV electrons which exhibit a similar range of much more uniform energy loss.

2.5 The Damage Mechanism

2.5.1 Defect production models

Numerous models have been proposed to account for the production of F centres in concentrations above the thermal vacancy equilibrium by ionizing radiations of energies insufficient to produce direct displacement. Seitz (1951) suggested the absorption of excitons at dislocation cores might cause movement of dislocation jogs to produce vacancies by

the mechanism outlined in §2.2.4. McLennan (1951) supposed that a halogen atom produced from a halide ion by ionization would wander off interstitially with thermal vibrations. Varley (1954a, b) proposed a double ionization of the halogen ion, so that it is removed as a positive ion by the lattice Madelung energy; subsequent electron capture would then produce an F centre and interstitial halide atom. Klick (1960) suggested that double ionization of a single halide ion or single ionization of two adjacent halide ions would lead to the production of a halogen molecule occupying adjacent halide ion sites; if the molecule were localised at one of these sites by jump of a nearby halide ion into the other site, a vacancy and interstitial would be formed converting by electron capture to an F centre and an H centre. Dexter (1960) used a band model to show that a locally doubly ionized state could not exist more than 10^{-15} sec before hole migration, and therefore could not lead to displacement. Smoluchowski and his colleagues (Smoluchowski and Wiegand 1961; Howard, Vosko and Smoluchowski 1961; Royce, Sharma and Smoluchowski 1962) criticised Dexter's use of a band model for holes in alkali halides and further proposed that the cross section for ionization was sufficiently large through an Auger emission process. Seitz (1961) proposed that a self trapped exciton may spontaneously generate a halogen ion vacancy and interstitial halogen ion analogous to the F^+ centre that is created when a U centre is excited with light at low temperatures. Williams (1962) calculated both electronic and atomic relaxation times of two adjacent ionized halide ions in the tight-binding approximation and concluded that appreciable atomic motion

could occur before hole separation; furthermore, he indicated the necessity for a replacement collision sequence along $\langle 110 \rangle$ to separate the vacancy and interstitial sufficiently far to prevent recombination. Balarin (1964) proposed the removal of an atom by the recoil energy given during the emission of a photoelectron, but the energies involved are far too small to initiate the replacement collision sequence necessary for interstitial-vacancy separation.

All of these models, apart from the Seitz (1951) mechanism, involve an actual high energy ionization process, viz. generation of photoelectrons, and cannot sensibly account for the sensitivity of defect production to impurities (Sibley, Sonder and Butler 1964) or temperature (Hall, Pooley and Wedepohl 1964), or for defect production by non-ionizing radiation viz. 6-10 eV ultraviolet radiation (Parker 1961; Hall et al. 1964; Pooley and Runciman 1966; Konitzer and Hersh 1966; Goldstein 1967). There is no evidence that existing lattice defects are necessary for damage production, invalidating the Seitz mechanism. In fact, the findings of this electron microscopical study clearly demonstrate that defect production is amply efficient in perfect crystal regions.

2.5.2 Excitonic mechanism: Pooley-Hersh model

To provide for these observed damage features, Pooley (1965, 1966a) and Hersh (1966) independently proposed that the non-radiative decay of an exciton state in the perfect lattice could impart sufficient momentum to a halogen ion to initiate the collision sequence necessary for displacement. That is, the model entails a strictly non-ionization

mechanism by which the electronic state of a halogen ion raised to an exciton level can lead to ionic displacements without ever going through the conduction band. The exciton configuration responsible is the $|X_2^-|^*$ molecular ion, i.e. a V_k centre (a hole self-trapped in the valence band) with a bound electron. Any radiation quanta having sufficient energy to create this exciton state, or indeed, to excite states of higher energy or free electrons, can result in displacement damage, since both Kabler (1964) and Murray and Keller (1965) have shown that electron-hole pairs in alkali halides recombine via states having the configuration of an electron bound to a V_k centre. Indeed, Keller and Patten (1969) have recently observed by EPR techniques Frenkel defect production accompanying post irradiation electron-hole recombination. The effect of impurities can be explained in that they provide alternative electron trapping sites to V_k centres, while the temperature dependence arises from relative efficiencies of the radiative and non-radiative modes of exciton decay.

2.5.2.1 The electron-hole recombination

Fig. 2.9 provides a configuration coordinate representation of the energy states of the V_k and associated electron which it subsequently traps as a function of the separation of the two halide ions forming the V_k centre for three halogen ion species. In the V_k ground state (upper curve) the two ions constituting the $|X_2^-|$ configuration are closer together than the normal $\langle 110 \rangle$ ion separation due to the molecular bonding introduced by the trapped hole. Upon trapping the electron the V_k centre finds itself in the excited $|X_2^-|^*$ state (lower curves) which

characteristically exhibits a surprisingly long lifetime ($\sim 10^{-8}$ sec in most alkali halides: Vasil'eva and Morgenshtern 1960; Ahrenkiel 1966; Pooley and Runciman 1970). There are four possible modes of decay for this excited state: (i) the electron and V_k centre can re-dissociate with an activation energy E_d ; (ii) the electron-hole pair (exciton) can together migrate with an activation energy E_m to some alternative recombination site, such as an impurity; (iii) recombination can proceed radiatively with emission of luminescence of energy E_r ; (iv) an internal non-radiative transition can occur with thermal activation energy E_{th} , imparting momentum to either of the two halogen ions, the two ions moving apart with kinetic energy E_{nr} ($\sim 5-10$ eV). Pooley (1966a) has made a fundamental calculation of the ratio $R(T)$ of non-radiative to radiative transition probabilities, based on the treatment by Huang and Rhys (1950) of radiationless transitions in the F centre, using one-phonon electric dipole transitions. He finds that for some alkali halides, such as KCl, there is little change in this ratio over the entire temperature range 0-300 K; while for others, for example NaCl and notably KI, the non-radiative transition probability decreases markedly at lower temperatures. Pooley and Runciman (1970) have made corroborative measurements of the competing luminescence process and compared these with F centre production efficiencies over the same temperature region (Hughes et al. 1967; Dawson and Pooley 1969), noting an anticorrelation between luminescence and F centre production, that is, between radiative and non-radiative transitions. This provides substantial support for the model of damage production based on non-radiative exciton decay.

2.5.2.2. The replacement collision sequence

It is not sufficient merely to impart to a halogen ion an energy E_{nr} in order to form a defect; there must be some mechanism for the removal of the ion sufficiently far from the vacancy to prevent recombination, a requirement largely ignored by Hersh (1966) but recognised by Pooley (1966b) who attempted calculation of the threshold energy necessary for such separation. The mechanism Pooley chose was the $\langle 110 \rangle$ replacement collision sequence, illustrated in fig. 2.10, involving close-packed rows of halogen ions; this model is particularly attractive because the electron-hole recombination cited above imparts momentum to the two halogen ions comprising the V_k centre in the $\langle 110 \rangle$ direction. Thus the collision is a focussed one and likely to proceed at energies considerably smaller than that necessary for isotropic displacement, where threshold is probably in the region 25-30 eV, clearly in excess of the energy contribution by non-radiative electron-hole recombination. The $\langle 110 \rangle$ sequence also provides the equal mass condition necessary for maximum energy transfer and minimises the Coulomb energy barrier, at the same time effecting separation of the vacancy and interstitial quickly enough ($\sim 10^{-12}$ sec) to prevent spontaneous recombination (Balarin 1964).

One technique by which to establish the energy threshold necessary to initiate a collision sequence is by computer simulation (e.g. Oen, Holmes and Robinson 1963). The principal difficulty in simulating a collision sequence is in the choice of a suitable potential; a serious difficulty for low energy collision processes is accounting for many-body effects. In his first attempt, Pooley used a Born-Mayer or Born-Mayer-Verwey potential and a linear model, representing the effect of other

ions not along the $\langle 110 \rangle$ line by a periodic potential; polarisation was neglected and the halogen atom was assumed to move away as an ion, leaving behind an empty vacancy (F^+) which subsequently captured an electron to become an F centre. This initial approach yielded very low $\langle 110 \rangle$ replacement thresholds, $\sim 4-10$ eV, except for very closely packed halogen ions in LiBr, LiI, and NaI. Torrens and Chadderton (1967) produced similar calculations for more realistic two- and three-dimensional models in NaCl and KCl and found that the calculated thresholds were not greatly affected by the form of the potential; however, thresholds calculated were very large $\sim 25-30$ eV. At the same time Rahman and Pooley (Hughes et al. 1967) made a comprehensive simulation for all f.c.c. alkali halides using a three-dimensional model, a Born-Mayer potential and this time including polarisation effects. Replacement thresholds nevertheless remained stubbornly in the 20-30 eV range.

The above simulations assumed that the primary products of the replacement sequence are F^+ : I^- which transform upon electron capture in $\sim 1 \mu s$ to F:H. Ueta et al. (1969) and Hirai et al. (1971), however, have shown from pulsed high flux irradiation damage experiments that F and not F^+ centres are a primary product and are formed with 20 ns of the time of irradiation ($\sim$ excited state lifetime). Hatcher and Pooley (1970) have subsequently modified the simulation model so that F:H are the primary products. The modified replacement sequence is indicated pictorially in fig. 2.10. The important feature of the revised model is that a halide ion ejected with 5-10 eV along a $\langle 110 \rangle$ direction will be ionized by the electric field of the vacancy when it reaches a point about midway to the site of the adjacent halide ion; the second ion will

in turn be ionized in moving towards the third, and so on. The replacement sequence thus proceeds accompanied by hole tunnelling which reduces the energy requirement considerably, since each knock-on ion spends a considerable fraction of its propagation time as a neutral atom experiencing fewer repulsive constraints. Smoluchowski et al. (1971) have calculated the total energy requirement for the modified sequence to be 5-7 eV in KCl, if the ejected Cl^0 atom immediately forms an H centre with the next Cl^- ion. The energy available from the V_k centre-electron recombination is 9 eV (6.4 eV from the non-radiative electron-hole recombination, 2.6 eV from potential energy of the two Cl^- ions after the Cl_2^- bond is broken), most of which is available for the replacement sequence if this energy is shared unequally between the Cl^- ions. An analysis of V_k centre dynamics suggests that such assymmetric energy distribution is likely. Thus we see the electronic structure of the alkali halide lattice is invoked in two separate ways to explain efficient damage production by ionizing or near-ionizing radiation.

There is good evidence that a replacement collision sequence involving considerable momentum does indeed take place rather than, for example, the crowdion diffusion process favoured by Konitzer and Herish (1966). Townsend and Kelly (1968) and Townsend and Elliott (1969) have shown that low energy electron irradiation of alkali halide surfaces is accompanied by efficient sputtering. F centre production by electron-hole recombination is not observed in alkaline earth oxides (MgO , CaO) where calculated replacement thresholds are very high, ~ 40 eV (Pooley 1966b). Furthermore, the replacement sequence model accounts for the difficulty

in coloration at room temperature of those alkali halides with exceptionally large anion/cation size ratios (LiI, NaI, LiBr, NaBr), since threshold energies for a replacement sequence rise with increasing anion size. The reduction of F centre production in mixed crystals (Arends, Den Hartog and Dekker 1965; Still and Pooley 1969) appears to correlate closely with the expected disruption of a replacement collision sequence from different anion masses (for mixed halogens) or from deflection of the anion collision train by dissimilar adjacent cations (for mixed alkalis). Finally, it will be shown by electron microscope observation in §5.4 that relatively large, widely-spaced interstitial halogen clusters can nucleate and grow in pure alkali halides at temperatures as low as 5 K where interstitial halogen bulk diffusion is absent; this observation can be adequately explained only if halogen interstitials are given significant momentum (extending over an appreciable number of lattice sites) in the initial damage process.

2.5.3 Frenkel pair production efficiency

Creation of Frenkel defect pairs in alkali halides is characterised by two production regimes, first distinguished by Gordon and Nowick (1956): a quickly saturating "early stage" of high efficiency strongly relating to existing defect concentration, previous mechanical history, plastic deformation, impurity content, irradiation intensity and irradiation temperature; a second "late stage" of lower efficiency, initially linear with radiation dose but eventually saturating at high defect concentrations, whose form and eventual saturation level depend mainly on irradiation temperature and to a lesser extent on irradiation rate. It is this last stage, of course, which is of primary interest

for the high irradiation doses and dose rates and the large defect concentrations inherent in transmission electron microscopy.

As temperature is an important experimental parameter, and about the only one that can be varied appreciably for the case of electron microscopy, we shall first investigate variation of the initial late stage defect production efficiency with temperature. Subsequent behaviour with time (i.e. with increasing defect concentration) will be treated in the discussion of saturation kinetics, §2.7. Fig. 2.11, compiled by Sonder and Sibley (1972) from a variety of sources, illustrates the qualitative temperature dependence of defect creation efficiency $\partial N/\partial E$ as evidenced by F centre production rates in KCl. The behaviour illustrated is typical, in all but one aspect discussed below, of most alkali halides; and it indicates three principal stages in the variation with temperature.

The decrease in production efficiency between liquid helium and liquid nitrogen temperatures reflects the instability of closely correlated Frenkel pairs upon supplying thermal activation for interstitial diffusion; it appears that a series of potential wells exists between the separated vacancy and interstitial, and that upon acquiring some modicum of mobility, a stable interstitial has a smaller barrier to overcome in returning to annihilate its correlated vacancy than for free migration, for example to interstitial sinks. The elimination of close Frenkel pairs continues until the interstitial has acquired sufficient mobility to escape the attractive field of the vacancy with high probability (generally $\sim 30-50$ K). In this connection it must be noted that the majority (often by a factor of as much as 10:1; Ritz (1966)) of these closely correlated Frenkel defects exist as F^+I^- rather

than F:H pairs. As the F^+ concentration is not accounted for in F band measurements, the actual drop in production efficiency in the 30-50 K region (where F^+ are unstable) may amount to as much as a factor of 50.

The increase between 100 and 200 K is not well understood, but it can be correlated with the temperature range within which the self-trapped hole becomes mobile (Vilu and Elango 1966; Comins and Wedepohl 1966). Such a correlation suggests that defect production is somehow more efficient for electron-hole recombination at special sites available to the mobile hole, an explanation rather unconvincing in view of the role of, for example, impurity sites in depressing defect production at temperatures where the self-trapped hole is mobile (Pooley 1966b). Two more likely explanations exist. The first involves the anticorrelation of recombination luminescence and defect production in this temperature range (Pooley 1966a ; Pooley and Runciman 1970) where luminescence intensity is increasing, previously detailed in §2.5.2.1. Comins (1969) has pointed out, however, that no such anticorrelation exists in KBr; nor does defect behaviour in KCl correlate with the large increase in recombination luminescence below 100 K noted by Giuliani (1967). A second explanation invokes differences in interstitial behaviour in the low and high temperature regions. At temperatures below 100 K in the early stages of irradiation, interstitials are apt to remain either isolated or in a high density of small clusters; at higher temperatures a lower density of rather larger clusters might be expected to result from increased interstitial mobility (interstitial mobility will be discussed in §2.6). The probability of an F centre being created near an interstitial is

considerably lessened when interstitials are in large clusters rather than dispersed, and this distribution then leads to increased production of stable defects. Indeed, such variation in interstitial distribution with temperature has been suggested by irradiation hardening (Sibley and Sonder 1963), bleaching (Sonder et al. 1967) and thermal conductivity (Sonder and Walton 1967) experiments, and has been demonstrated in the electron microscopical observations described in §5.4.

The decrease in production efficiency noted about 200 K is largely related to irradiation dose rates, as indicated in fig 2.11. Such behaviour suggests influence of a marginally mobile (i.e. slowly moving) irradiation species; in this case the anion vacancy is strongly suspected, probably migrating to interstitial clusters and annihilating (Sonder and Templeton 1967). Vilu and Elango (1966) have found similar behaviour in NaCl, KBr and KI. In fact, as Sonder and Sibley (1972) have pointed out, if one orders the alkali halides by the temperature at which such depression occurs (viz. KI, KBr, KCl, NaCl), one finds from fig. 2.13 (see §2.6.3) that F^+ centre mobility scales similarly. The inverse dose rate dependence suggests that at irradiation intensities obtaining in the electron microscope ($\sim 10^{23}$ eV cm⁻³ sec⁻¹), little variation in production efficiency will be noted in this temperature range. A similar conclusion will be found to hold for the influence of anion vacancy mobility in saturation kinetics at room temperature at high dose rates, §2.7.

Pooley and co-workers (Pooley 1966c; Hughes et al. 1967; Pooley and Runciman 1970) have demonstrated that in some alkali halides, notably the iodides, a dramatic rise in recombination luminescence

inhibits defect production on a scale swamping small variations in efficiency of the sort illustrated in fig. 2.11. Fig 2.12 contrasts F centre production efficiency R as a function of temperature for a number of representative alkali halides. Three sorts of behaviour are indicated: (i) a high ($< 2000 \text{ eV F}^{-1}$) and fairly constant (within an order of magnitude) defect production efficiency at all temperatures, of the sort depicted in fig. 2.11, for most of the commonly studied alkali halides (KCl, KBr, LiF, RbCl); (ii) a marked depression in defect production at low temperature in those alkali halides (KI, NaCl, NaBr, RbI, LiCl) for which there is an increasing efficiency of radiative exciton decay; and (iii) a very much reduced defect production at all temperatures for those alkali halides (NaBr, NaI, LiI, LiBr) with large anion/cation size ratios. The point about group (i) (and group (ii) at room temperature) is the extraordinarily large number of defects one is apt to encounter with energy deposition rates $> 10^{23} \text{ eV cm}^{-3} \text{ sec}^{-1}$ characteristic of intense radiation sources such as the electron microscope; in under 20 sec of irradiation, every lattice site will have been displaced at least once in the course of a collision sequence. Considerable advantage, therefore, accrues from utilisation of those group (ii) and (iii) alkali halides with defect production rates diminished by orders of magnitude, either at room temperature or at low temperatures, from this level. The four alkali halides that exhibit reduced room temperature defect production are generally those with the largest anion/cation size ratio, Table 1.1. Indeed, it might well be expected that the replacement collision sequence saddle point energies are appreciably higher and defect production correspondingly less

efficient where there is proportionately less room for the propagating anion interstitial. The relationship between anion size and defect production efficiency was, in fact, first noted by Rabin and Klick (1960) in an attempt to explain different defect production rates at low temperatures, a discrepancy now better explained for low temperature data on the basis of non-radiative recombination efficiency, but still generally valid for room temperature comparisons.

Two prominent exceptions, LiF and LiCl, with large anion/cation ratios nevertheless damage extremely efficiently and appear to invalidate the simple anion size criterion. There are, however, at least three reasons why LiF and LiCl should damage efficiently, despite ion size disparity. First, there is more energy available from the non-radiative exciton decay (E_{nr} in fig. 2.9) in the lithium halides than in the sodium halides. Second, because of the strong $F^- - F^-$ or $Cl^- - Cl^-$ ion repulsion, the alkali fluoride or chlorine structures are less densely packed than the apparent ion size disparity would indicate. Third, the stronger anion-anion repulsion in the fluorides and the chlorides implies that the replacement collision sequences are more efficient. Consequently we conclude that the low defect production efficiency of certain alkali halides at room temperature can be tentatively explained by ion size criteria.

In view of the rather low efficiency of damage production from ionization processes in some alkali halides at some temperatures, it is worthwhile to re-examine the role of simple knock-on displacement damage, inherent in the measurements of F centre production obtained by 400 keV electron irradiation, fig. 2.12, and potentially significant for 1 MeV

electron microscopy. In Table 2.4 we have compared the minimum ionization damage cross section exhibited over the temperature range 4-300 K for a selection of alkali halides with the corresponding displacement cross sections, assuming a 25 eV displacement threshold, for 400 keV and 1 MeV electron irradiation. The comparison indicates that even under these conditions, ionization damage is still a dominant feature and is certainly worthwhile reducing as much as possible. Experience at low temperature (§5.4) also indicates that actual defect production rates by ionization at low temperature are considerably larger than indicated by the F centre measurements alone.

2.6 Defect Mobility and Aggregation

We have seen in §2.3 and §2.5 that the primary pair products of irradiation are $F:H$ or F^+I^- which either recombine or apparently aggregate under various conditions of temperature and irradiation to F_2, F_3 etc. and H_2 configurations, beyond which aggregations the information attainable from optical absorption or EPR spectra dwindles. On the other hand, individual point defects cannot be detected in the electron microscope, and defect clusters less than about 3 nm diameter are virtually invisible. At the very least, if defect aggregates are planar, such resolution implies >30 clustered defects; if aggregates are spherical, >300 clustered defects. Clearly, considerable aggregation must occur for electron microscopical observations to be relevant. Defect mobility has particular relevance then to the possibility of prolonged electron microscopy at temperatures below defect mobility thresholds where one might expect increased examination time to be

available before observable defect aggregates accumulate in such density as to obscure other observable features.

However, other more subtle effects also exist. Defect mobility and defect aggregation can influence the primary defect production mechanism by affecting non-radiative exciton decay efficiency and subsequent defect recombination. Conditions of both interstitial and vacancy mobility effectively set saturation defect levels attainable in crystals and control the kinetics of that saturation. The latter will be elaborated in the discussion of saturation, §2.7. The mobilities of the hole (self-trapped as a V_k centre) and the V_k^* exciton are particularly important at intermediate temperatures, as their motion opens up to the exciton decay process a wealth of alternative recombination sites at the impurities which inevitably exist in even the best available crystals. This role of impurities will be discussed in §2.8.

Fig.2.13 illustrates graphically the three principal defect mobility thresholds in all alkali halides for which data are available. We note that there is a particularly large region centred on liquid nitrogen temperatures in which only the interstitial defect is mobile, and in which rather straightforward experiments with interstitials can be conducted. At liquid helium temperature we might expect that all defects have been frozen, at least from random bulk diffusion. Conversely, at room temperature there is significant mobility in all defect species, which makes analysis somewhat more ambiguous.

2.6.1 Halogen interstitial mobility

The halogen interstitial apparently exists in two forms, the ion

(I^-) and the neutral atom (H), see §2.3.3.2. Isochronal and isothermal annealing experiments in the range 6-100 K have provided a great deal of information about the mobility of the interstitial halogen ion (Rüchardt 1955, 1956; Gebhardt 1962; Kurz and Gebhardt 1964; Giuliani et al. 1965; Itoh, Royce and Smoluchowski 1965; Hertz, Peisl and Waidelich 1967; Balzer, Peisl and Waidelich 1968; Giuliani and Reguzzoni 1968) and the interstitial atom (Känzig 1958; Käuzig and Woodruff 1958; Schnatterly and Compton 1964; Konitzer and Hersh 1966; Behr, Peisl and Waidelich 1967a; Ueta 1967; Chu and Micher 1968; Durand, Farge and Lambert 1969). These experiments measure such properties as H and I^- band optical absorption, H centre spin resonance, correlated F and F^+ band optical absorptions, lattice parameter, thermal expansion and thermal conductivity. The results of these measurements indicate a number of stages in the mobility of halogen interstitials, summarised in Table 2.5 for KCl.

2.6.1.1 Interstitial ion

The interstitial I^- halogen ion, formed at very low temperatures as the complement of the F^+ centre, presumably occupies a tetrahedral interstitial site in the halogen sublattice (being unstable in the crowdion configuration; this assignment, however, is uncertain), and moves via an interstitialcy mechanism along $\langle 111 \rangle$ at temperatures as low as 11 K. The activation energy for this interstitial mobility has been calculated by Tharmalingam (1964) on both Born-Mayer and Born-Mayer-Verwey models. The complementary F^+ defect exhibits up to four distinct annealing stages below 50 K which (in KBr) Itoh, Royce and Smoluchowski

(1965a) have attributed to release of mobile interstitials from different occupied interstitial sites relative to the halogen vacancy. In KCl Giuliani and Reguzzoni (1968) have noticed that a very small fraction of the complementary F^+ centres appear to remain stable above this temperature and to decay somewhere between 30 and 77 K; they attribute this behaviour to trapping of mobile interstitial ions at impurity sites subsequently released at higher temperatures.

The first three stages are first order annihilation reactions, i.e. described by kinetics of the form

$$\frac{dI^-}{dt} = K_1 I^- \exp (-E_1/kT) \quad (2.55)$$

where I^- is the interstitial ion concentration and E_1 an activation energy for interstitials separated less than three $\langle 110 \rangle$ ion distances from the vacancy. The last stage is a second order reaction, i.e. kinetics described by

$$\frac{dI^-}{dt} = K_2 (I^-)^2 \exp (-E_2/kT) \quad (2.56)$$

corresponding to random (free) migration of interstitial ions initially separated more than three $\langle 110 \rangle$ lattice distances from the vacancy, $E_2 > E_1$. A particularly significant feature of this analysis is that there are correlated with each vacancy a series of interstitial sites each with a specific activation energy for migration; interstitials in some of these sites have a preferred migration direction actually away from the vacancy and cannot return to the vacancy because of the repulsive interaction until the random walk stage. The relative population of these sites, which determines the average activation energy observed for each stage, will be peaked in the twelve $\langle 110 \rangle$ directions of the

replacement collision sequence.

Before the first annealing stage an appreciable number ($> 50\%$) of the interstitial halogen ions are actually situated within about three $\langle 110 \rangle$ lattice distances of a halogen vacancy at liquid helium temperatures. As a result, there is a high ratio of $F^+ : I^-$ to $F : H$ at liquid helium temperature in the presence of restricted interstitial mobility. One way of explaining the number and stability of $F^+ : I^-$ pairs is to consider the $F^+ : I^-$ creation mechanism. It seems likely that intrinsic luminescence (which is usually strong at low temperatures) and to some extent the radiation field can excite F centres. The F^* excited state is known to be long-lived (Swank and Brown 1963), and in the presence of a nearby halogen atom interstitial the excited electron may tunnel with high probability to the interstitial crowdion site to form an interstitial ion and thus an $F^+ : I^-$ pair. Once the interstitial is ionized, the polarisation induced at the F^+ site keep the vacancy ionized, as suggested by Lütty (1961). and stabilises the F^+ state.

Convincing evidence for this mechanism comes from the observation of Kabler (1964) that the F^+ / F ratio drops dramatically when radiation-induced luminescence disappears at higher temperatures, also from the observation of Ritz (1966) that the F^+ / F ratio depends on the F band absorption coefficient of the sample. The fact that the F^- centre is rarely observed at low temperature (Kabler 1964) supports the thesis that electron excitations readily occur during low temperature irradiation. For more widely spaced $F : H$ pairs, the F electron must be ionized into the conduction band to reach the interstitial, an event which is considerably less probable.

Annealing experiments for closely correlated F^+I^- pairs suggest that the largest number of these interstitial ions simply annihilate with their complementary vacancy centres upon acquiring thermal mobility, and thus are of little consequence to subsequent thermal aggregation. However, the more isolated interstitial ions created from an initial H centre under ionizing radiation, by capture of an electron either from a fully ionized F centre or from other radiation-induced ionization processes, are considerably more likely to survive thermal annealing and contribute to aggregation at higher temperatures. Nevertheless, a large concentration of stable interstitial ions may be of considerable consequence to eventual statistical accumulation of interstitial clusters at very low temperatures (§5.4).

2.6.1.2 Interstitial atom

The interstitial atom lies in the $\langle 110 \rangle$ "crowdion" H centre configuration and is associated with its complement, the F centre. Information about H centre mobility has been obtained both by spin resonance (Känzig 1958; Hänzig and Woodruff 1958; Konitzer and Hersh 1966; Chu and Mieher 1968) and from H band optical absorption (Behr, Peisl, and Waidelich 1967a, b). The last workers have detected two correlated annealing stages in the H and F absorption bands above 30 K in KCl during isochronal anneal, which they attribute to, respectively, a first order annihilation reaction for H and F centres closer than six lattice sites and a second order reaction corresponding to free migration of H centres more than six lattice sites distance from F centres. Schnatterly and Compton (1964) have detected a process for

M centre annihilation in KCl at about 90 K with an activation energy (0.07 eV) similar to those derived by Behr, Peisl and Waidelich from their F^+ annealing data. An identical value has been obtained in LiF by Durand, Farge and Lambert (1969) from analysis of saturation kinetics. It should be noted that the H centre can migrate along $\langle 110 \rangle$ by relatively simple electron transfer accompanied by only minor relaxations; furthermore the $|X_2^-|^0$ molecular ion (which is bound to the two neighbouring halogen ions to comprise the $|X_4^{3-}|^0$ configuration) occupies a space scarcely larger than the single halogen ion it replaces. It thus exhibits comparatively greater mobility than "hard sphere" crowdion configurations in non-ionic materials, beginning to move thermally at temperatures as low as 20 K in some alkali halides. Once again, the electronic character of alkali halide defects has altered their behaviour from those in simpler materials. The low temperature electron microscopical observations detailed in §5.4 confirm the existence of these small mobility thresholds; indeed, these thresholds necessitate liquid helium microscopy to prevent rapid aggregation of the interstitial species.

Nevertheless, the same observations also indicate that even below interstitial mobility thresholds, considerably more interstitial aggregation occurs than can be accounted for by statistical redistribution of isolated entities to a clustered species by prolonged irradiation. Indeed, two other experiments suggest that considerable interstitial mobility exists at sub-threshold temperatures during irradiation. Itoh and Saidoh (1969) have observed both H_2 and H_A formation actually saturating at 4 K and from the kinetics have calculated interaction

volumes of 1500 and 150 lattice volumes respectively for interstitial-interstitial and interstitial-alkali impurity reactions. F centre saturation kinetics at 4 K (Pooley 1966c; Hughes and Pooley 1971) can also be explained by assuming that an interstitial annihilates vacancies within a volume comprising about 7000 halogen sites. These volumes correspond to an interstitial range >15 lattice sites for random diffusive motion. One explanation for these large interaction volumes is that some form of radiation-enhanced interstitial diffusion may be occurring, perhaps via a thermal spike, concurrent with ionization of H centres. A slightly different way of looking at this process is to consider that the replacement collision sequence offers an assist; at low temperature reduced lattice vibration renders even a longer replacement collision sequence more probable. For example a collision sequence 10 lattice sites in extent requires an interaction radius of only 7 lattice sites, a sequence 20 sites in extent requires an interaction radius only 5 lattice sites, etc.

It should be noted that a distance of about 20 lattice sites represents about the order of separation of adjacent defects at saturation ($\sim 10^{19} \text{ N cm}^{-3}$) if they were isotropically distributed, which supports the view that for saturation defect concentrations at any temperature, one can expect appreciable interstitial aggregation. The inescapable consequence for electron microscopy is that recourse to low temperature observation does not serve to inhibit defect clustering by rendering defects completely immobile; in fact, it will be shown in §2.7 that one major effect is simply to retard interstitial diffusion sufficiently to induce rather different Frenkel pair saturation

kinetics. Saturation defect levels attained at any temperature appear to preclude successful microscopy.

2.6.2 Self-trapped hole mobility

In alkali halides, only electrons can move freely at any temperature once they are excited into the conduction band. The self-trapped hole, or V_k centre, ultimately responsible for damage production only acquires mobility somewhere in the temperature range 100-200 K, moving by a diffusive process controlled by thermally-activated jumps. Investigations of the thermal stability of the V_k centre were first undertaken by Delbecq, Smaller and Yuster (1958) in KCl and Känzig (1960) in LiF shortly after its initial discovery. Subsequently, Murray and Keller (Murray and Keller 1965, 1967; Keller and Murray 1965, 1966) and others have made detailed studies of hole motion in several alkali halides. Since the V_k centre lies along $\langle 110 \rangle$, equivalent positions lie at 60° or 90° to the initial orientation. It is found that the V_k centre changes orientation principally in steps of 60° , for which reorientation the jump frequency has the form $\nu_h = A \exp(-E_h/kT)$. Known values of the pre-exponential factor A and the activation energy E_h are tabulated in Table 2.6 together with mobility threshold temperatures. Notably, rather large differences exist between alkali halides.

A principal consequence of V_k centre mobility is the effect of impurity sites on defect production; a hole may migrate preferentially to an impurity site where recombination may take place without leading to defect production. The inhibition thus afforded is discussed in §2.8. Hole migration is also important in Goldstein's (1967) model of F

saturation by perturbation of the generating V_k^* exciton (see §2.7).

2.6.3 Halogen vacancy mobility

The unaggregated halogen vacancy exists in four forms; the F centre, the ionized F^+ centre, the F^- centre and the excited F^* centre. Each of these electronic states of the vacancy exhibits quite different ionic transport properties, and models for F centre aggregation have found it necessary to invoke the electronic contribution to explain observed aggregation kinetics. Vacancy diffusion parameters for vacancies in the various electron states in KCl are compared in Table 2.7 and contrasted for different alkali halides in fig. 2.13.

2.6.3.1 F centre

Step diffusion of the F centre has been measured by Wolf (1966) using EPR techniques at high temperatures to yield a jump frequency and activation energy for F centre self diffusion. These measurements obtain an activation energy for KCl of 1.6 eV, far too high to be of much importance to vacancy aggregation reported at and below room temperature. Lüty (1968) has utilised the orientation and dissociation information provided by the F_A centre to determine by extrapolation the thermal mobility of the F centre in pure crystals; this extrapolation concurs with Wolf's measurements. Hirai and Matsuyama (1967, 1970; Matsuyama and Hirai 1969) have attempted to explain a much lower observed 0.9 eV energy for thermal formation of M centres from F centres by the covalent interactions between F centres.

2.6.3.2 F⁻ centre

The F centre that has captured an extra electron, a centre which develops along with F⁺ centres upon ionization of F centres, does not appear to be really mobile in the same sense as other vacancy centres, as it is electronically unstable even below room temperature in most alkali halides, and measurements of its stability indicate actual alteration, i.e. decomposition into F + e⁻ (Rabin 1963), recombination with mobile holes (Delbecq, Ghosh and Yuster 1966) or annihilation by mobile interstitials (Sonder, Sibley and Mallard 1967) rather than vacancy motion. Luty (1968) has attempted to detect dichroism (i.e. a reorientation) in F_A⁻ centres in KCl:Na using pulse annealing, without success, although F_A⁺ centres could be reoriented under similar treatment. The conclusion is that the F⁺ centre is more mobile than the F⁻ centre, and the former is apt to be responsible for the increased vacancy mobility after optical ionization of F centres. (This result is to be expected, as the additional polarisation from two electrons must induce an inward displacement of the vacancy's nearest neighbours to further stabilise it).

2.6.3.3 F⁺ centre

Determination of the mobility of the empty halogen vacancy can be made by thermal diffusion and ionic conductivity measurements in the high temperature extrinsic region (see §2.2; also Süptitz and Teltow 1967). Fuller (1966) has conducted measurements of the former sort using radioactive tracer chlorine in KCl, Beaumont and Jacobs (1967) the latter sort

with highly pure KCl crystals; their results for anion vacancy migration activation energy agree closely, 0.95 eV and 1.05 eV respectively, as do their determinations of pre-exponential factors. These measurements clearly preclude anion transport around room temperature.

A serious discrepancy exists, however, between these data and results of $F_2(M)$ accumulation after optical ionization of F centres, which has also been shown (Delbecq 1963; Giuliani 1967; Lütty 1968) to involve migration of the empty vacancy. An activation energy corresponding to growth of the F_2 optical absorption band has been established at 0.6 eV, appreciable anion transport occurring even below room temperature. Below about 200 K, the upper limit for F^- stability, the activation energy decreases still further to 0.14 eV (with a much smaller pre-exponential, of course).

Similar behaviour is observed for other alkali halides, as indicated by the mobility threshold temperatures in Table 2.8. One possible explanation of the discrepancy is indicated below in the discussion of the excited F centre state. Another, indicated by Farge, Lambert and Smoluchowski (1967) is the covalent bonding attraction between F^+ and F centres, extending to quite large separations, which could satisfactorily explain observed aggregation kinetics.

2.6.3.4 Excited F centre (F^*)

Fedders, Hunger and Lütty (1961) have demonstrated that electrons continuously released from F centres during $F \rightarrow F^+$ conversion above the

F^- stability threshold become trapped with high probability at the resulting ionized F centres but are captured only via the excited F state, F^* , thermal emission being the dominating subsequent process. Thus excited F centres are repeatedly formed by temporary electron capture in anion vacancies. Luty and his co-workers (Fritz, Luty and Rausch 1965; Luty 1968; Luty 1971) have subsequently shown that F centres in the excited state can have extremely high ionic mobility, as evidence by experimental F_A^* reorientation. The extrapolation of various alkali halide:alkali F_A combinations leads to a thermal reorientation activation energy of 0.6 eV for KCl:K, coinciding with F_2 aggregation results. This energy comprises the thermal activation energy for F^- ionization (0.5 eV) less the energy for ionizing the F^* state (~ 0.15 eV) which determines the lifetime of the excited F centre, plus the thermal migration energy. The latter is then computed to be at least as low as 0.25 eV; experimentally Luty and co-workers have been able to induce F_A reorientation via the excited F_A^* state with thermal energies ~ 0.1 eV. Measurements with different alkali halide:alkali F_A combinations extrapolate to a migration energy as small as 0.13 eV in pure KCl.

If initial ionization of the F centre is induced by the irradiation itself, as obtained under dynamical irradiating conditions in the electron microscope, we are left with only the migration energy (0.13 eV) which is incredibly low. We might therefore propose that considerable radiation enhanced vacancy mobility may result at room temperature under heavy irradiating conditions. However, enhanced mobility can occur only for those intervals during which the excited

F state exists. The continual ionization induced by irradiation will doubtless render the F^* lifetime small, which has the effect of reducing the pre-exponential factor for the jump frequency.

2.6.4 Halogen interstitial aggregates

2.6.4.1 Low temperature region: di-interstitials

Evidence for the clustering of two interstitial defects (H_2 centres) comes from growth of the V optical absorption bands above the interstitial mobility threshold. Itoh and co-workers (Itoh 1966; Itoh et al. 1967; Itoh and Saidoh 1969) have shown that at temperatures where the H centre becomes thermally unstable, a broad composite H' band including the V_4 band (which is associated with a di-interstitial halogen centre) is observed. Above 77 K the V_4 band predominates, together with a marked reduction in the H' band and disappearance of the H band, suggesting that whatever centre is responsible for the V_4 band is the most stable of the di-interstitial configurations comprising the H' band. The V_4 band is most prominently produced by irradiation between 140 and 200 K (Itoh 1966), decaying above 230 K (Ishii 1966). Kingsley (1962) has shown that a symmetry axis of the V_4 defect lies along $\langle 100 \rangle$ while Dienes, Hatcher and Smoluchowski (1970) have considered the elastic interaction of two H centres. White and Greene (1969) have calculated an interaction energy between two isolated H centres as 1.5 eV and have shown that if an interstitial molecule results from their interaction a $\langle 100 \rangle$ orientation is at least stable. Dienes et al. (1970) in fact show that the energy of an interstitial halogen molecule is less than two H centres, and suggest that this is

the ultimate fate of the H centre. Both Dienes, Hatcher and Smoluchowski (1967) and Bachmann and Peisl (1970) have shown that the elastic strain field of the H centre is highly anisotropic and extends to some distance from the centre (appreciable even to about 5 neighbours away). There is, therefore, a rather large interaction volume for aggregate H centre formation, even below the interstitial diffusion threshold, for a replacement sequence more than ten ions long.

Itoh and Saidoh (1969) have developed a formalism for describing di-interstitial aggregation. If u is the effective interaction volume between two H centres, the growth rate of H_2 centres (here understood to mean any di-interstitial configuration) may be expressed as

$$\dot{H}_2 = u H \dot{N} \quad (2.57)$$

where H_2 and H represent the concentrations of these centres, N the number of stable Frenkel pairs and $\dot{N}$ the basic production rate of H centres which survive initial annihilation with their F centres. Since the H_2 centre is composed of two H centres, and assuming no further aggregation,

$$N = H + 2H_2 \quad (2.58)$$

and solving (2.57) we find

$$H = \frac{1}{4u} \ln \left\{ \frac{1}{1 - 2uH} \right\} - \frac{1}{2} H. \quad (2.59)$$

The concentration of H_2 centres then exhibits two distinct states: the first when $2uH \ll 1$ and H_2 production is parabolic with H ,

$$H_2 = \frac{uH^2}{2} ; \quad (2.60)$$

the second when $uH \sim \frac{1}{2}$ predicts saturation of H centre concentration

$$\frac{H_2}{H} \rightarrow \infty . \quad (2.61)$$

This saturation of H centre concentration is actually observed and implies that further production adds only to the aggregate population. The interaction volume is found to be at least 1500 lattice volumes at liquid helium temperature where no thermal activation take place, implying an interaction radius of ~ 5 lattice sites for an interstitial ejected 20 lattice sites in the replacement sequence. This radius accords with the calculation of Dienes, Hatcher and Smoluchowski (1967) that there is an appreciable displacement field to the fifth nearest neighbour of an H centre. The H centre concentration at H saturation is then $1/2u \sim 5 \times 10^{18} \text{ cm}^{-3}$.

Actual nucleation of di-interstitials may take place heterogeneously at impurities, particularly at higher temperatures. For example, Saidoh and Itoh (1970) and Giuliani, Gustinetti and Stella (1971) have suggested that an alkali impurity ion (e.g. Li^+ or Na^+ in KBr) can stabilise an otherwise unstable di-interstitial configuration at 77 K, giving rise to the V(306) band in KBr, i.e. an $(\text{H}_2)_A$ centre. Concentrations of these impurities are in the 10 ppm range or a potential nucleation site density $\sim 10^{17} \text{ cm}^{-3}$.

2.6.4.2 High temperature region: higher aggregates

Evidence for larger aggregates comes from observation of the V absorption bands upon irradiating at higher temperatures or annealing lower temperature irradiation products. Much confusion arises in the interpretation of V bands, principally because different workers have chosen to work in different alkali halides (KCl, KBr, KI) and because several separate absorption bands appear to coincide at the same

wavelengths; some workers have separated these by their dichroic properties, but this precaution has not been universally practiced. The relevant bands are the V_2 , V_3 and V_7 and what are loosely termed "V aggregate" or "slow growing" bands.

Ishii (1966) found that for KBr (and somewhat similarly in KCl) the V_4 band forms strongly between 77 K and 190 K, together with a small V_7 band, but is not formed at 230 K (Dutton and Maurer 1953 found a similar result). Irradiation at 230 K or above instead produces first the V_2 and V_7 bands, then upon prolonged irradiation a broader band at slightly higher energy growing slowly with irradiation, this band also being produced by the annealing of lower temperature irradiation products at room temperature. The V_2 band nearly coincides with this slow growth band, but exhibits different dichroism. The V (306) band attributed to an $(H_2)_A$ centre, nearly coincides with the V_7 band but also exhibits different dichroic properties. Finally, prolonged irradiation at 300 K produces a strong V_3 band which can be very slightly thermally bleached at room temperature. Winter, Wolfe and Christy (1969) have shown that the transition $V_4 \rightarrow V_2 \rightarrow V_3$ occurs identically in KCl, KBr, KI, RbCl, RbBr and RbI, and that the positions of these bands depends primarily only on the anion concerned. Both Christy and Phelps (1961) and Herrmann and Pinard (1970) have noted that in KCl the V_3 band grows in constant proportion to the F band at room temperature, the latter workers carrying their measurements right up to saturation where the two bands obey the same saturation behaviour. This implies that the entity responsible for the V_3 band is somehow the complement (or some fixed multiple thereof) of the F centre, for example

V_3 absorption may correspond to some transition associated with constituent interstitials within an interstitial cluster, becoming important only when clusters reach a size large enough that most interstitials experience identical surroundings. Ishii and Rolfe (1966) also found a slowly growing band at longer wavelengths for long irradiation times in KBr or in additively coloured KBr; they identified this band with the W band of Mollwo (1937) and attributed it to clusters of bromine molecules because of similarity with absorption by adsorbed or dissolved Br_2 .

About the same time, Konitzer and Hersh (1966) studied V band production in KI between 5 K and room temperature, finding two V bands which corresponded closely to the V_2 and V_3 absorptions of KI additively coloured with halogen gas, and to those of halogen molecules in solution. They found that the two bands were both associated with a single centre for which production was marginal at 4 K, rose dramatically above 90 K, and reached a maximum at 130 K, decreasing somewhat thereafter, but at each stage paralleling F centre production. Irradiation at room temperature (as opposed to 195 K) produced a broad V_3 band whose absorption peaked at slightly higher energy than the V_2 band and was more resistant to optical bleaching. This suggests that the broad room temperature band may arise from further aggregation.

Additional evidence for interstitial clusters comes from the kinetics of saturation (Pooley 1966c ; Sonder and Templeton 1967; Durand, Farge and Lambert 1969) discussed in §2.7, which require large interstitial aggregates to account for the observed form of vacancy-interstitial recombination. Sonder and Templeton (1967) have estimated at least 200

interstitials per cluster for a saturation F centre concentration of $\sim 10^{18} \text{ cm}^{-3}$.

Sonder et al. (1967) noted from vacancy centre bleaching rates that defects produced at 80 K irradiation were more easily bleached than those created at progressively higher temperatures; their observation implies that the cross section per interstitial for vacancy trapping decreases with increasing irradiation temperature, which may be explained by interstitial clusters of progressively larger size.

Whapham and Makin (1960), Sibley and Sonder (1963) and Nadeau (1962, 1963, 1964) have shown that irradiation hardening of alkali halide crystals arises from interstitials, rather than vacancy defects. (cf. hardening by additive F colouration, Suzuki and Doyama, 1959). Subsequently, Sonder et al. (1966) noted that interstitial centres produced by irradiation at 80 K were less effective barriers than those produced by irradiation above 150 K; from this observation it has been inferred that interstitial clusters of different size are formed depending upon irradiation temperature. (While the latter is true, it does not explain the hardening behaviour; see §5.4 and §5.7.1.) Sibley and Russell (1965) noted that crystals doped with interstitial-trapping impurities exhibited less severe radiation hardening, suggesting that interstitial-trapping impurities altered the size (or number) of these aggregates.

Finally, several more direct techniques have suggested the existence of large defect clusters in irradiated alkali halides. Sonder and Walton (1967) measured phonon scattering from clusters by thermal conductivity measurements between 0.2 and 2 K. A size of 7 nm was

indicated for F centre concentrations $\sim 5 \times 10^{18} \text{ cm}^{-3}$ produced by irradiation at room temperature, but no clustering was indicated for irradiation at 77 K. Recently Spalt and coworkers (Spalt 1970; Spalt and Peisl 1971; Trinkaus et al. 1970) have measured x-ray diffuse scattering from defect clusters in crystals irradiated at 77 K and 300 K; room temperature irradiation to $\sim 10^{18} \text{ F cm}^{-3}$ results in cluster volume ~ 350 lattice volumes. Lastly and most convincingly, the electron microscopical experiments of this study (§5.3 - §5.5) have provided definitive evidence for and considerable information about the form of interstitial clustering, which make possible a tentative interpretation of the V band absorptions.

2.6.5 Halogen vacancy aggregates

2.6.5.1 Simple halogen vacancy aggregate centres

The van Doorn (1962) models for the simple halogen vacancy aggregate centres, the M, R, N centres corresponding to F_2 , F_3 , F_4 , are now well established. Although the last assignment is still open to interpretation (Schneider and Kabler 1966), considerable experimental evidence (Schnatterly and Compton 1964; Nahum 1967; Durand, Farge and Lambert 1969) suggests that simple aggregates larger than F_3 nevertheless exist. There is also evidence that these aggregates can exist in positive and negative, as well as neutral, charge states (i.e. M^+ , M^- , R^+ , R^- , etc.; see Nahum 1967). Aggregates may be produced in three ways: (i) dynamically during irradiation (Thommen 1962; Sibley and Sonder 1963; Harrison 1963; Rabin 1963), (ii) by thermal annealing of dispersed F centres (Hirai and Matsuyama 1967), and (iii) by optical bleaching of

dispersed F centres (Asai and Okuda 1966; Delbecq 1963; Itoh and Suita 1960, 1962; Bron 1960). Each procedure presents inherently different production conditions. During irradiation there is a continual production of F centres (and ionized F centres as well) and interstitials building towards saturation; because of interstitial production, there is simultaneous creation and destruction of F centres, and thus of M centres, until at saturation the two processes are equal. On the other hand, for a fixed concentration of dispersed F centres initially present in the crystal, for example by additive colouration, conversion to aggregate centres by thermal or optical excitation is governed only by depletion of F centre population (Agathonikou-Rokofyllou, Costikas and Manos 1967). Similarly if F centres are introduced by prior irradiation above liquid nitrogen temperature, the interstitials also produced are presumed to have clustered and have little effect on subsequent thermal or optical conversion to aggregates. Optical excitation leads to a species of different mobility, the ionized F^+ centre, as indeed does irradiation, which alters aggregate kinetics from those of simple thermal F aggregation.

Thommen (1962) was able to show that F and M centres are in dynamical thermal equilibrium at room temperature during and after irradiation. Sonder and Sibley (1963) observed dependence of the equilibrium on dose rate and suggested that the equilibrium arises from simultaneous creation and destruction of F and M centres during irradiation. Harrison (1963) has proposed that a dynamical equilibrium exists between F centres and all F aggregate centres. The relationship between aggregate centres in a crystal has been shown (Faraday, Rabin and

Compton 1961; Sibley and Sonder 1962; Sonder and Sibley 1963; Wallis and Faraday 1964; Schnatterly and Compton 1964) to be of the form

$$F_{n-1} + F \rightleftharpoons F_n; \quad (2.62)$$

thus

$$F_n = K_n F^n, \quad K_n = \prod_{i=1}^n K_i'; \quad (2.63)$$

where F_n is the concentration of the n 'th aggregate and the equilibrium constants K_i' are functions of aggregation conditions. Compton and Rabin (1964) showed easily that the relation (2.63) arises for the case of the M centre. We now generalise their approach in a manner that lends significance to the equilibrium constants K_i' .

Suppose an incremental increase dF in F results in an incremental increase dF_n in F_n . If we assume some number of sites k_n surrounding an F_{n-1} centre which if converted to F centres result in F_n centre formation, it follows that

$$dF_n = \frac{k_n F_{n-1}}{N_0}, \quad (2.64)$$

where $k_n F_{n-1}/N_0$ is that fraction of sites out of a total N_0 halogen sites leading to F_n centre production. Integrating (2.64) we have

$$F_n = \frac{\prod_{i=1}^n k_i}{n! N_0^{n-1}} F^n. \quad (2.65)$$

If we assume that k is approximately the same for each successive aggregate (this assumption will hold for small aggregates or if appreciable vacancy mobility exists), we can write

$$F_n = \frac{1}{n!} \left(\frac{k}{N_0}\right)^{n-1} F^n = K_n F^n. \quad (2.66)$$

(k/N) clearly corresponds to some aggregation volume w per aggregate within which further aggregation proceeds, i.e.

$$F_n = \frac{(wF)^n}{n! w} \quad (2.67)$$

For the case of M centre formation in the absence of vacancy diffusion, only the 12 nearest neighbour sites to an F centre are expected to contribute, i.e. $k_M = 12$ (cf. 16 for an R centre). Faraday, Rabin and Compton (1961) and Horn and Peisl (1966) have observed $k_M \sim 12$ for KCl x-irradiation below 220 K. Above this temperature k_M was found to increase in Boltzmann fashion with an activation energy ~ 0.5 eV, evidently related in some way to vacancy mobility. (Seager, Welch and Royce (1969) have found, however, that a plot of $\ln k_M$ vs temperature in the range 200-350 K is not necessarily constant, but alters with temperature, impurity and dose rate; it must be noted that the activation energy for hole mobility is also ~ 0.5 eV and may alter M centre formation rates.) At room temperature Horn and Peisl obtained $k_M \sim 1750$ in reasonable agreement with earlier measurements by Thommen (1962). Sibley and Sonder (1963) observed a dose rate dependence of the equilibrium constant, with k_M in the range 250-1250. An extrapolation of their data to low dose rates (Crawford 1964) yields $k_M \sim 1600$, corresponding to an aggregation volume $w \sim 0.4 \text{ nm}^3$, i.e. a radius 7-8 sites about each F centre.

The relation (2.66) neither correlates simultaneous buildup of higher order aggregates (i.e. presumes $F \gg M$ for M formation, $M \gg R$ for R formation, etc.) nor allows for overlapping aggregation volumes. A more useful approach (Vaisburd and Melik-Gaikazyan 1965) is to treat F centre production as an event random in both space and time and to apply Poisson statistics to show that the probability of n F centres occurring within an aggregation volume w is

$$p(N,n) = \frac{(Nw)^n}{n!} \exp(-Nw), \quad (2.68)$$

where

$$N = F + 2F_2 + 3F_3 + \dots = \sum_{i=1}^n i F_i \quad (2.69)$$

is the total vacancy concentration. If R is the rate of F centre generation (assumed constant), $N = Rt$ and the concentration of the n 'th aggregate is given by

$$F_n = \frac{(wRt)^n}{n! w} \exp(-wRt), \quad (2.70)$$

which for small t ($wRt \ll 1$) reduces to (2.66). The solution (2.70) predicts that concentration of the n 'th aggregate will go through a maximum for $wRt = n$; this has not been observed in constant temperature experiments (i.e. where t is the only variable) even for large dose rates and post-saturation irradiation (Soul 1970). Typically, the M centre concentration saturates at about 10% of the F centre concentration in most irradiation experiments at room temperature. There are two reasons for this: (i) continued irradiation has been shown to destroy F aggregates due to recombination of their vacancy constituents with interstitials produced during the irradiation (Schnatterly and Compton 1964; Durand, Farge and Lambert 1969; Soul 1970); and (ii) it will be shown in §2.7 that the effective vacancy production rate $R(t)$ for use in (2.70) is not constant but diminishes with time due to vacancy-interstitial recombination; basically the diminution arises because the recombination volume v for interstitial-vacancy annihilation is at least of the order of the aggregation volume w . A typical vacancy concentration (Rt) at saturation is in all cases $< 10^{20} \text{ cm}^{-3}$ (Pooley 1966c; Monpagnens 1968; Herrmann and Pinard 1970; Durand, Farge and Lambert 1969; Soul 1970), while a typical aggregation volume at room temperature (Thommen 1962;

Sibley and Sonder 1963; Horn and Peisl 1966; Soul 1970) is $w \sim 0.5 \text{ nm}^3$; therefore $wRt_{\text{max}} = 5 \times 10^{-3}$ and never reaches $n = 1$, much less $n = 2$. Even if all the halogen sites were vacant ($Rt \sim 10^{22} \text{ cm}^{-3}$) we should expect no more than the $n=5$ aggregate to be present in appreciable concentrations, unless the aggregation volume is considerably increased, which may occur at higher temperatures where there is appreciable vacancy mobility.

Some support for the statistical approach of (2.70) is lent by the data of Durand, Farge and Lambert (1969) for aggregation in x-irradiated LiF. They irradiated crystals for equal periods of time at progressively higher temperatures and obtained F, M, R, N and higher order aggregate growth curves of the sort predicted by (2.70), plotting aggregate concentration against temperature rather than time. In this case w rather than t is made to increase (as the temperature increases so also does the vacancy mobility and the effective aggregation volume).

Equation (2.70) does not take into account the radiative destruction of F aggregate centres, e.g. $(F + I) + M \rightarrow F + (I + M) \rightarrow F + F$. Schnatterly and Compton (1964) and Wallis and Faraday (1964) have observed that F, M and R centre growth kinetics can be reasonably well described by relations of the form

$$\dot{F}_n = k_n R F_{n-1} - n D F_n \quad (2.71)$$

where R and D are the creation and destruction rates for vacancies, whether in isolated or aggregated form. Differentiating (2.70) leads to the relation

$$\dot{F}_n = w R F_{n-1} - w R F_n \quad (2.72)$$

which evidently differs from (2.71). Assuming that rate of radiative destruction of vacancies is proportional to the interstitial creation rate R , i.e. that the rate of destruction for the n 'th aggregate is $nk'RF_n$, we have

$$\begin{aligned} \dot{F}_n &= w R F_{n-1} - w R F_n - n k' R F_n \\ &= w R F_{n-1} - (w + n k') R F_n \end{aligned} \quad (2.73)$$

Soul (1970) found that for M centres in KCl at room temperature $nk' \sim 450 w$, so that $(w + nk')R/wR \approx 450$, in reasonable agreement with the result from Wallis and Faraday's (1964) data that $nD/k_M R \approx 530$ in KCl at liquid nitrogen temperature. This agreement suggests that the same sorts of interstitial-vacancy recombination processes are occurring at both liquid nitrogen and room temperatures.

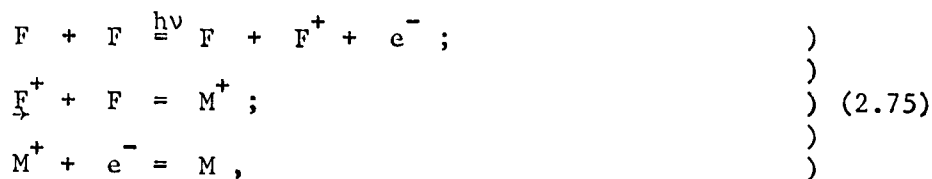
Equation (2.70) does not take into account, either, that aggregates of a given order may be thermally unstable above a certain temperature and may dissociate thermally. This dissociation has been investigated by Tomiki (1960) and Jain and Sootha (1968) in additively coloured KCl and by Jain and Jain (1969) in KBr. Dissociation temperatures as listed in Table 2.8 are observed. These data indicate that at temperatures where there begins to be sufficient vacancy mobility for larger aggregate formation, a stable aggregation nucleus is not available. This finding undoubtedly explains the sensitisation of higher order aggregate formation (see discussion of colloids in the next section) by various impurities. Significantly the LiF crystals used by Durand, Farge and Lambert (1969) in which they were able to sustain appreciable aggregate concentrations above 500 K had appreciable

oxygen impurity present: this impurity has been shown to stabilise very high order aggregate clusters (Tsal', Pashkovskii and Kabotovich 1964).

Considerable thought has been expended in deciding the mechanism by which F aggregation actually takes place. In particular there is a considerable discrepancy between determinations of halogen vacancy mobility (in any electron charge stage, §2.6.3) and the activation energy for M centre formation (~ 0.6 eV). In optically bleached crystals (and also irradiated crystals) the presence of F^- and F^+ centres led Luty (1961a) to propose the mechanism



where $\rightarrow$ denotes a mobile species. Since $F^+ : F^-$ pairs are liable to be found in close proximity, they diffuse towards each other under Coulomb attraction until the F^- centre decays thermally, whereupon the cycle repeats at the next ionization. On the basis of bleaching kinetics in additively coloured KCl, Delbecq (1963) proposed the alternative mechanism



where the F^+ centre is the mobile entity and diffuses to the F centre under the monopole-dipole interaction between F^+ and F. Farge, Lambert and Smoluchowski (1967) have argued (as do also Hirai and Scott 1967) that the monopole-dipole attraction is not sufficiently long range, varying as the inverse fourth power of separation, and they suggest

instead that the covalent bonding between F^+ and F centres can account for the anomalously low activation energy for M centre formation; their calculations show that significant bond strength exists for separations up to five lattice sites. Brothers and Lynch (1968) point out that an $F^+:F^-$ covalent bond would be equally likely (and also more uniform than the simple Coulomb attraction) and propose the mechanism



As indicated in §2.6.3 the F^+ centre is apt to be the mobile entity for either mechanism (2.75) or (2.76), rather than the F^- which has been proposed by Crawford (1964). In the event of appreciable covalent bonding for close separations of F^+ and F^- , it is more difficult to assign an identity, and thus a unique mobility, to each. One would expect, however, that as the pair approach the diffusion would become more F-like, with a higher diffusion energy than an $F^+:F$ pair.

The choice of one of these mechanisms ultimately rests with identification of the M^+ centre as a principal temporary entity in the process of M centre formation under bleaching or irradiation. Schneider and Rabin (1965) identified the M^+ and R^+ centres in KCl and KBr by re-irradiation and bleaching at liquid helium temperature, and subsequently also at room temperature. Farge, Toulouse and Lambert (1966) found similar evidence for M^+ and R^+ at room temperature in LiF. Nahum and Wiegand (1967) and Nahum (1967) have studied the properties of M^+ and R^+ in LiF and have demonstrated that dynamic equilibrium between F and F aggregates exists for F_2^+ and F_3^+ as well, suggesting that these centres

are party to the M and R aggregation process. Evidence was also offered for the existence of F_4^+ . Interestingly, R^+ was apparently formed from the reaction $M^+ + F = R^+$ and not $F^+ + M = R^+$, since R^+ formation was found to terminate when the M^+ concentration is exhausted, suggesting that M^+ is a mobile entity. In a novel experiment, Matsuyama and Hirai (1969) doped KCl with Tl^+ in order to produce a large number of electron traps to stabilise F^+ centres. F_2^+ lifetime was thus prolonged so that its formation could be studied; upon warming above 290 K, electrons released from the Tl^+ traps converted the F_2^+ centres to M centres. An activation energy for F_2^+ formation of 0.52 eV was found and a dissociation energy of 0.74 eV (F_2^+ binding energy, 0.14 eV). In comparison F^- centres were found to be unstable above 220 K.

Although these results favour the M^+ involvement, there is certainly the possibility that both processes contribute to M centre aggregation. Kubo and Ozawa (1963), for example, have observed simultaneous decrease of the F^- band and increase of the M band in LiF electron irradiated at liquid nitrogen temperature and annealed to room temperature.

Hirai and Matsuyama (1969, 1970) have also investigated the thermal growth of M centres in the absence of optical excitation in additively coloured KCl. In this case F centres are the only mobile entity, and an equilibrium of the form



was observed, where K_1 and K_2 are rate constants for the processes of creation and destruction. Thermal growth kinetics could be described by the relation

$$\begin{aligned} \dot{M} &= K_1 (F_0 - 2M)^2 - K_2 M \\ &= K_1 F^2 - K_2 M \end{aligned} \quad \begin{array}{l}) \\) \\) \end{array} \quad (2.78)$$

which is not quite equivalent to (2.71). Activation energies for both processes were obtained from K_1 and K_2 as follows:

$$\begin{aligned} F + F &= M \quad 0.95 \text{ eV} \\ M &= F + F \quad 0.11 \text{ eV} \quad (\text{M binding energy, } 0.18 \text{ eV}). \end{aligned}$$

Good agreement with these energies was obtained from a model incorporating covalent F:F bonding. This result is particularly relevant to M centre formation by the F^+F^- mechanism in the case of optical or radiative bleaching; since M centre formation is found only for relatively close pairs, the covalent bonding will produce a situation closer to F:F and a higher activation energy for M centre formation.

2.6.5.2 Colloids

If alkali halide crystals containing atomically dispersed F centres are annealed to several hundred degrees above room temperature, a new optical absorption band is formed and the crystal exhibits Tyndall scattering. Savost'yanova (1930) interpreted this behaviour as scattering from a colloidal suspension of alkali metal in the dielectric medium of the crystal, predicting a particle size over 80 nm. Colloidal alkali is understood to be produced from the coagulation of F centres, precipitation of the metallic phase occurring as the F centre contributes its electron to a lattice alkali ion trapped in the F centre coagulation volume. We review work on colloids here principally for two reasons: (i) the only other significant electron microscopical study of defects -

in alkali halides (Izumi 1969) has interpreted observed defect clusters (which will be shown in §5.5 to be anion interstitial clusters) as alkali metal colloids, and (ii) a second spherically symmetric defect is observed under heavy irradiation of alkali halide foils or at elevated temperatures which roughly correlate with the onset of anion vacancy mobility (§5.3.3).

The classical way to produce colloids has been the slow cooling of crystals additively coloured with excess alkali from the additive colouration temperature (see Schulman and Compton 1962). There is evidence also (Compton 1957; Geck 1957; Yoshida and Ikeda 1957, 1959; Ikeda and Yoshida 1967; Tsal', Pashkovskii and Didyk 1967; Durand, Farge and Lambert 1969) that colloids can be produced by irradiation. However, irradiated crystals are unsuitable for subsequent prolonged annealing due to recombination of vacancies and interstitials. The evidence customarily quoted for the presence of the alkali metal phase has been the observation by McLennan (1951) of electron diffraction patterns from metallic Na in NaCl films heavily electron irradiated in the electron microscope; in fact, these observations were accompanied by appreciable surface decomposition, and it can be shown in light of more recent work (Townsend and Kelly 1968; Townsend and Elliott 1969; Lord 1971) that such irradiation is accompanied by efficient sputtering and desorption of halogen ions from the crystal surfaces by the replacement collision sequence of defect production. A similar comment applies to the detection of colloids by energy loss measurements in thin evaporated films of alkali halides during 50 keV electron irradiation (Creuzberg 1966) and by recent electron diffraction studies of irradiated NaCl (Jain 1970).

A second absorption band not associated with scattering by particles also develops during conditions of colloid evolution (Scott and Bupp 1950; Scott and Smith 1951), often referred to as the "Scott R' band" or the "X band" (Shatalov 1956), and has been associated with the presence of very small colloids or colloidal precursors. Scott, Smith and Thompson (1953) attempted replication electron microscopy of X centres without success, indicating they must be less than 5 nm diameter. Scott and his co-workers, also Doyle (1960) and Penley and Witte (1962) have attempted explanation of X band characteristics based on optical and electrical properties of alkali metal, with poor agreement. On the other hand, Shatalov (1956, 1957, 1958), Etzel (1960) and Sonder (1962) have shown that the optical and diamagnetic properties of the centre suggest the the X band arises instead from atomically dispersed vacancy centres. Recently Jain and Sootha (1968) have rather convincingly shown that the X band arises from the presence of divalent cation impurities and is attributable to association of an F centre with a divalent impurity-cation vacancy pair; the true colloid absorption band peaks at slightly higher energy and forms at somewhat higher temperatures. In fact, the presence in concentrations > 10 ppm of those divalent impurities which enhance X band formation has been shown to depress true colloid formation (Tsal' and Pashkovskii 1964; Jain and Radhakrishna 1968; Jain and Jain 1969). The shift in the absorption peak during progressively higher annealing temperatures, previously interpreted as corresponding to growths of colloid dimensions, was shown to be the transition from atomically dispersed X centres to true vacancy aggregates. For colloids produced by heating in the dark, colloid size was shown from EPR measurements to remain roughly constant at < 700 atoms/colloid (< 1 nm diameter)

for $9.10^{17} \text{ F cm}^{-3}$; however, heating in light appeared to produce a larger colloid size (consistent with increased vacancy mobility before aggregate dissociation).

Unfortunately, because of the proximity of the X and colloid bands and their formation under similar thermal treatment (particularly in those crystals of low purity used several years ago), considerable confusion has arisen in the literature as to which of these two centres was actually being studied in any series of experiments. This confusion has been increased by the tendency to refer to both bands indiscriminately as colloidal.

Jain and Jain (1968, 1969) and Jain and Sootha (1968) have made careful studies of the production and stability of colloids during the annealing of KBr and KCl crystals generated from additive colouration temperatures (Jain and Mehendru 1965), employing both optical absorption and the increase in electrical conductivity afforded by thermionic emission of electrons from metallic colloids into the alkali halide conduction band (Kothari and Jain 1964; Jain and Sootha 1965). They have observed heterogeneous equilibrium, $\text{F} \rightleftharpoons \text{colloid}$, upon annealing from room temperature with a temperature dependence indicated in Table 2.8. Colloids formed in the presence of light were shown to be larger and appear at lower temperatures than those formed in the dark; both observations are consistent with halogen vacancy mobility enhanced ($\text{F} \rightarrow \text{F}^+$) relative to the thermal stability of colloid clusters. The bonding energy of an F to a colloid was obtained as 0.8 eV in KCl (considerably larger than for M centres) and appears to be related primarily to association of the electron derived from the F centre with the alkali metal (Glauberger and Tsai' 1968).

As a consequence, all but 10% of the F centres have dissociated from colloids in KBr by 340° C and all by 500° C in KCl. According to the analysis of electrical conductivity by Kothari and Jain (1964) the maximum number of F centres per colloid does not exceed 20.

Durand, Farge and Lambert (1969) have found similar behaviour for LiF x-irradiated at progressively higher temperatures, detecting colloids by sensitive small angle x-ray scattering techniques. They found that for $\sim 10^{19}$ F cm⁻³, 1/4 of the F centres have aggregated into colloids of 1 nm diameter at 473, 1/3 by 523 K and $\frac{1}{2}$ by 593 K. The number of colloids remained constant at 7×10^{16} cm⁻³, while the colloids grew to a maximum of 1.5 nm diameter; the density suggests that colloids nucleate at specific sites, probably impurities.

Impurity effects are known to be important for colloid formation. Compton (1957) and Etzel and Patterson (1958) demonstrated that the hydroxyl $|\text{OH}^-|$ ion appears necessary for colloid formation in irradiated NaCl; Jain and Jain (1969) have observed a very large effect of humidity on colloid formation, while oxygen-bearing anion radicals $|\text{OH}^-|$, $|\text{SO}_4^{2-}|$, $|\text{O}_3^{2-}|$, $|\text{NO}_3^{2-}|$ were found to sensitise colloid formation in both additively coloured (Tsal' and Pashkovskii 1964; Tsal', Pashkovskii and Nabitovich 1964) and γ irradiated (Tsal', Pashkovskii and Didyk 1967) NaCl and KCl. On the other hand, divalent cation impurities were found to depress colloid formation (Tsal' and Pashkovskii 1964; Jain and Radhakrishna 1968; Jain and Jain 1969).

Study of colloids by electron microscopical replication of freshly cleaved alkali halide surfaces has proved a particularly fruitful, if perhaps currently ambiguous, technique. Scott, Smith and Thompson (1953)

first employed replication to search without success for colloids associated with the X band. Subsequently, Tomiki and Hibi (1959) and Simon and Sproull (1960) successfully detected large, nearly hemispherical pits (up to 2.5 μm diameter) in additively coloured KCl slowly cooled from the colouration temperature. The latter workers noted a monotonic anticorrelation between cooling rate and pit size, from 20 nm diameter (forced air cooling) to 2.5 μm diameter (slowly cooled over 12 h), the larger pits exhibiting distinct geometrical (8 sided) structure; no pits (at least none > 10 nm) were observed for water-quenched crystals or those treated to produce the X band (14 h at 523 K). On the other hand, 20-800 nm diameter pits have been detected in additively coloured crystals doped with oxygen-bearing anion impurities and rapidly quenched from the colouration temperature (Tsal', Pashkovskii and Nabitovich 1964) and in presumably pure electrolytically coloured crystals similarly quenched (Shvarts et al. 1970). Significantly, when KCl crystals from the latter study were subsequently annealed to 623 K, pits of largest diameter (75 nm) were formed, and annealing to 673 K reduced pit size (43 nm), in precise temperature agreement with the optical data of Jain and Sootha (1965, 1968) presented in Table 2.8. Most remarkably pits formed even in crystals having only the F band in their absorption spectra.

Radchenko and Vdod (1970) have replicated "colloids" in electrolytically coloured KCl, KBr and KI produced by photoexcitation at 523-553 K. Jensen (1967) has ostensibly replicated colloids in additively coloured CsBr bleached with light at room temperature. The size of these "colloids" could be increased by heating from 313-473 K during exposure to light. The variation of colloid band width and that of the temperature dependence suggested that the Cs colloids contained substantial impurity

concentrations, probably lighter alkali metals.

Tsal', Pashkovskii and Didyk (1967) attempted to observe colloids in KCl and NaCl containing oxygen-bearing anion impurities and irradiated with ^{60}Co radiation. They found that NaCl containing 1 mole % OH^- developed an intense colloid absorption band for γ doses $> 10^8$ R; heating to 473 K reduced this band and shifted its maximum to shorter wavelengths. KCl-1% KOH under similar irradiation developed a weak colloid band. Significantly, no colloids were observed by electron microscopical replication.

There are, then, two important observations relating to replication studies: (i) large colloids (or some form of precipitation) may be formed even during rapid quenching in additively coloured crystals in the presence of only the F absorption band and (ii) these large colloids are not observed in irradiated crystals, even when sensitised by large OH^- additions, in the presence of a strong colloid absorption band. These observations suggest that we may be dealing with two different sorts of aggregation, one somehow inherent in cooling additively or electrolytically coloured crystals and leading to large spherical precipitates and the other applying to the thermal aggregation of F centres and resulting in very small aggregates. The former sort has particular relevance to the discovery of Dawson and Hughes (1971, private communication) that modern pure crystals that have been additively coloured need not be quenched from their colouration temperature to preserve dispersed F centres (the procedure of Jain and Mehendru 1965), but they may be furnace cooled; if the observations of Tsal' et al. are correct, large colloids may nevertheless nucleate with this procedure, though only F band absorption is evident. In the absence of further evidence, this dilemma remains

unsolved; thus we must use the term colloid advisedly. Though direct transmission electron microscopy might be expected to supply some of the evidence required (see §5.3.3.2), it appears unlikely that in the case of crystals irradiated in bulk at or above room temperature, aggregate clusters of observable size would form. On the other hand, additively coloured crystals should result in large observable aggregates, if the replication results are to be believed, and certain irradiation conditions peculiar to thin foils may induce colloidal aggregation. These points will be discussed further in §5.3.3 in conjunction with actual microscopical observations.

2.7 Saturation

It was indicated in §2.4.2.5 and Table 2.3 that the rates of energy loss from electron irradiation in the electron microscope are so large that saturation damage levels are unavoidable. While the specific implications for electron microscopy will be treated more fully at the end of this section a more general consideration of saturation behaviour will be given first.

The defect concentration at which most defect measurements have been carried out, in typical x ray or γ ray colouration experiments, occurs in that region where the growth of F centres is linear with increasing irradiation dose (Table 2.3 indicates the low dose rates applying to x and γ irradiation). It is clear that linear growth cannot continue indefinitely, but that damage saturation must eventually occur at some concentration limit less than 1.0, i.e. < the

lattice anion density $\sim 10^{22} \text{ cm}^{-3}$. It is, moreover, reasonable to expect that alteration of growth kinetics, if not saturation itself, may occur a good deal sooner, since the elastic interactions between defects of opposite sign and even of the same sign are known to extend further than nearest neighbour sites. Therefore, defect recombination will inevitably occur with greater frequency with increasing defect concentration, and there will also be alteration both of growth kinetics and of ultimate saturation level.

2.7.1 Saturation data

Saturation behaviour has been reported by a large number of workers (Fischer 1959; Vaisburd and Melik-Gaikazyan 1965; Pooley 1966c; Sonder and Templeton 1967; Monpagens 1968; Durand, Farge and Lambert 1969; Soul and Tubbs 1969; Herrmann and Pinard 1970a; Soul 1970; Choudhury, Goswami and Choudhuri 1970; Hughes and Pooley 1971), and attempts have been made to account for observed kinetics by several mechanisms. From what can be surmised from these experiments saturation is temperature, impurity and dose rate dependent, as evidenced by the whole range of irradiating conditions and equally wide scatter of reported behaviour.

A typical saturation curve is depicted in fig. 2.14 taken from the data of Hughes and Pooley (1971) for 300 keV proton irradiation of KCl at room temperature. In the early stages of F centre growth, F centre production appears nearly linear with dose E , but at a later stage the production rate begins to diminish steadily and falls to zero at saturation, which occurs typically at an F centre fraction $\sim 10^{-3}$

(i.e. $\sim 10^{19}$ F cm⁻³). Various attempts have been made to perform analytical fits to such growth curves, with results that illustrate substantial differences in the curves themselves. Goldstein (1967) found good experimental fit to $F \propto E^{\frac{1}{2}}$ in ultraviolet colouration of KI, as did Durand, Farge and Lambert (1969) for x irradiated LiF. Sonder and Templeton (1967) approximated saturation of γ irradiated KCl with first order kinetics, while Pooley (1966c) found kinetics appropriate to $F \propto E/(1 + KE)$ for proton irradiated KCl. Herrmann and Pinard (1969) discovered an empirical fit of the form $F \propto 1 - \sqrt{KE + 1}$ for electron irradiated KCl, while Hughes and Pooley (1971) have used $F \propto \ln (KE + 1)$ for proton irradiated KCl. A comparison of growth kinetics is interesting and has been set out in Table 2.9. Thus, three sorts of behaviour have emerged: (i) growth which proceeds as $\sqrt{E}$; (ii) growth which is eventually logarithmic with E; and (iii) growth which obeys n'th order kinetics.

Models accounting for F centre saturation behaviour are as numerous as the differences in observed saturation kinetics. There are basically five rate limiting mechanisms which can be postulated to explain either the approach to saturation or the eventual saturation level. These are:

- (1) exciton decay quenching
- (2) athermal recombination
- (3) recombination by interstitial diffusion
- (4) recombination by vacancy diffusion
- (5) vacancy aggregation.

Goldstein (1967) has proposed that the presence of created defects in the proximity of a V_k^* exciton can lead to quenching of intrinsic

luminescence and presumably of the non-radiative exciton decay also, i.e. offering a third alternative to those of radiative and defect production; such a mechanism would yield a defect production rate inversely proportional to the defect concentration, as observed experimentally by Goldstein. As it appeared unlikely that the presence of F centres led to luminescence quenching, he postulated that interstitial centres were somehow responsible. Pooley (1966c) and subsequently Hughes and Pooley (1971) have suggested that associated with each F centre is some prohibited volume within which recombination of the F centre and an interstitial created therein proceeds spontaneously, i.e. athermally. As the irradiation proceeds the volume of the crystal within which spontaneous recombination takes place increases, with a correlated decrease in the F centre production rate. The model does not lead to absolute saturation, for which secondary processes must be invoked, but appears to describe correctly the approach to saturation. Farge (Durand, Farge and Lambert 1969; Farge 1969) has used Pooley's recombination volume concept and proposed that, apart from athermal recombination, interstitials also annihilate F centres on their way to interstitial sinks, the latter presumed to be small, planar dislocation loops. Farge's analysis does not, however, reproduce his experimental results. Sonder and Templeton (1967) have proposed, on the evidence of temperature cycling experiments in the ambient range, that mobile vacancies (in this case, undoubtedly F^+ centres) migrate to interstitial sinks and annihilate with an activation energy ~ 0.4 eV. These experiments were conducted at very low dose rates (γ irradiation), allowing the mobile vacancy plenty of time to find an interstitial; an

alternative fate is the formation of M centres. Finally, Soul (1970) has proposed that vacancy aggregation might be able to explain F centre saturation ($F \rightarrow M$, R, etc. with destruction of the isolated F centre) and particularly post-saturation behaviour. It will be noted that such a mechanism does not imply defect saturation but only isolated F centre saturation. Hughes and Pooley (1971) tend to favour this mechanism as the back reaction necessary for absolute F saturation on their model.

We have plotted in fig. 2.15 the results of five different room - temperature F centre saturation experiments in KCl over a wide range of dose rates together with the low temperature result, using a necessarily logarithmic abscissa. Two features are immediately evident: (i) each curve exhibits approximately logarithmic behaviour over a major portion of its length, and (ii) there is a general dose rate dependence of the eventual saturation level. At least part of the apparent absolute saturation for the room temperature data of Pooley and of Pooley and Hughes is the use of protons with inevitable $F \rightarrow U$ conversion at the ends of their trajectories. Upon closer inspection we note further that there is an evident dose rate dependence of growth rate as well. It is also clear that there are two sorts of behaviour with temperature: (i) a marked depression of growth rate during irradiation at liquid helium temperature, and (ii) the same effect for small temperature rises in the ambient range at low dose rates.

We have elected to utilise the athermal recombination approach of Hughes and Pooley in order to attempt a general explanation of these features. This approach is particularly useful because it embodies the most basic growth rate limiting process. Also, other mechanisms can be

treated simply as perturbations on this solution. We outline this approach in the following sub-section and examine the data of fig. 2.15 in the next.

2.7.2 Athermal recombination

Pooley (1966c) first proposed that athermal interstitial-vacancy recombination (athermal in the sense of not requiring thermally activated defect diffusion) could explain F centre growth curves at both room temperature and low temperature, where either one or both of the primary products of irradiation are immobile. He introduced the notion that around each vacancy (or interstitial) there is some prohibitive volume v within which annihilation with a defect of opposite sign created therein will proceed spontaneously without activation energy. This notion can be shown to lead to an expression relating the rate of increase of F centre concentration to the initial creation rate, the dose and the total prohibitive volume associated with the immobile species. Recently Hughes and Pooley (1971) have reformulated this rate equation more rigorously; we further extend their analysis below. Two cases must be considered: (i) room temperature where it is assumed vacancies are immobile but interstitials diffuse rapidly to sinks (the existence of these interstitial sinks will be demonstrated in §5.5); and (ii) below the interstitial mobility threshold where both defects are presumed immobile. These assumptions will be examined critically later.

2.7.2.1 Room temperature

We suppose that rate of energy deposition $\dot{E}$ is constant in time, that for a given deposited energy E the number of vacancies initially created is RE per unit volume and that the number surviving at any stage of the irradiation is N where

$$N = F + 2F_2 + 3F_3 + \dots = \sum_i i F_i$$

is the number of Frenkel pairs existing within the crystal. If the total prohibited volume associated with them (taking overlap into consideration) is V , the rate equation becomes

$$\frac{dN}{dE} = R(1-V), \quad (2.79)$$

since $(1-V)$ is the probability that a correlated interstitial will survive. For small F centre concentrations, clearly $V \sim vN$; however, as the concentration increases individual volumes of influence may overlap, and the dependence of V on N must be sought. In this treatment we neglect that F aggregates may be formed for more than nearest neighbour separations.

If P is the probability that a new vacancy falls outside the existing forbidden volume, the incremental increase dV in V will be vP , i.e.

$$\frac{dV}{dN} = vP. \quad (2.80)$$

Since $P = (1-V)$ we integrate (2.80) to obtain

$$V = 1 - \exp(-vN). \quad (2.81)$$

Substituting into (2.79) we obtain

$$\frac{dN}{dE} = R \exp(-vN), \quad (2.82)$$

whence

$$N = \frac{1}{v} \ln(vRE + 1). \quad (2.83)$$

Of particular interest is the logarithmic dependence on dose predicted by (2.83). Differentiating, we find

$$\left(\frac{dN}{dE}\right)^{-1} = vE + 1/R, \quad (2.84)$$

whence v can be obtained. Values of v calculated from (2.84) for the data of fig. 2.15 remain roughly constant over the dose range and are listed in Table 2.10.

There is clearly a monotonic dependence of recombination volume on dose rate indicated. The limiting volume of $2 \times 10^{-19} \text{ cm}^3$ corresponds to a radius of 4 nm and contains ~ 3000 halogen sites. This radius encompasses ~ 8 halogen ion sites along a $\langle 110 \rangle$ line, which is about what we might expect (and has been calculated by Pooley, 1966b) for the necessary extent of a replacement collision sequence to produce a stable defect pair. The dose rate dependence at room temperature undoubtedly arises from the mobility of vacancies (principally F^+ centres) which can diffuse to form F aggregate clusters or annihilate at interstitial clusters. Both reactions lead to an increase in the value of v obtained from (2.84). However, as the dose rate increases, thermally activated recombination becomes increasingly less important, and we shall suppose that for the high dose rates obtaining in the electron microscope ($> 10^{23} \text{ eV cm}^{-3}$) only the athermal recombination volume is effective in determining the kinetics of the approach to saturation.

2.7.2.2 Low temperature

The assumptions for the low temperature case ($< 30 \text{ K}$) are identical to those at high temperature, with the added condition that interstitials as well are now frozen into the lattice as H centres. We

label interstitial defects I, and we have in addition to v_F and V_F associated with vacancies also v_I and V_I associated with interstitials. There are then nine possible fates for a newly created vacancy-interstitial pair: each defect species can be created within the influence volume of the same species or the opposite species or neither, i.e. within V_F , V_I or $(1-V_F-V_I)$, and we can calculate the probability for each of the nine possible combinations in terms of V_F and V_I . We shall for the moment assume isotropic interaction between vacancy and interstitial ($v_F=v_I=v$) and also similar distribution ($V_F=V_I=V$). Asymptotic solutions for the rate equation are then possible, and for high doses

$$N = \frac{1}{4v} \{ \ln(4v RE + 1) + 1 \} , \quad (2.85)$$

which is analagous to (2.83) with v replaced by $4v$. Differentiating we find

$$\frac{1}{R} \{ \ln R \left(\frac{dN}{dE} \right)^{-1} + R \left(\frac{dN}{dE} \right)^{-1} \} = 4vE + 1/R . \quad (2.86)$$

We note that when dN/dE is small so that (2.85) is valid, (2.86) reduces to

$$\left(\frac{dN}{dE} \right)^{-1} = 4vE + 1/R , \quad (2.87)$$

which is (2.84) with v replaced by $4v$, and from which we derive v . The liquid helium temperature data of Hughes and Pooley indicate that for KCl at a dose rate of $6 \times 10^{20} \text{ eV cm}^{-3} \text{ sec}^{-1}$, $v \sim 5 \times 10^{-19} \text{ cm}^3$, a factor of 2.5 larger than the limiting value at room temperature. This factor may arise because at room temperature the interstitial has a finite chance of diffusing out of the region of influence before annihilation can occur, or because F^+ centres are not measured; it is not particularly important, and we shall neglect it.

A more illustrative approach is to differentiate (2.84) and (2.87)

with respect to $\ln E$ in the high dose region where $vRE \gg 1$, giving

$$\frac{dN}{d \ln E} = \frac{1}{v} \quad \text{at room temperature;} \quad (2.88a)$$

$$\frac{dN}{d \ln E} = \frac{1}{4v} \quad \text{at low temperature.} \quad (2.88b)$$

Comparison of (2.88a) and (2.88b) implies that for irradiation at low temperatures, a plot of N vs $\ln E$ should have a slope only one-quarter (or less) as large as a corresponding irradiation at room temperature. This claim is borne out by comparison of the low temperature and room temperature curves of fig. 2.15, which show that at low temperature a given defect level will be approached considerably more slowly with a greater expenditure of irradiation energy than at room temperature, providing considerably more time for electron microscope observation at low temperature even in those alkali halides (such as KCl) exhibiting no reduction of defect production rates at low temperature. This is an important result, and it suggests that the most important effect of retarding interstitial defect mobility at low temperatures is not necessarily to reduce the scale of observable cluster formation but instead to prolong the approach to defect saturation.

The increase in permissible dose is readily seen by rewriting equations (2.84) and (2.87) in the form

$$E \approx \frac{\exp vN}{vR} \quad \text{for room temperature;} \quad (2.89a)$$

$$E \approx \frac{\exp 4vN}{4vR} \quad \text{for low temperature,} \quad (2.89b)$$

with the expectation that

$$\frac{E_{LT}}{E_{RT}} = \begin{cases} \frac{\exp 3vN}{4} & \text{if } v_{LT} = v_{RT} ; \\ \frac{\exp 9vN}{10} & \text{if } v_{LT} = 2.5 v_{RT} . \end{cases} \quad (2.90)$$

The ratio (2.90) can amount to an inordinately large effect for defect concentrations near 10^{19} cm^{-3} . Fig. 2.15 indicates, however, a distinct change in the kinetics of approach at about $5 \times 10^{18} \text{ cm}^{-3}$, with a slope thereafter approaching the room temperature condition. We believe this transition may indicate saturation of the isolated interstitial H concentration, as observed by Itoh and Saidoh (1969) at about this defect level, and the subsequent build-up of interstitial clusters. Indeed, we note the same effect in the earliest stages of room temperature irradiating before much interstitial clustering could have occurred. Such clusters can be eventually produced even under low temperature irradiating conditions (see §5.4); and, of course, with their presence, the assumptions of the low temperature case break down and approach those of the late room temperature analysis. Thus, what we may expect for low temperature microscopy is a prolonged period of cluster-free observation followed by a period of relatively rapid and quickly saturating cluster growth. The difference in total dose between low temperature and room temperature conditions for a concentration of $10^{19} \text{ defects cm}^{-3}$ is a factor of 20, which is nearly exactly the increase in observation time afforded by low temperature electron microscopy in KCl before onset of serious radiation damage (see §5.4).

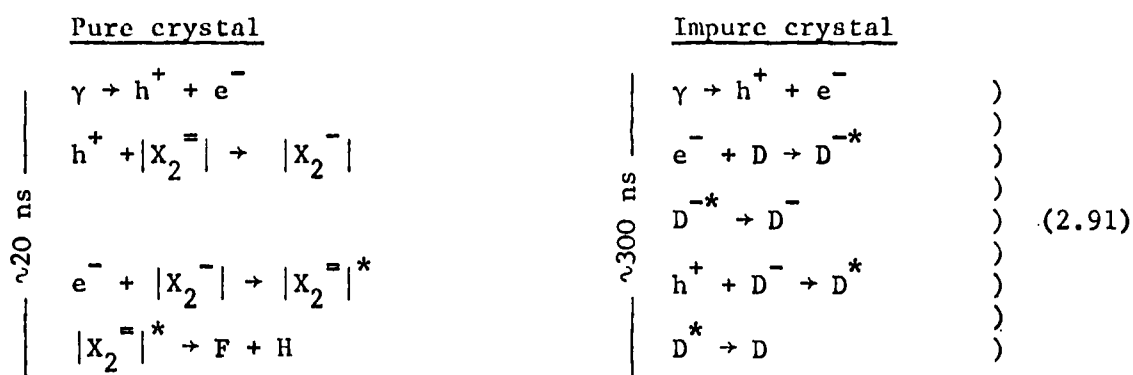
2.8 Impurity Effects

Since the production and aggregation of point defects in alkali halides is a rather complex process, nearly all impurities have some measurable effect on the final stabilised defect distribution; indeed,

a few of these have already been mentioned in discussion of the replacement collision sequence (§2.5.2.2) and vacancy aggregation (§2.6.5). In this section we shall discuss three specific impurity effects which are of consequence to efficiency of defect production as well as of defect aggregation in the late stage of alkali halide irradiation.

2.8.1 Electron-trapping impurities

At temperatures where the self-trapped hole is mobile, electron-trapping impurities (notably divalent cations) should be able to act as considerably slower alternative electron-hole recombination sites and thus prevent normal defect production occurring via the non-radiative exciton decay mechanism. The sequences in pure and impurity-containing crystals would be as follows.



D represents the impurity in its initial ionic charge state: for example, a divalent impurity may have an ionic charge of +2 or a charge of +1 with respect to the neutral lattice; if associated with an adjacent cation vacancy the pair may have no overall net lattice charge, but the impurity may still be a more efficient electron trap than a normal lattice site. It is clear that the sequence in impure crystals, involving electron-trapping impurities, by-passes or "short-circuits" the normal exciton

sequence. It should be stressed that on this model alternative recombination sites are available only at temperatures at which the self-trapped hole (V_k centre) is appreciably mobile (indicated in Table 2.6), with the result that inhibition by electron-trapping impurities is unlikely to be effective below about 200 K in most alkali halides.

Each step in the recombination sequences has associated with it a rate constant, and Pooley (1966c) has constructed from these an inhibition parameter s reflecting both irradiation rate $\dot{E}$ and the hole jumping rate v_h ,

$$s \approx \frac{1}{60} \frac{\dot{E} N_o}{v_h N_D^2}, \quad (2.92)$$

where $\dot{E}$ is in $\text{eV cm}^{-3} \text{ sec}^{-1}$, N_o is the halogen site concentration, N_D the electron-trapping impurity concentration, and $v_h = A \exp(-E_h/kT)$. For $s \gg 1$ little inhibition is predicted; for $s = 1$ defect production is down by a factor of 2; for $s \ll 1$ the depression of production rate relative to that in the pure crystal is given by

$$\frac{\dot{F}}{F_o} = s^{\frac{1}{2}} \approx \frac{1}{N_D} \left\{ \frac{\dot{E} N_o}{60 v_h} \right\}^{\frac{1}{2}} \propto \frac{\sqrt{\dot{E}}}{N_D \exp(-E_h/2kT)}. \quad (2.93)$$

The jump rate pre-exponential A and the activation energy E_h are known for only a few alkali halides (KCl, KI; see Table 2.7), though mobility threshold temperatures are more generally available. Dawson and Pooley (1969) have measured F centre production rates as a function of temperature in KCl:Pb^{++} and KI:Tl^+ and find activation energies for inhibition which correlate directly with hole jump activation, as predicted in (2.93).

The dose rate dependence predicted by (2.93) is particularly significant. There is considerable evidence for F centre suppression

for modest impurity concentrations (100 ppm) and moderate irradiation rates ($\sim 10^{19}$ eV cm⁻³ sec⁻¹) from the work of Sibley, Sonder and Butler (1964), Hall, Pooley and Wedepohl (1964) and Sibley and Sonder (1965). Nevertheless, dose rate dependence has been observed from the differences in γ irradiation ($\sim 10^{17}$ eV cm⁻³ sec⁻¹) and 1.5 MeV electrons ($\sim 10^{19}$ eV cm⁻³ sec⁻¹); for example 250 ppm Pb⁺⁺ was required to suppress late stage colouration in KCl under high intensity electron irradiation compared with only 60 ppm for low intensity γ irradiation (Sibley and Sonder 1965). For the electron microscope $\dot{E}$ is so high (10^{23} eV cm⁻³ sec⁻¹) that despite the $\sqrt{\dot{E}}$ dependence, exceptionally large impurity concentrations may be needed to offset the high irradiation rate. We have listed in Table 2.11 for three alkali halides specifically studied by electron microscopy, the concentration of electron-trapping impurities necessary for a ten-fold reduction in defect production rate for a radiation intensity $\dot{E} \sim 10^{23}$ eV cm⁻³ sec⁻¹. A value of E_h for NaCl has been assumed from comparison of mobility threshold temperatures in KCl, KI and NaCl. The factor of ten was chosen because electron microscopical studies of crystals externally irradiated to one-tenth saturation exhibit measurably smaller defect clusters.

The result for NaCl is important because Yagi and Honjo (1964, 1967) have reported significant suppression of observable damage during electron microscopy of NaCl:1 000-10 000 ppm Ca⁺⁺ (see §5.2). It must be noted, however, that impurity concentrations of this magnitude are in excess of the irradiation defect concentration, and inhibition of defect mobility may equally account for absence of observable defect clustering; this possibility will be discussed in §2.8.3. The particularly small

value for KI suggests that normally occurring impurities (obtainable KI is not exceptionally pure) may have had a measurable effect on the measurements of F centre production obtained at lower dose rates $\sim 10^{21}$ eV cm⁻³ sec⁻¹ by Hughes et al. (1967). There should certainly be an effect for trace impurities in NaI with its very mobile hole ($E_h = 0.15$ eV); this may help to explain the remarkably low defect production rates in NaI at room temperature.

An alternative role for electron-trapping impurities, at least at temperatures considerably above 200 K, is the stabilisation of F^+ centres, leading to an increased rate of defect recombination via vacancy mobility (Sonder and Sibley 1965; Sonder et al. 1967; Crawford, Sibley and Sonder 1967). That is, impurities cause an increased rate of back reactions, rather than affecting the primary production process (Sonder and Templeton 1967). However, pulse experiments by Pooley (1968) appear to suggest that the form of observed F centre decay processes cannot principally account for the inhibition of coloration, while further defect production efficiency measurements (Dawson and Pooley 1969) extending to temperatures below the F^+ mobility threshold still reveal marked inhibition by impurities. The conclusion is that the inhibition process is strongly V_k dominated. Recent uv coloration experiments (Lushchik, Vitol and Elango 1969) tend to support this view. Irradiation by uv ensures that impurities affect the forward production rate (since free electrons and holes are not produced, only self-trapped excitons); under these conditions no impurity inhibition is observed.

Two further observations appear to contradict the predictions of the two previous models. One is the observation (Sibley and Russell 1965) that Ca^{++} and Sr^{++} impurities in $KCl:Ca^{++}$ and $KCl:Sr^{++}$ induce marked

late stage suppression at room temperature, but high irradiation intensities ($5 \times 10^{18} \text{ eV cm}^{-3} \text{ sec}^{-1}$) are considerably more effective than low irradiation rates ($10^{17} \text{ eV cm}^{-3} \text{ sec}^{-1}$), reversing the order found earlier in KCl:Pb^{++} (Sibley and Sonder 1965). This inverse intensity dependence is difficult to correlate with either the model of alternative recombination sites or that of F^+ stabilisation, both of which predict the opposite behaviour. The other observation is the consistent enhancement of production efficiency by electron-trapping impurities, particularly divalent ones in the early stages of coloration (Sibley and Russell 1965; Ikeya et al. 1966) and at low temperatures (Hall, Pooley and Wedepohl 1964; Sibley and Sonder 1965).

These observations suggest yet a further role for impurities, almost certainly that of stabilising the mobile interstitial species. For example, at low temperatures or in the early stages of coloration, impurities stabilising interstitials act as a sink as effective as large interstitial clusters, inducing "high temperature/late stage" recombination kinetics (§2.7), thus increasing defect production efficiency over that obtained in "low temperature/early stage" (isolated interstitial) kinetics (see fig 2.15). At higher temperatures or in later stages of irradiation as interstitial aggregation proceeds randomly distributed impurities then act as nucleation sites for interstitial clusters more numerous than in pure crystals, thus distributing interstitials into a larger number of smaller clusters; mobile F^+ vacancy centres, created by electron trapping, then reach interstitials more quickly, on average, resulting in a faster annihilation rate. The differences in the ways different impurities affect defect production may well be due to varying efficiency in the stabilisation of interstitial species, as well as to

differences in electron-trapping cross section. The form of interstitial stabilisation (interstitials trapped singly or aggregated into large observable clusters) is, of course, of profound importance to the success of alkali halide electron microscopy, equally as much as defect production rates. The process of interstitial stabilisation is therefore considered in the next two sections for two sorts of impurity species.

2.8.2 Monovalent cation impurities

It is now reasonably well established that a stable monovalent impurity cation-anion interstitial complex exists at low temperatures in alkali halides in the form of the H_A centre, giving rise to the V_1 absorption band (Kolopus et al. 1967; Giuliani 1968, 1970; Delbecq et al. 1969; Patten and Keller 1969; Schoemaker and Kolopus 1970). The configuration is depicted in fig. 2.4d, from which it can be seen that an H centre lying along $\langle 110 \rangle$ has rotated slightly off-axis in the presence of a monovalent cation impurity. The favourable elastic interaction only exists, of course, for substitutional cations of smaller size than the lattice cations they replace, for example Na^+ or Li^+ in KCl or KBr, but not Rb^+ (Giuliani 1970). Information about the H_A centre and its stability is obtained, not only from the V_1 absorption band, but also from EPR spectra and the complementary F absorption band. For example, both Giuliani (1970) and Saidoh and Itoh (1970) have obtained a linear relation between growth of the F band and growth of the V_1 band during irradiation.

Giuliani (1969) and Saidoh and Itoh (1970) have further shown that there is an absorption band in $KBr:Na^+$ and $KBr:Li^+$ correlating with the

F^+ band and due to the association of an interstitial halogen ion with the cation impurity, i.e. I_A^- ; this configuration, along with the H_A centre is, moreover, stable even above liquid nitrogen temperature, whereas I^- is unstable above 21 K in pure crystals (Itoh, Royce and Smoluchowski 1965). Saidoh and Itoh (1970) and Giuliani, Gustinetti and Stella (1971) have also detected absorption in the V_4 region which appears to be associated with di-interstitial anion-cation impurity complex, i.e. $(H_2)_A$. It appears, therefore, that all known anion interstitial species are stabilised by monovalent cation impurities to considerably higher temperatures than in pure crystals, and there is every reason to suppose that these impurities act as effective nucleation sites for further interstitial aggregation at still higher temperatures.

Itoh and Saidoh (1969) have determined an interaction volume of 150 lattice volumes for Na^+ -interstitial association in $KBr:Na^+$ from the same analysis as described in §2.6.4.1. Assuming interstitial capture is assisted by a replacement sequence ten lattice sites in length implies an interaction radius only two to three lattice sites. Saidoh and Itoh (1970) have, in fact, calculated an interaction energy between an H centre and a Na^+ impurity in KBr, using the approach of Bachmann and Peisl (1970) for H_2 interaction, obtaining an interaction energy $\sim 0.007 (r_0/r)^3$ eV, where r_0 is the halogen nearest neighbour separation; this compares with an interaction energy $\sim 0.25 (r_0/r)^3$ between two H centres and suggests that rather large concentrations of monovalent cation impurity are necessary to obtain an appreciable redistribution of interstitial aggregation. Since the interaction radii for H_A and H_2 formation are, respectively, $2r_0$ and $7r_0$, an interaction energy $\sim 10^{-3}$ eV is

apparently sufficient to induce association, perhaps by defocussing the crowdion replacement sequence.

The calculations of Dick (1966) for elastic field gradients in $\text{KBr}:\text{Na}^+$ imply that surrounding each Na^+ impurity are 24 lattice sites which provide more stable positions for interstitial atoms or ions than normal, though all 24 positions are by no means simultaneously populated; this calculation supports the interaction radius value derived from Itoh and Saidoh (1969).

Both Giuliani (1969) and Saidoh and Itoh have performed annealing experiments on H_A and I_A^- configurations to determine bond energies, monitoring H_A and I_A^- absorption bands and the correlated F and F^+ concentrations. Table 2.12 lists the temperatures at which each configuration becomes unstable in $\text{KBr}:\text{Na}^+$ and $\text{KBr}:\text{Li}^+$, together with dissociation energies from annealing and other experiments, compared with those relating to H and I^- centre stability in pure crystals. It is clear that stability is maintained to considerably higher temperatures in both species. It is also evident that the Li^+ ion is a more efficient interstitial stabiliser than Na^+ , as might be expected from relative ion sizes. Similar stability experiments have not yet been performed for the di-interstitial-monovalent cation impurity complex.

Giuliani (1969) has shown that monovalent cation impurities enhance both F and F^+ production in the early stages of irradiation at 80K, this enhancement correlates with growth of the V_1 band and is almost certainly due to stabilisation of interstitial anions, altering initial recombination kinetics. It is not known how late stage defect production behaves, but it might be expected that such interstitial

stabilization should depress late stage efficiency at intermediate temperatures by imposing essentially low temperature athermal recombination conditions. If the impurity concentration is large enough, interstitial clustering may never occur on a scale sufficient to alter recombination kinetics towards the high temperature form. The utility of interstitial stabilisation for microscopy is in simply altering observable clustering behaviour without appreciable need to influence fundamental defect production rate. There is ample evidence from low temperature electron microscopy experiments in $\text{KI}:\text{Na}^+$, detailed in §5.4, that 200 ppm Na^+ impurity is sufficient to inhibit observable clustering completely; in fact, use is made of this property to extend the time available for microscopy at low temperature. At temperatures above the H_A or I_A^- dissociation thresholds the doping is ineffective; there is, of course, no influence at room temperature.

2.8.3 Divalent cation impurities

The introduction of alkaline earth impurities into an alkali halide lattice complicates matters by introducing electrostatic as well as elastic considerations. As indicated in §2.8.1 it is accordingly difficult to separate the processes of production alteration and defect stabilization. There is the additional problem that defect stabilization may occur through electrostatic as well as elastic interactions. Moreover, there is considerable evidence that the cation vacancy which is created in equal numbers with divalent cation additions (to maintain overall charge neutrality), readily associates with the divalent impurity to provide a considerably more complex impurity centre. These

two defects attract each other because they are oppositely charged in the lattice.

The number of isolated cation vacancies N_V^+ , isolated divalent cation impurities N_D^{++} and associated pairs N_{VD} are functions of the temperature, association entropy change S_A and association energy E_A , and are related by an expression of the form (Crawford 1968)

$$\frac{N_V^+ N_D^{++}}{N_{VD}} = \exp(S_A/k) \exp(-E_A/kT). \quad (2.94)$$

If divalent impurities are the only source of vacancies, and the total divalent impurity concentration is N_D , $N_{VD} = N_D - N_V^+$; and if $N_V^+ \ll N_D$, we find

$$N_V^+ = N_D^{1/2} \exp(-E_A/2kT). \quad (2.95)$$

Ikeya et al. (1965) have measured an association energy $E_A \sim 0.3-0.4$ eV. Thus at room temperature one expects most divalent impurity-cation vacancy pairs to be associated. In this connection, it is worth noting that many impurity-vacancy pairs are found in higher complexes: dimers and especially trimers (Cook and Dryden 1962).

Hayes and Nichols (1960) found a paramagnetic $|Cl_2^-|$ centre with $\langle 100 \rangle$ symmetry in KBr doped with divalent impurities and irradiated at 195 K, which they attributed to a V_k centre perturbed by the presence of a divalent cation-cation vacancy pair, i.e. a hole trapped at an associated impurity-vacancy complex. Crawford and Nelson (1960) subsequently suggested that the centre was instead due to a halogen ion which had captured a hole, forming a halogen atom which thereafter relaxed into an adjacent cation vacancy introduced by the divalent cation concentration. This model explained the enhancement of early

stage F centre production in doped crystals, since the resulting anion vacancy could then trap an electron to become an F centre. As an obvious corollary, Varley (1962) proposed that an interstitial halogen species created instead by irradiation could be subsequently trapped in a cation vacancy.

Ishii and Rolfe (1966) investigated the V bands introduced in KBr:Ca^{++} and KBr:Sr^{++} by irradiation and found three separate components, in addition to the Hayes-Nichols band, which they called D bands. The D_3 band grew under irradiation at liquid nitrogen temperature and exhibited $\langle 100 \rangle$ dichroism. Annealing the D_3 band to room temperature resulted in a broader D_1 band, maintaining the $\langle 100 \rangle$ symmetry. Irradiation at room temperature produced two related bands, D_{2A} and D_{2B} , exhibiting $\langle 111 \rangle$ dichroism, as well as a D_1 component. Two models were proposed for the $\langle 100 \rangle$ and $\langle 111 \rangle$ type centres involving association of a $|\text{Br}_3^-|$ molecule ion situated at an anion site and surrounded by three impurity-vacancy pairs.

Itoh and Ikeya (1967) studied the growth of the optical absorption bands associated with the divalent impurities in KBr:Ca^{++} x-irradiated at 195 K. Both the Hayes-Nichols (H-N) and the D_3 bands were produced, and both were shown to be complementary to the F centre. The H-N band saturated early on in the irradiation and was, in fact, shown to be proportional to the square root of the impurity concentration, and thus from (2.95) to the isolated cation vacancy concentration, suggesting that the model of Crawford and Nelson is reasonable. Recent positron annihilation measurements in NaCl (Waung, Brandt, and Levy 1968) have indeed shown that isolated cation vacancies are destroyed during x irradiation at room temperature. However, a plot of the initial formation rate of the H-N band

against $1/T$ (Ikeya et al. 1966) yields an activation energy of 0.08 eV, which is consistent with interstitial halogen mobility and suggests that the model of Varley (1962) is more nearly correct, i.e. the isolated cation vacancy acts as a trap for mobile interstitials created by irradiation. An observed increase in early stage F coloration at 195 K was found to be correlated with H-N band formation, which is consistent with interstitial stabilisation. Accordingly, we shall refer to this centre an anion interstitial stabilised by a cation vacancy as an H_V centre, in keeping with Sonder and Sibley's (1972) use of V for cation vacancy centres.

The D_3 band continued to grow together with the V_4 band well into late stage coloration, and saturated only when all divalent impurities were exhausted, after which the V_4 band only continued to grow. Conductivity measurements indicated that most of the divalent impurities were associated with cation vacancies. These two results strongly suggest that the D_3 band is associated with interstitial trapping by divalent impurity-cation vacancy complexes. The D_3 band was not formed at room temperature, possibly indicating that at 195 K the D_3 band arises from singly trapped interstitials, and that at room temperature impurity-vacancy complexes act as nucleation sites for further interstitial aggregation. For example, the D_1 band of Ishii and Rolfe might be associated with trapped di-interstitials, and the D_2 bands with higher interstitial aggregates nucleated at the complexes. On the basis of this evidence, we shall denote the centre responsible for at least the D_3 band as an H_Z centre, an H centre trapped at a divalent cation impurity-cation vacancy complex. Models for the H_V and H_Z centres are indicated in fig. 2.4e.

Substantial evidence for interstitial trapping derives also from other sources. For example, most recently Ikeya, Itoh and Suita (1969)

have discovered by EPR measurements a Mn paramagnetic centre in NaCl:Mn^{++} irradiated at liquid nitrogen temperature, which appears to be associated with an interstitial halogen species bound along $\langle 100 \rangle$. The concentration of this centre decreased with prolonged irradiation and annealed at 180 K, both results suggesting further interstitial aggregation. Sibley and Russell (1965) conducted room temperature irradiation hardening experiments in KCl:Sr^{++} and KCl:Ca^{++} using 1.5 MeV electrons and ^{60}Co γ irradiations. It was found that early stage coloration did not contribute to irradiation hardening, even though impurities were found to enhance early stage coloration. Late stage coloration, however, contributed markedly to hardening, as previously demonstrated in pure crystals where the increase in flow stress is attributable to strain-producing interstitials (Sonder et al. 1967) and scales with square root of the F centre concentration (Sibley and Sonder 1963). However, doping with divalent impurities was found to reduce the hardening for the same irradiation dose. This result is particularly significant, as it is well known that addition of divalent impurities itself raises the flow stress (Brown and Pratt 1963). Production efficiency measurements of Sonder and Sibley (1965) in KCl:Pb^{++} at 80 K revealed that addition of 5 ppm Pb^{++} results in an increase of 15 ppm in F centre concentration, suggesting that a divalent impurity can stabilise at least three interstitials; this increase saturates at ~ 150 ppm Pb^{++} where presumably all those interstitials which would have been unstable at 80 K are stabilised. Sonder et al. (1967) have found that optical bleaching of Frenkel pairs at room temperature is much faster in doped crystals and suggest that impurities induce a higher density of smaller interstitial clusters which accelerates the rate of annihilation by mobile vacancies

created during bleaching. Some indication of the stability of interstitials trapped by divalent impurities comes from the F^+ centre annealing experiments of Giuliani and Reguzzoni (1968). Additions of Sr^{++} and Pb^{++} to KCl prolong stability of F^+ centres to 150 K, after which a slow annealing stage extends nearly to room temperature. It is probable, then, that interstitial stabilisation occurs even at room temperature in crystals with substantial divalent impurity concentrations. Coupled with a defect production efficiency reduced by electron trapping mechanisms, such stabilisation reduces the scale of observable interstitial clustering. Once aggregation has begun at an impurity nucleation site, the resulting configuration is apt to be very much more stable thermally than the initial trapped entity.

The influence, then, of divalent impurities is expected to be similar to that of monovalent impurities, but extending to considerably higher temperatures (possibly room temperature). Whenever interstitial stabilisation occurs via attachment to dispersed impurities, the kinetics of saturation are altered towards low temperature recombination conditions, permitting considerably extended observation time for electron microscopy; electron trapping effects may be simultaneously present to reduce production rate, even for high irradiation intensities, provided impurity concentrations are large enough. Observable interstitial clustering is, of course, also inhibited. The cost, however, is high: mechanical and coloration properties are remarkably altered in divalent impurity-doped crystals and no longer reflect pure crystal behaviour at any temperature.

Table 2.1

Equilibrium Thermal Defect Concentration

<u>T, K</u>	<u>N_s (cm⁻³)</u>
0	0
298	5×10^5
473	6×10^8
673	8×10^{14}
873	4×10^{16}
1073 (m.p.)	4×10^{17}

Table 2.2

Colour Centre Notation

The notation below was adopted for consistent use in this thesis but is not necessarily standard throughout the literature. Symbols are meant to refer to their respective centres and not to any spectroscopic manifestation.

<u>Centre</u>	<u>Notation</u>	<u>Principal Optical Absorption Band(s)</u>
Vacancy Centres		
1. Anion vacancy, trapped electron	F	F, β
2. Excited F centre	F*	K, L
3. Anion vacancy (ionised F centre)	F ⁺	α
4. Anion vacancy, two trapped electrons	F ⁻	F'
5. Di-F centre	F ₂ , M	M
6. Ionised F ₂ centre	F ₂ ⁺	F ₂ ⁺
7. Tri-F centre	F ₃ , R	R ₁ , R ₂ , ?N ₁ , N ₂
8. Ionised F ₃ centre	F ₃ ⁺	F ₃ ⁺
9. F centre adjacent to monovalent cation impurity	F _A	A
10. F centre adjacent to divalent cation-cation vacancy complex	F _Z	Z
11. Hydrogen ion incorporated substitutionally	U	U

Table 2.2 (contd)

Self-Trapped Hole Centres

12. Self-trapped hole	$V_k, X_2^- $	V_k
13. Self-trapped exciton	$V_k^*, X_2^{2-} ^*$	exciton

Interstitial Centres

14. Interstitial halogen atom in crowdion position	$H, X_4^{3-} $	H
15. Interstitial halogen ion in interstitial position	I^-	I^-
16. Di-interstitial	H_2	V_4
17. Interstitial molecule	$ X_2 ^0$	V_2, V_3
18. H centre trapped at monovalent cation impurity	H_A	V_1
19. I^- centre trapped at monovalent cation impurity	I_A^-	I_A^-
20. H centre trapped at cation vacancy	H_V	Hayes-Nicols
21. H centre trapped at divalent cation-cation vacancy complex	H_Z	D

Table 2.3

Comparative Irradiation Rates

<u>Radiation type</u>	<u>Typical Dose Rate</u> (eV cm ⁻³ sec ⁻¹)	<u>Time to</u> <u>saturation</u>
50 keV x-rays (W target)	3×10^{16}	4 months
1 MeV γ rays (Co ⁶⁰)	2×10^{17}	3 weeks
400 keV electrons (Van de Graaff)	10^{20}	1 hour
400 keV protons (Van de Graaff)	2×10^{21}	3 minutes
100 keV electrons (electron microscope)	10^{24}	0.4 seconds

Table 2.4

Comparison of Minimum Ionization and Displacement Damage Cross
Sections

		(units of 10^{-24} cm^2)			
		<u>400 keV electrons</u>		<u>1 MeV electrons</u>	
		$\bar{\sigma}_I \text{ (min)}^\dagger$	$\bar{\sigma}_N^*$	$\bar{\sigma}_I \text{ (min)}^\dagger$	$\bar{\sigma}_N^*$
NaCl	(4K)	1050	8	950	29
KCl	(77K)	30000	6	27000	19
NaBr	(4K)	60	-	50	27
KI	(4K)	30	-	20	12

† from $\{\partial F/\partial E\}_0$ F centre measurements; $F^+ : I^-$ production excluded.

* 25 eV displacement threshold assumed.

Table 2.5

Interstitial Annealing Stages in KCl

Unbracketed values indicate threshold temperature (K) for onset of each annealing stage. Values in brackets () are estimated activation energies in eV. Bold lines set off indicated stage of bulk diffusion. Superscripts refer to references and techniques listed below data.

(a) Interstitial ion

(I)	11 ¹				
(II)	14				
(III)	19	18 ² (0.025)	18 ³ (0.06-0.11)	23 ⁴	
(IV)	27	27		29 ⁵	28 ⁶ (0.17) ⁷
(V)	30-77	45	36	35	

(b) Interstitial atom

(I)	33 ⁸ (0.04)		
(II)	44 (0.09)	42-60 ⁹	(0.17) ⁷
(III)		90 ¹⁰ (0.07)	

References for Table 2.5

- ¹Guiliani and Reguzzoni (1968): Isochronal anneal, α , I band opt. abs.
- ²Behr, Peisl and Waidelich (1967b): Isochronal anneal, H band opt. abs.
- ³Gebhardt (1962): Isothermal anneal, thermal conductivity
- ⁴Giuliani et al. (1965): Isothermal anneal, II band opt. abs.
- ⁵Hertz, Peisl and Waidelich (1967): Isothermal anneal, lattice parameter
- ⁶Balzer, Peisl and Waidelich (1968): Isothermal anneal, lattice parameter
and thermal expansion
- ⁷Tharmaligam (1964): theoretical calculation, Born-Mayer potential
- ⁸Behr, Peisl and Waidelich (1967a): Isothermal anneal, H band opt. abs.
- ⁹Känzig and Woodruff (1958): Isothermal anneal, H centre spin resonance
- ¹⁰Schnatterly and Compton (1964): Isothermal anneal, M centre decay time

Table 2.6

Stability of Self-Trapped Holes

<u>Alkali halide</u>	<u>A (sec⁻¹)</u>	<u>E_h (eV)</u>	<u>Mobility temperature (K)</u>
LiF		0.32 ¹	120 ¹
NaF			140-160 ²
NaCl		(~0.39)	160 ³
NaI		0.15 ⁴	58 ⁴
KCl	1 x 10 ¹³ ⁵	0.54 ^{5,6}	170-200 ^{5,6}
KBr		0.39 ⁷	140 ⁷
KI	4 x 10 ¹³ ⁸	0.273 ⁸	100 ⁸
RbI		0.32 ⁴	125 ⁴

¹Känzig (1960) ²Bass and Mieher (1965) ³Pung and Khaldre (1966)

⁴Murray and Keller (1967) ⁵Keller et al. (1967) ⁶Neubert and

Keffner (1962) ⁷Delbecq, Hayes and Yuster (1961) ⁸Keller and
Murray (1965).

Table 2.7

Vacancy Diffusion in KCl

	E_m (eV)	ν (sec ⁻¹)
F	1.6 ¹	3.7×10^{15} ¹
	1.6 ²	4×10^5 ²
	0.94 ³	-
F ⁺	0.95 ⁴	3.3×10^{12} ⁴
	1.04 ⁵	2.7×10^{12} ⁵
	1.18 ⁶	
	-	
	0.60 ⁷	
	0.60 ⁸	
F [*]	0.1 ⁹	6.9×10^9
	0.13 ²	

¹Wolf (1966): EPR; ²Lüty (1968): F_A, F_A⁺, F_A^{*} reorientation;

³Hirai and Matsuyama (1967): F₂ kinetics; ⁴Fuller (1966):

diffusivity; ⁵Beaumont and Jacobs (1967): electrical conductivity;

⁶Guccione, Tosi and Asdente (1959): theoretical; ⁷Van Doorn (1962):

F₂ formation; ⁸Härtel and Lüty (1963,1964): F_A⁺ reorientation;

⁹Fritz, Lüty and Rausch (1965): F_A^{*} reorientation.

Table 2.8

Vacancy Aggregate Behaviour

	KCl	KBr	KI	LiF
R → F, M, N	323	~273		
N → F, M	>373	>373		
M → F	>403	>373		
F → colloid	553	423	433	373 (neutron irradiated)
Colloid → F	623	523		

(All temperatures in K)

Table 2.9

Comparative F Centre Growth Kinetics

<u>Data</u>	<u>dF/dE $\propto$</u>
Sonder and Templeton (1967)	$(1 - KF)^1$
Pooley (1966c)	$(1 - KF)^2$
Herrmann and Pinard (1970a)	$(1 - KF)^3$
Goldstein (1967)	$(KF)^{-1}$
Durand, Farge and Lambert (1969)	
Hughes and Pooley (1971)	$\exp (-KF)$

Table 2.10

Recombination Volumes

<u>Data</u>	Dose Rate (<u>eV cm⁻³ sec⁻¹</u>)	ν (<u>cm³</u>)
Sonder and Templeton (1967)	6×10^{16}	1×10^{-18}
Herrmann and Pinard (1970a)	6×10^{20}	5×10^{-19}
Pooley (1966c)	10^{21}	3×10^{-19}
Hughes and Pooley (1971)	2×10^{21}	2×10^{-19}
Soul (1970)	2×10^{22}	2×10^{-19}

Table 2.11

Electron Trapping Impurity Levelfor $\dot{F}/\dot{F}_0 = 0.1$

<u>Alkali halide</u>	<u>E_h (eV)</u>	<u>ν_h (sec⁻¹)</u>	<u>N_D (ppm)</u>
KCl	0.54 ¹	60 ¹	50 000
NaCl	~0.37	~2 x 10 ³	~2 000
KI	0.273 ²	2.5 x 10 ⁴ ²	100

¹Keller et al. (1967)²Keller and Murray(1965)

Table 2.12

Thermal Stability of H and H_A Centres in KBr

		KBr	KBr:Na ⁺		KBr:Li ⁺	
Atom {	T, K	40 ¹	130, ⁴	145 ³	195, ⁴	210 ³
	E, eV	0.09, ² 0.1 ³	0.25, ²	0.3 ³	0.4 ³	
Ion {	T, K	21 ⁵	80 - 110 ⁶		-	
	E, eV	0.06 ⁵	0.3 ³		0.5 ³	

¹Künzig and Woodruff (1958) ²Ueta (1967) ³Saidoh and Itoh (1970)

⁴Giuliani (1970) ⁵Itoh, Royce and Smoluchowski (1965a) ⁶Giuliani (1968)

Fig. 2.1. Electron-excess optical absorption bands in KCl. All bands are not necessarily present under the same conditions, but are illustrated for completeness.

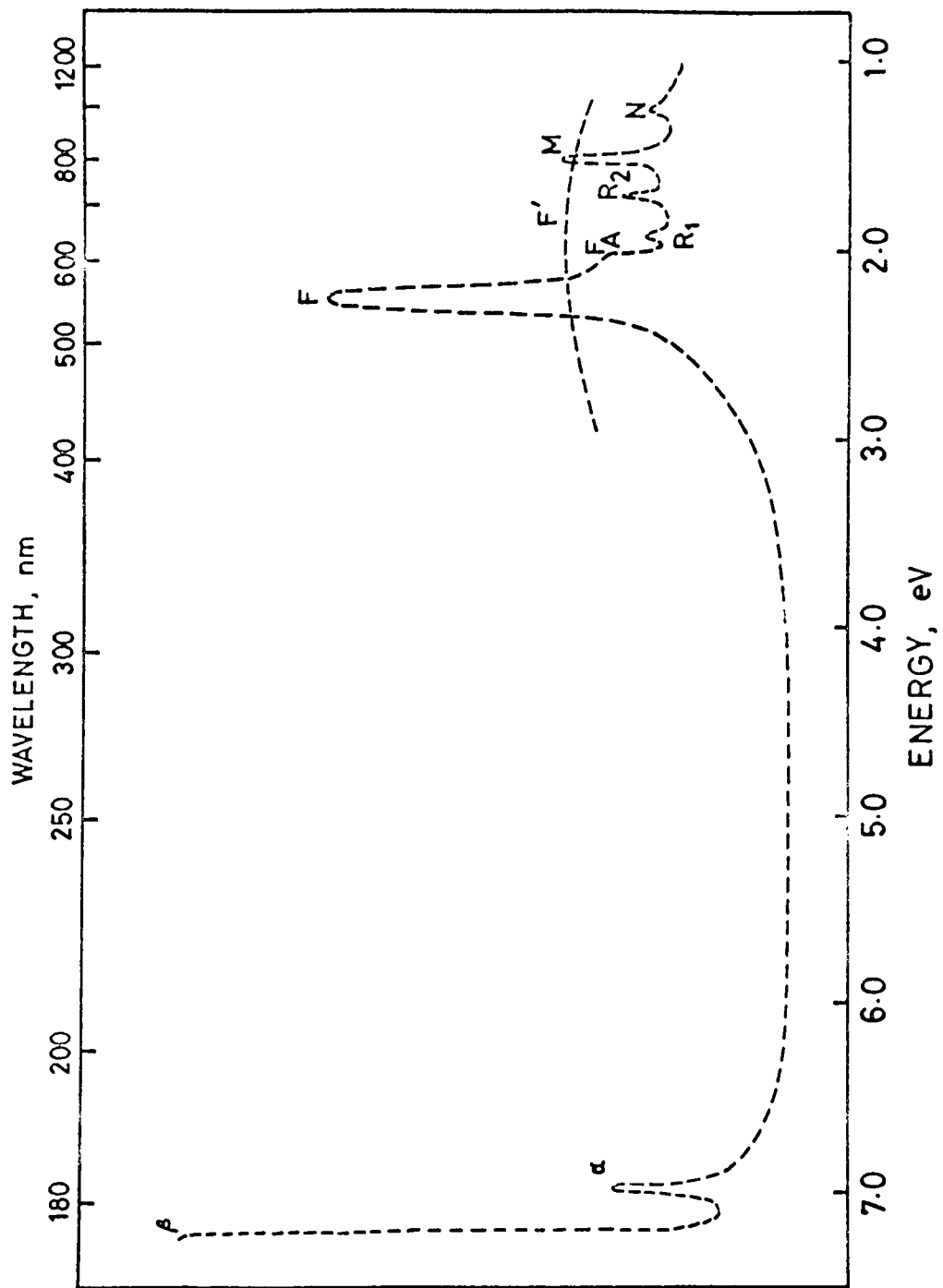


Fig. 2.2. The hole-excess optical absorption bands in KCl. All bands are not necessarily present under the same conditions, but are illustrated for completeness.

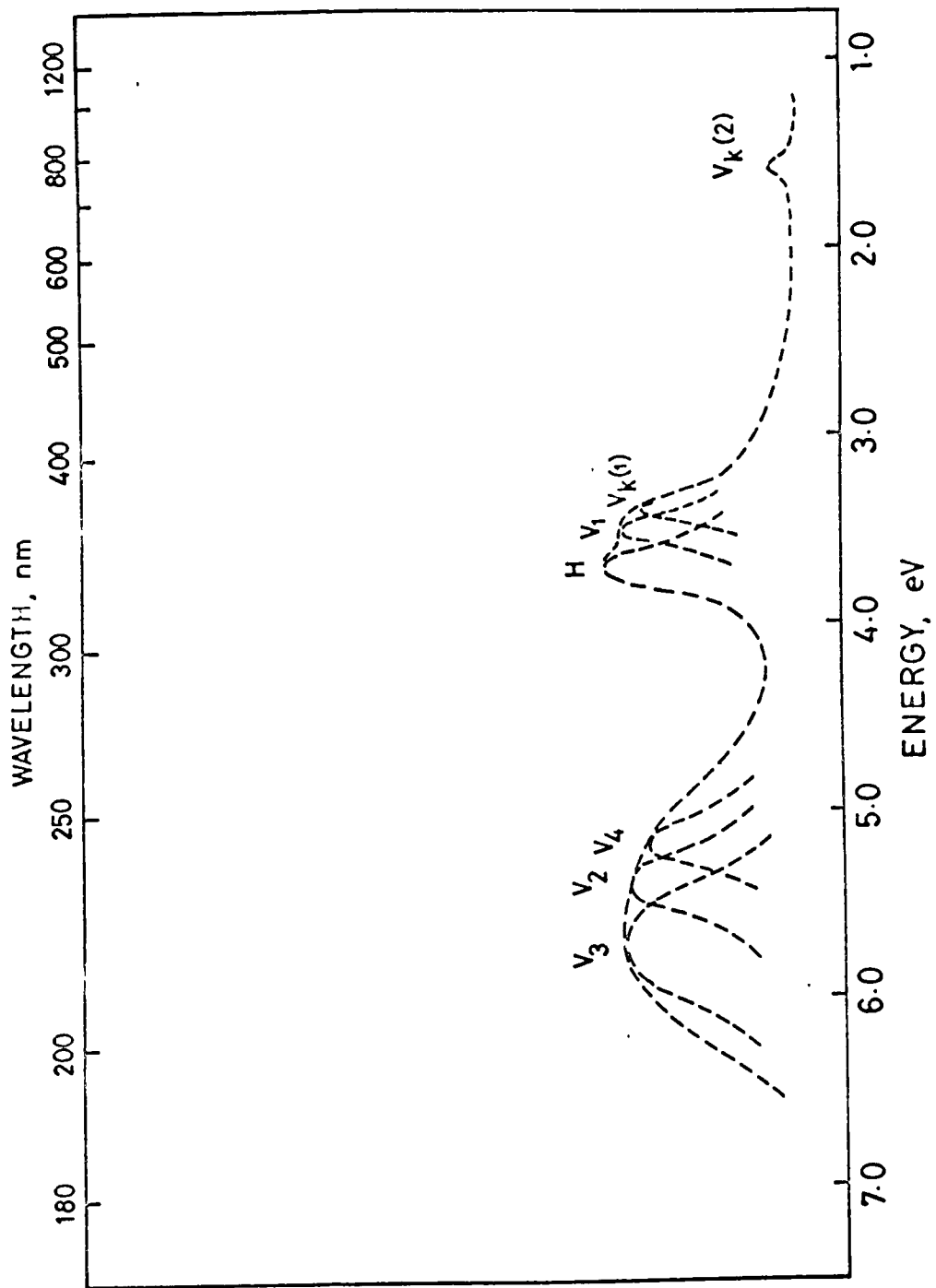


Fig. 2.3. The electron-excess centre configurations F , F^+ , F^- , $M(F_2)$, $R(F_3)$, F_A and F_Z . No attempt has been made to depict surrounding lattice relaxations.

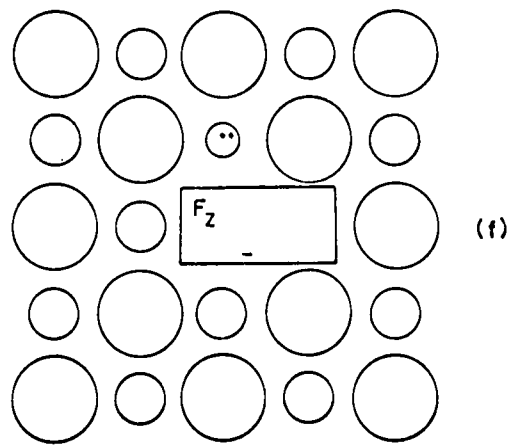
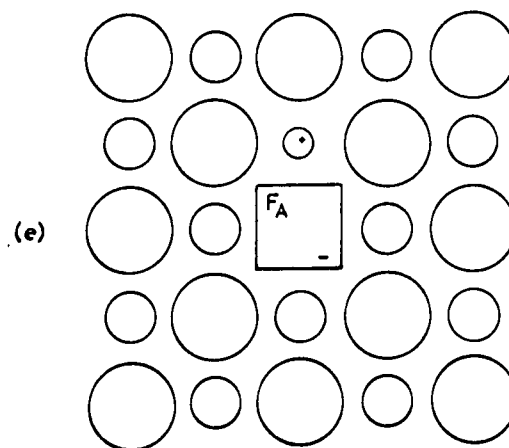
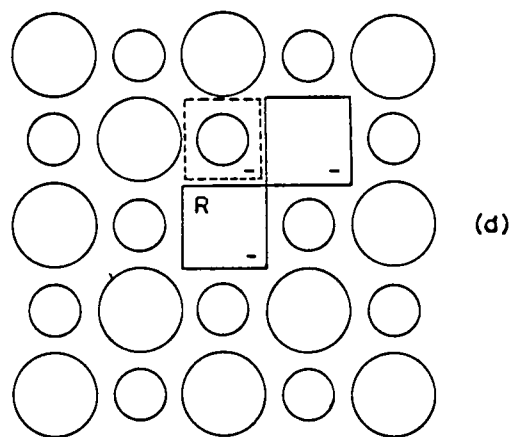
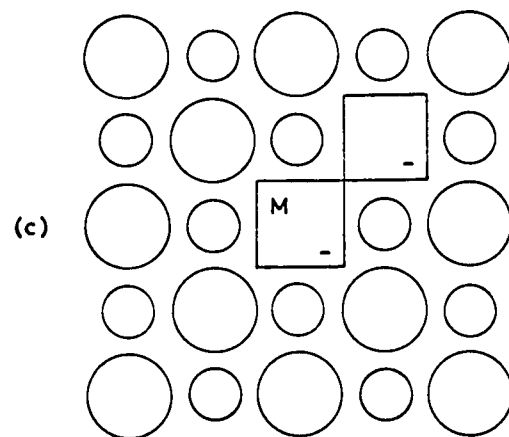
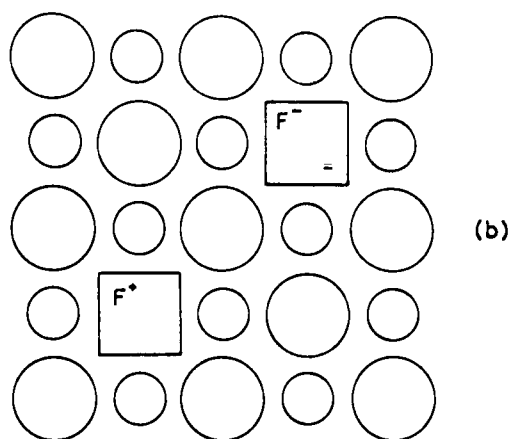
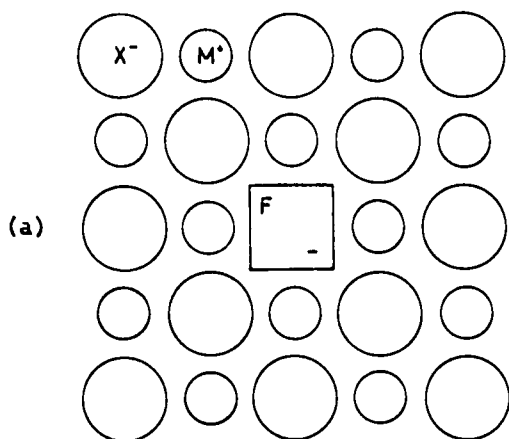


Fig. 2.4. The hole excess centre configurations' V_k , H , I^- , H_A , H_V and H_Z . No attempt has been made to depict surrounding lattice relaxations nor hole delocalisation.

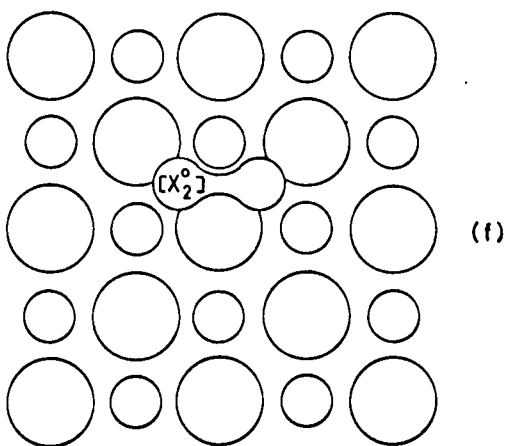
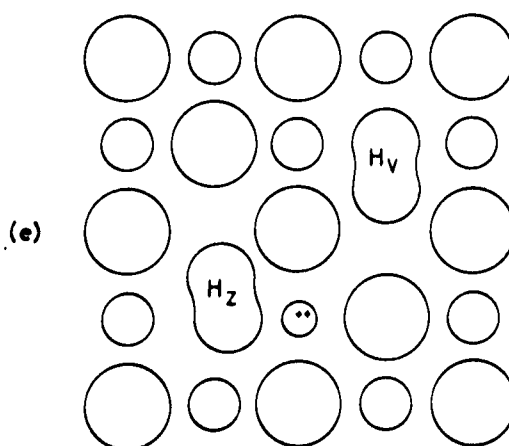
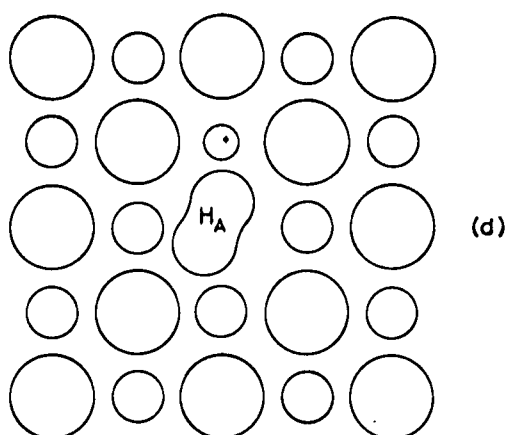
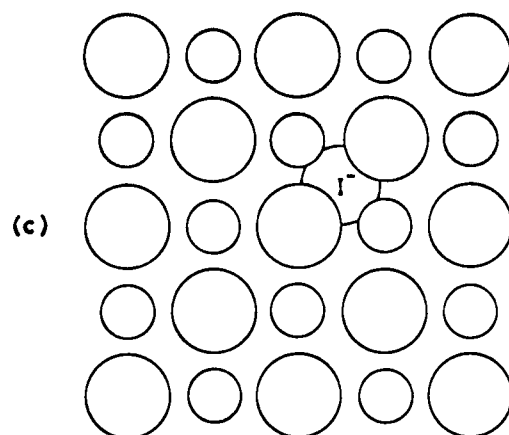
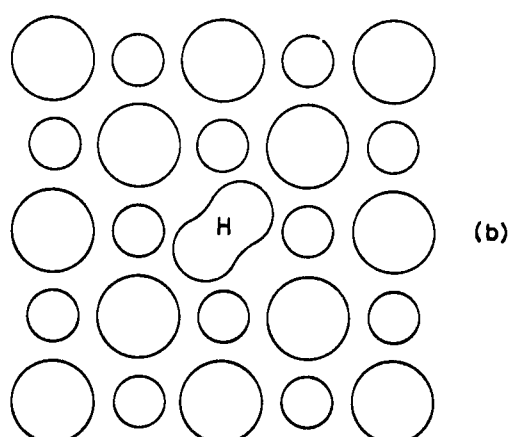
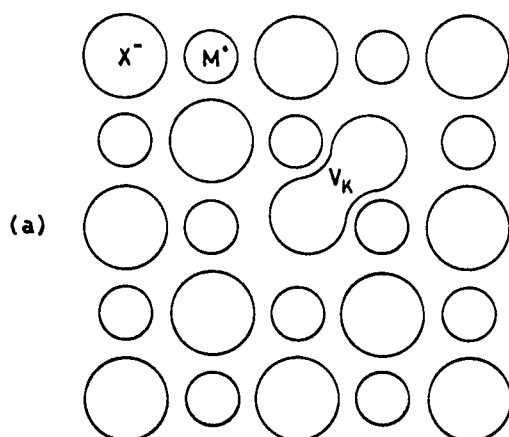


Fig. 2.5. Electron energy loss spectra for 100 KeV electrons in single crystal thin foils of (a) KCl and (b) NaCl irradiated at room temperature. The labelled peaks correspond to similar losses found by Creuzberg (1966b) in evaporated films. The peaks at ~ 14 eV (KCl) and ~ 15 eV (NaCl) represent plasma losses, other peaks exciton losses. An extra peak at 3.4 eV occurs in KCl and is discussed in §5.3.3.3 with reference to alkali colloid bulk plasmon loss.

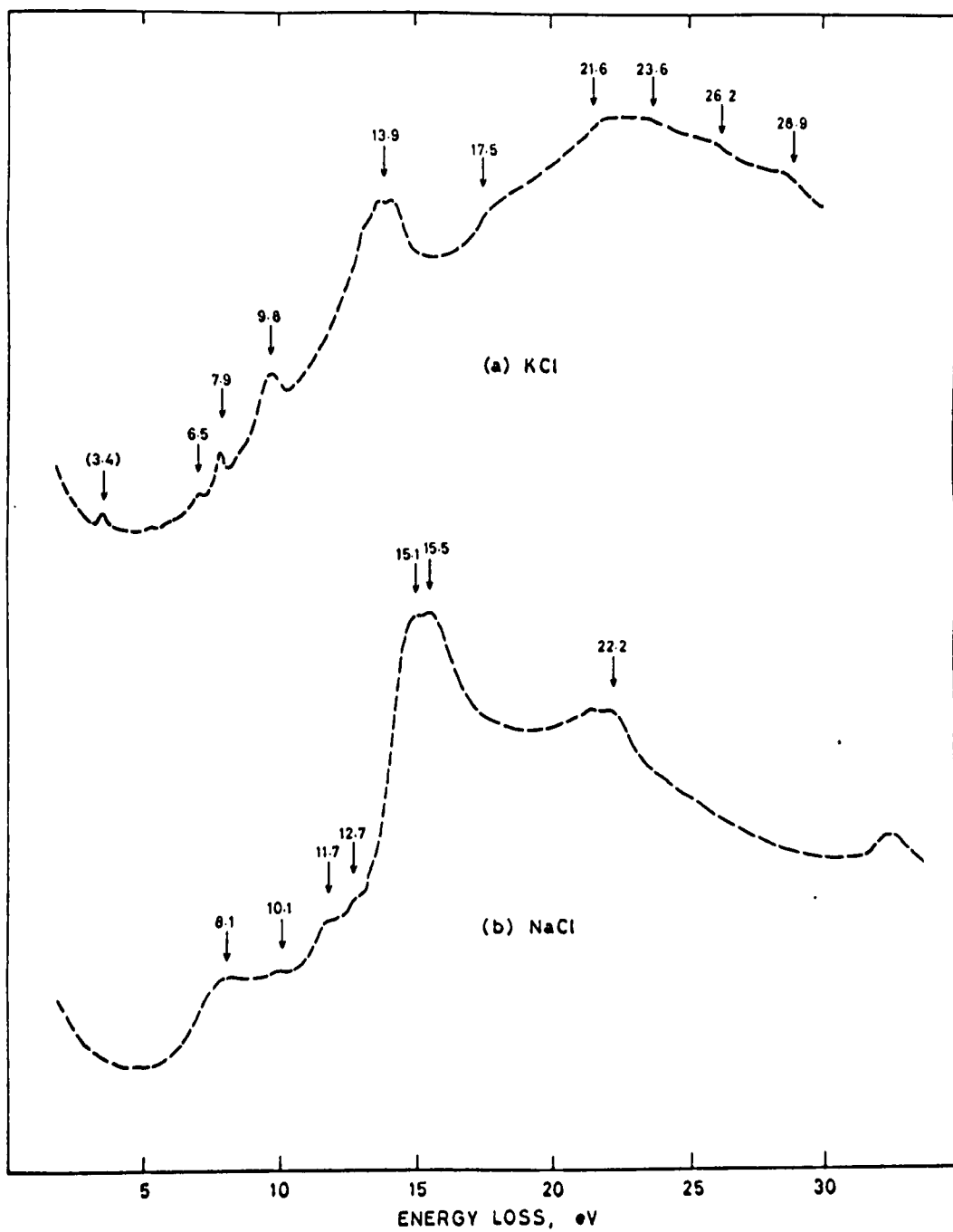


Fig. 2.6. Bethe energy loss for 40 KeV to 1 MeV electron irradiation of NaCl, NaBr, KCl, KBr and KI. Note the sharp increase in energy loss rate below 100 KeV. A factor of 2 or so advantage obtains in going from 100 KeV to 1 MeV.

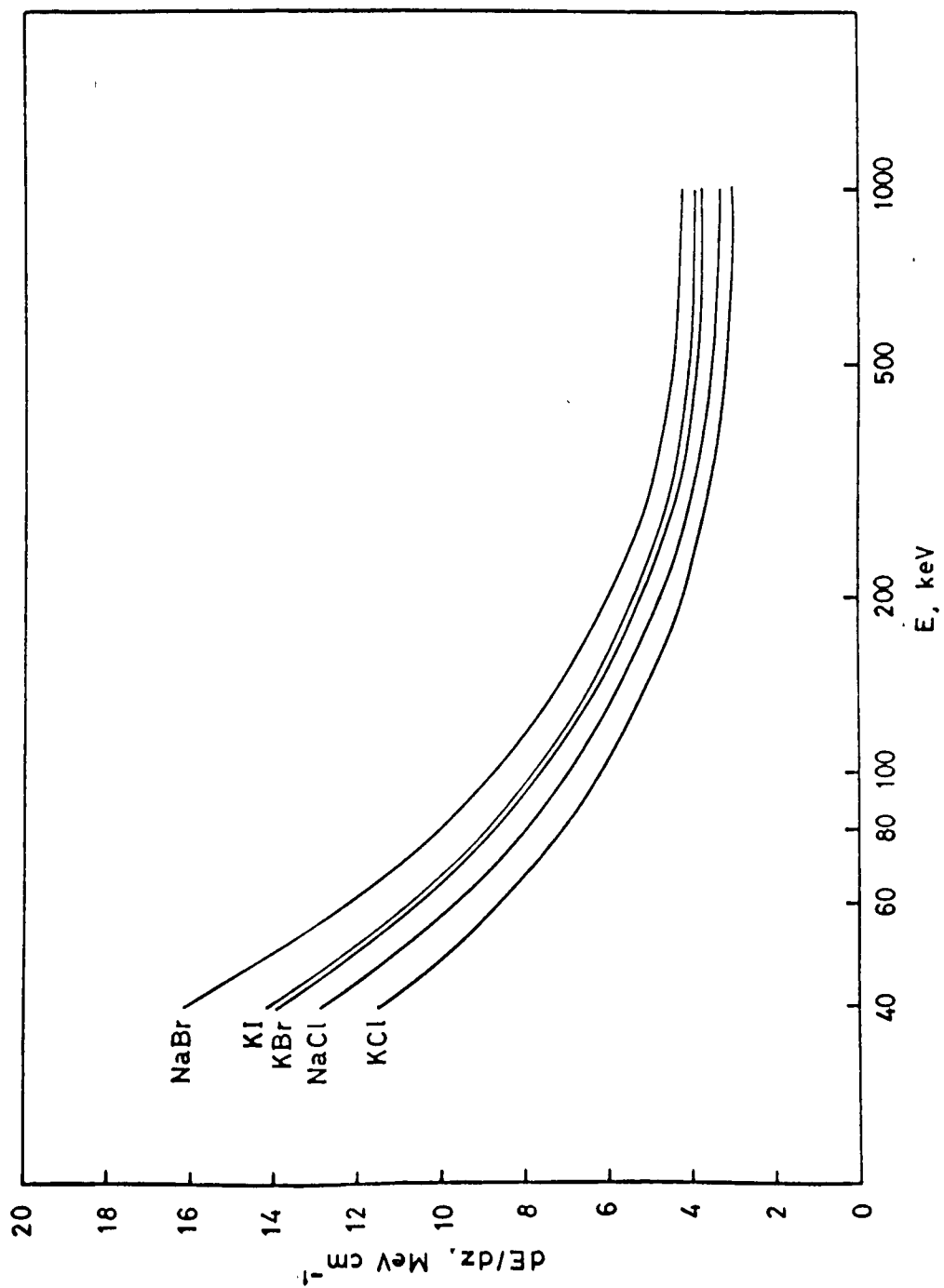


Fig. 2.7. Typical X-ray emission from a tungsten target bombarded with 50 KeV electrons. The most probable X-ray quantum occurs in the region ~ 25 KeV.

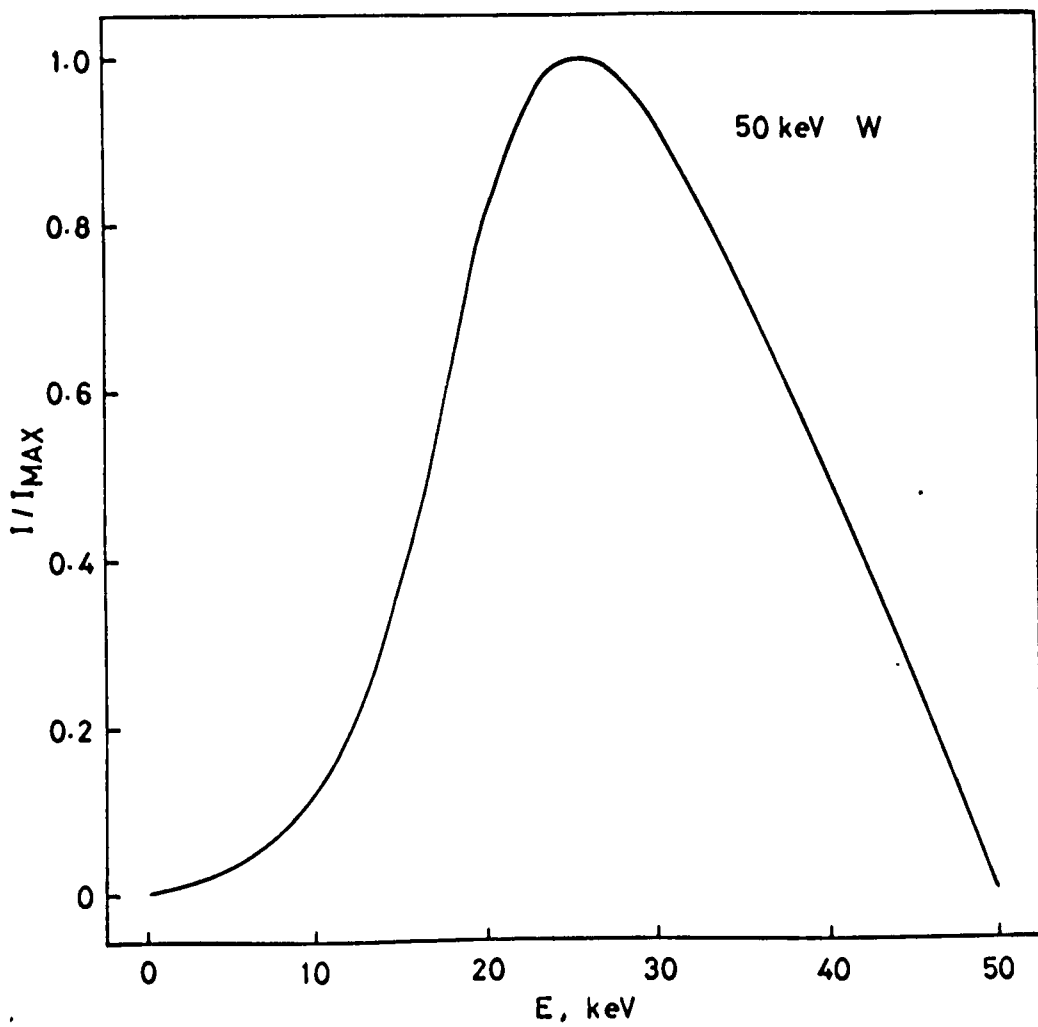


Fig. 2.8. Energy loss rate as a function of penetration by various irradiation types in KCl. An attempt has been made to depict the high initial loss of X-rays and the straggling of electrons. Note the uniform loss rate inherent in proton irradiation and the range and uniformity of γ irradiation.

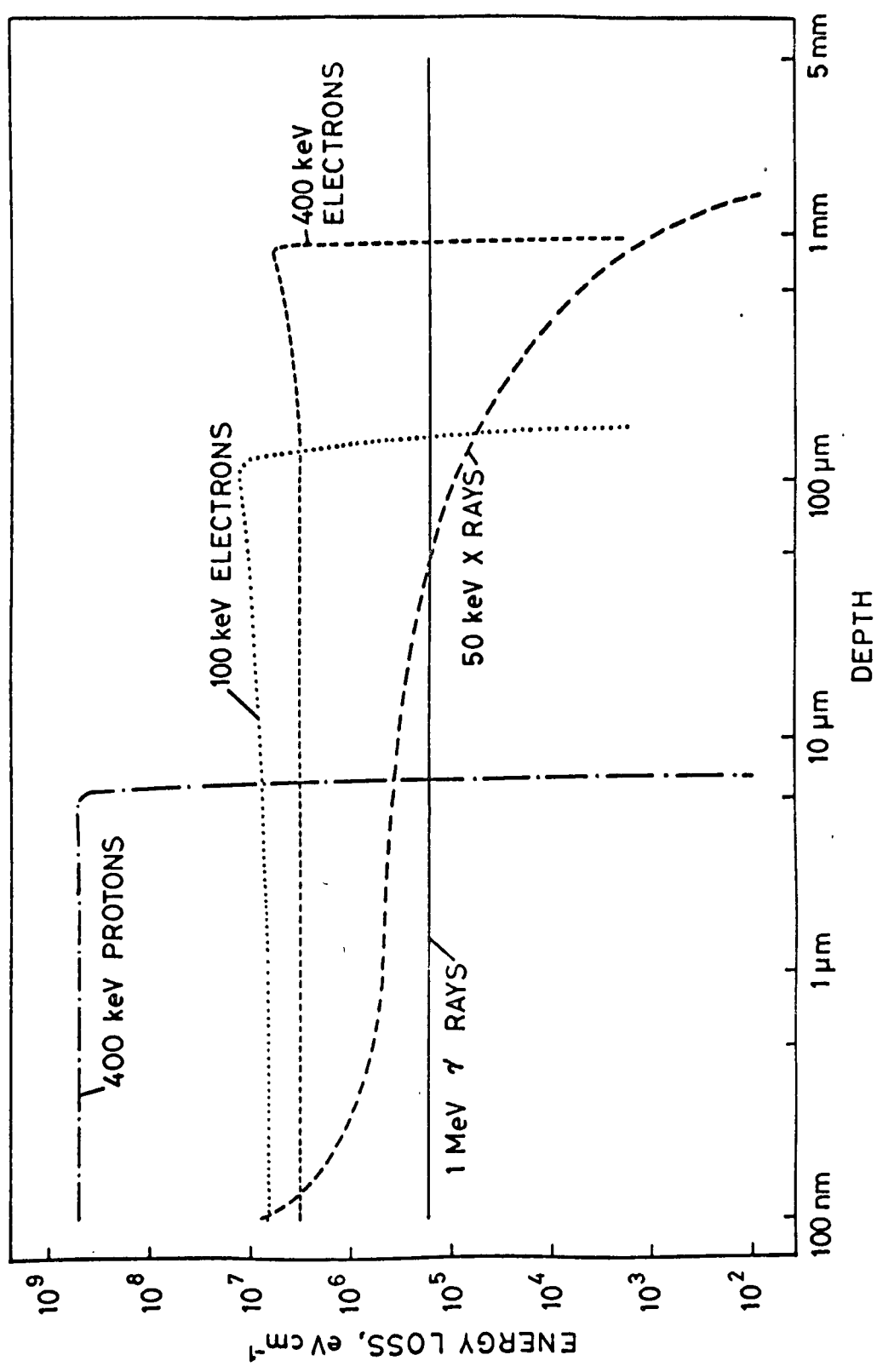


Fig. 2.9. Configuration coordinate energy diagram for the V_k^* exciton in three potassium halides. r_0 is the equilibrium anion separation, E_{th} the thermal activation energy for non-radiative exciton decay and E_{nr} the energy derived from the non-radiative electron-hole recombination (illustrated here for KBr). V_k motion can quench the entire process if a suitable impurity sink is available to serve as an alternative recombination site.

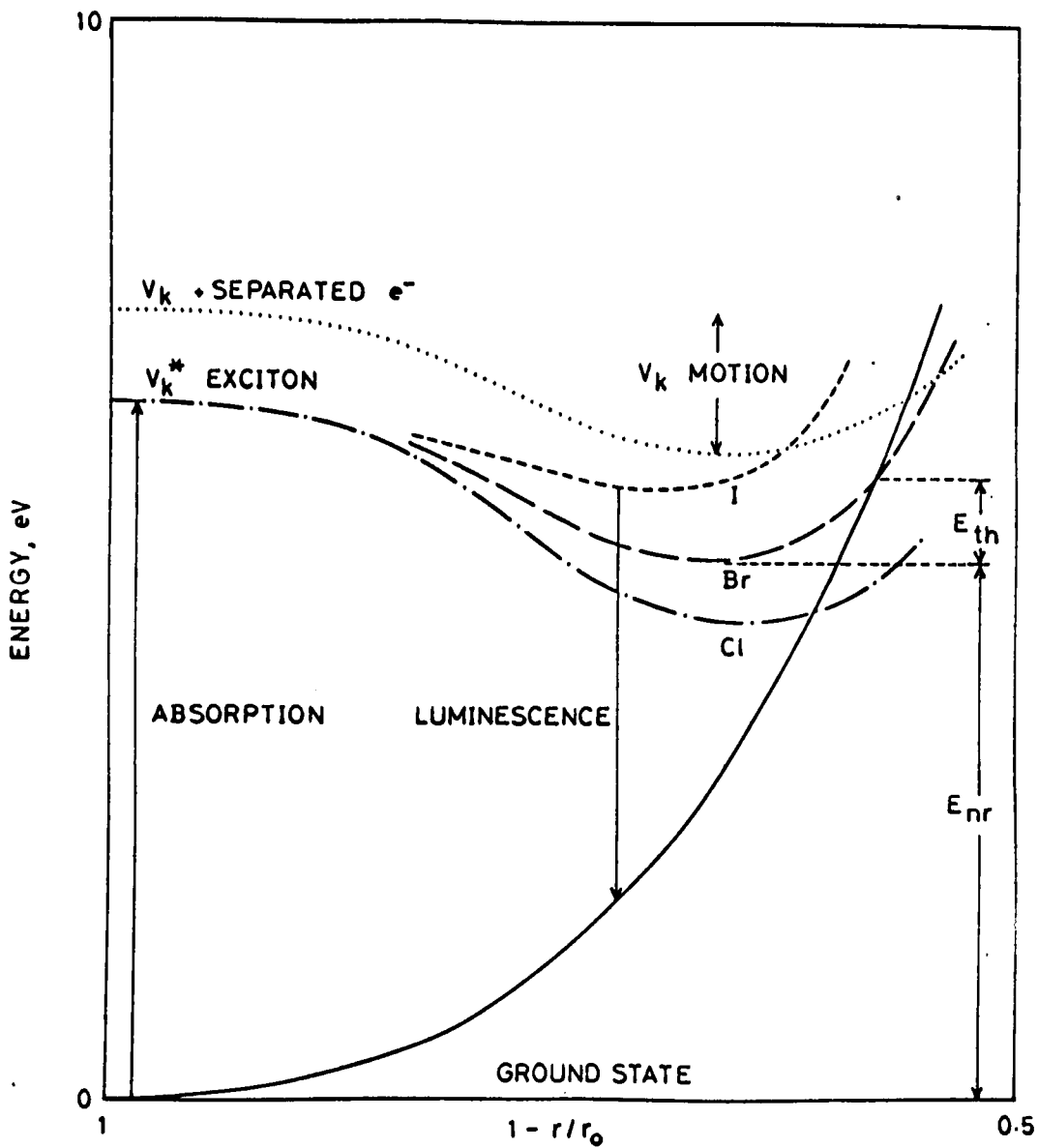
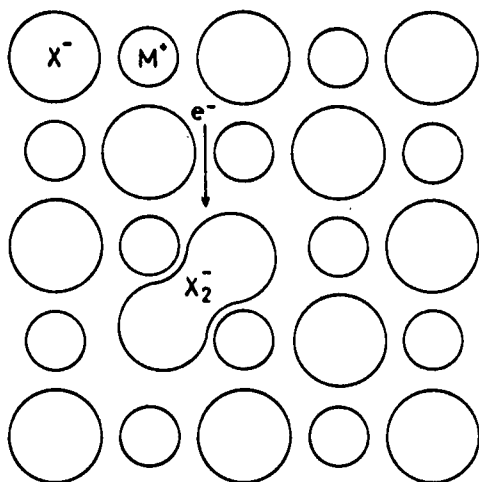
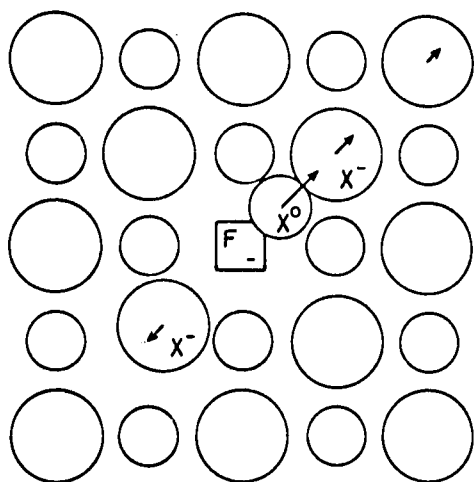


Fig. 2.10. Schematic representation of the Pooley (1966a, b) mechanism as modified by Hatcher and Pooley (1970). A hole is trapped in the valence band as a V_k centre, which subsequently traps an electron, the excited V_k^* state decaying non-radiatively. If the recombination energy is unequally shared, a halogen atom is ejected within 10 nsec along a $\langle 110 \rangle$ close-packed halogen row, leaving behind an F centre in its ground electronic state. The interstitial atom propagates by forward hole tunnelling (reverse electron tunnelling) until it comes to rest as an H centre at some distance from the F centre. Subsequent ionisation of the H centre during low temperature irradiation may produce an $F^+ : I^-$ pair replacing the initial F:H Frenkel defect.

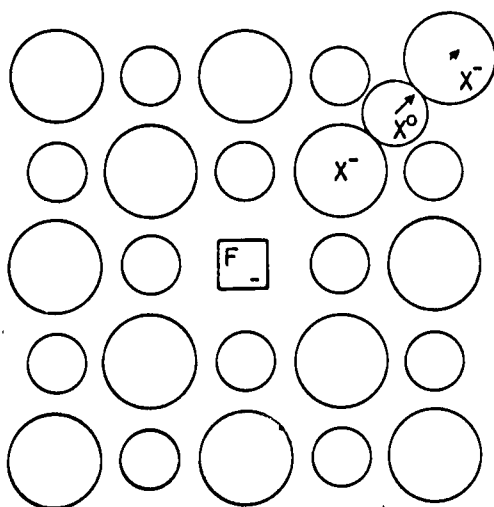
(a)



(b)



(c)



(d)

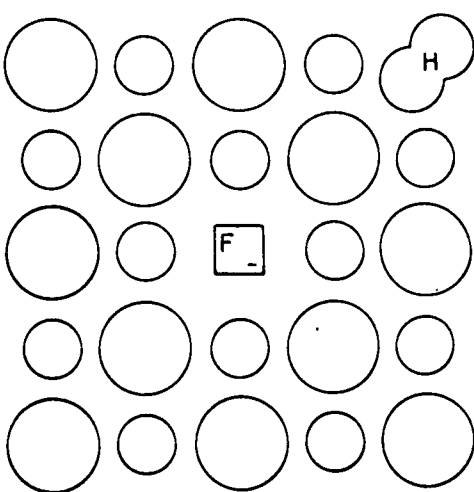


Fig. 2.11. Defect creation efficiency in KCl as a function of temperature T and irradiation intensity (in brackets). The decrease above 200K and relating to irradiation intensity almost certainly arises from mobility of the F^+ species. The decrease between 50K and 150K may relate either to V_k mobility or behaviour of the mobile interstitial.

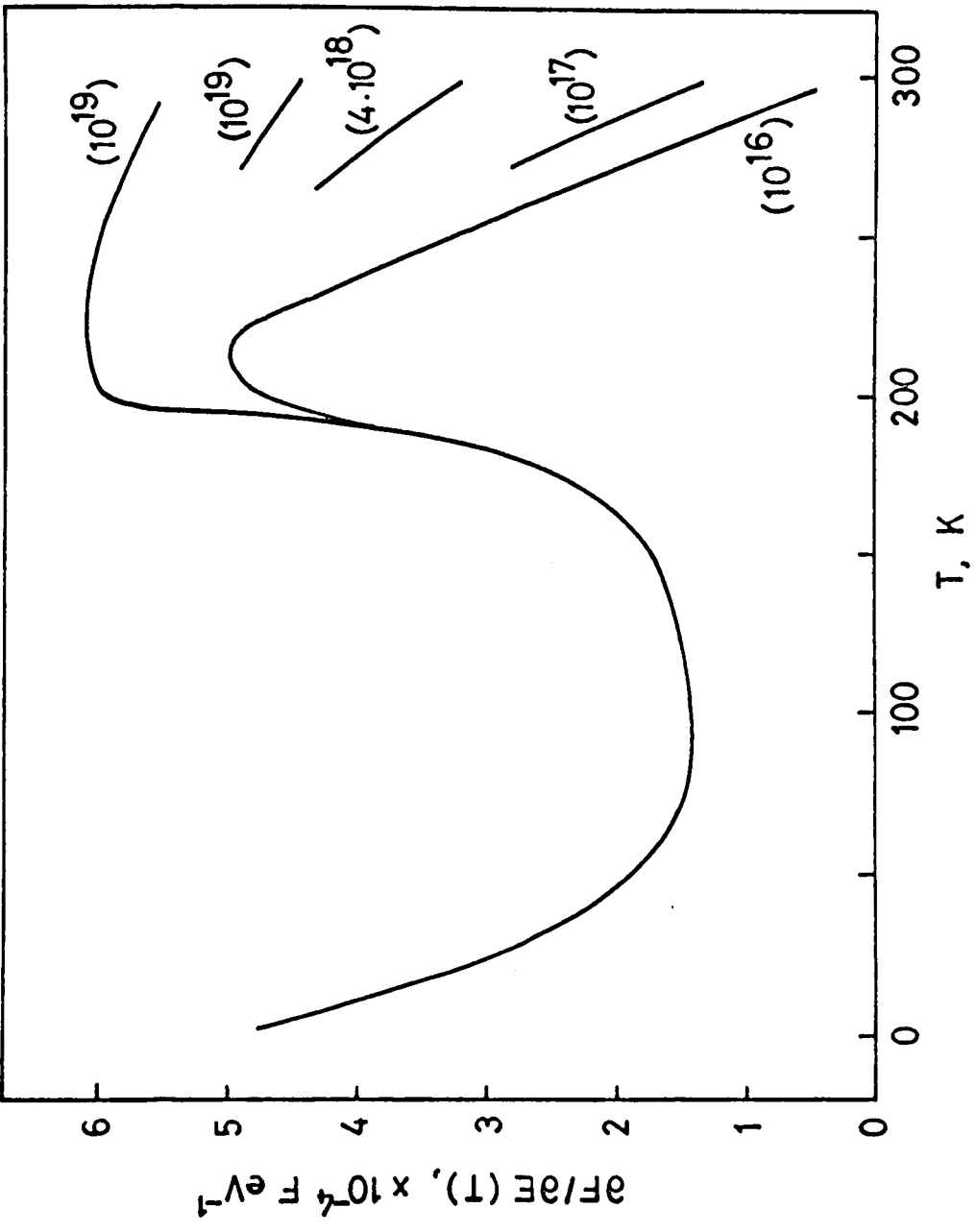


Fig. 2.12. Defect creation efficiencies as a function of temperature in six representative alkali halides. The large decrease in efficiency with decreasing temperature for NaCl, KI and NaBr parallels a corresponding increase in luminescence. The low high-temperature efficiencies in NaBr and NaI probably relate to ion size considerations.

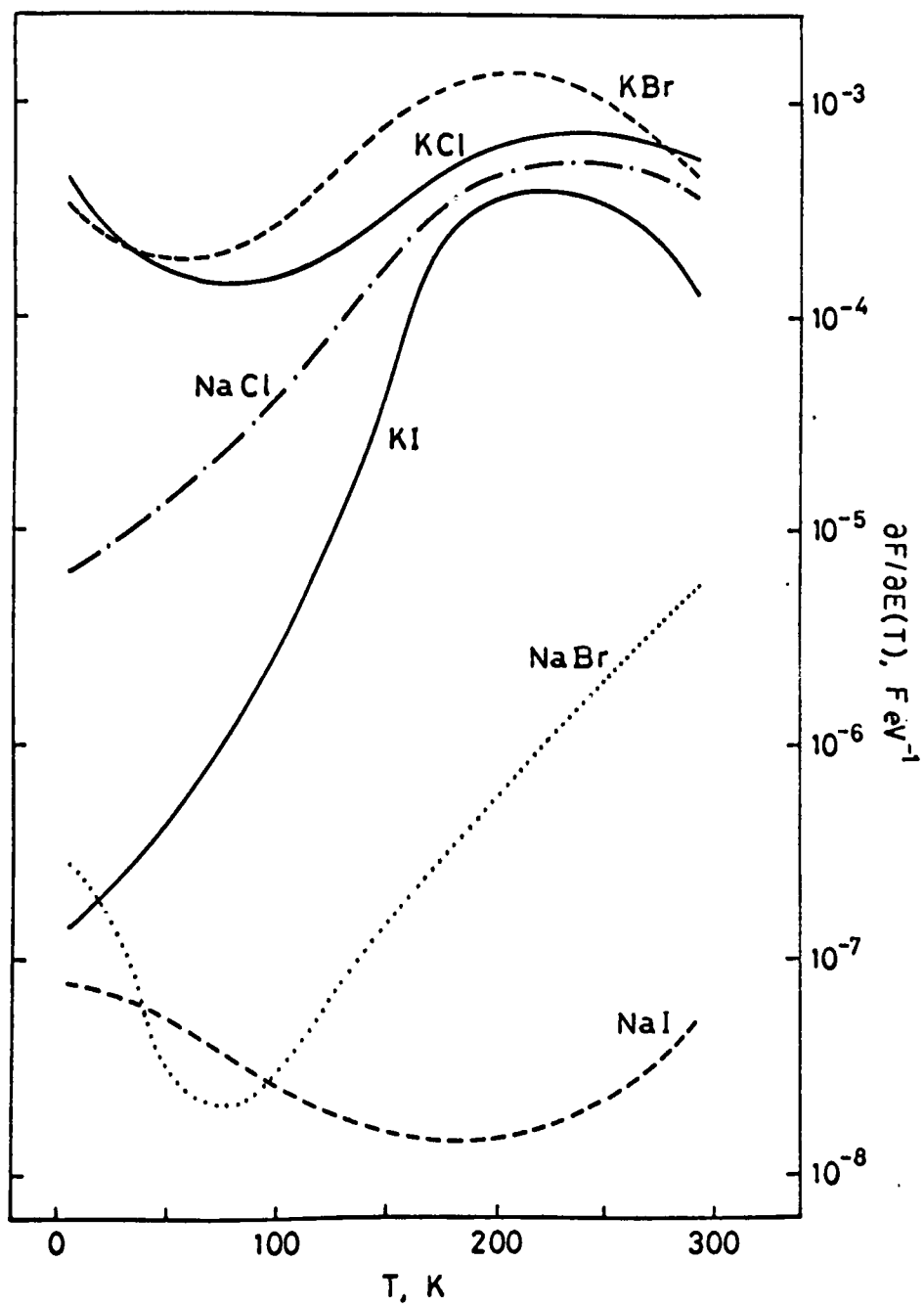


Fig. 2.13. Principal defect mobility thresholds for five alkali halides. The bars indicate the temperature range over which measurements reported in the literature indicate onset of appreciable defect mobility. Note that defect mobility conditions can be divided into three separable regimes.

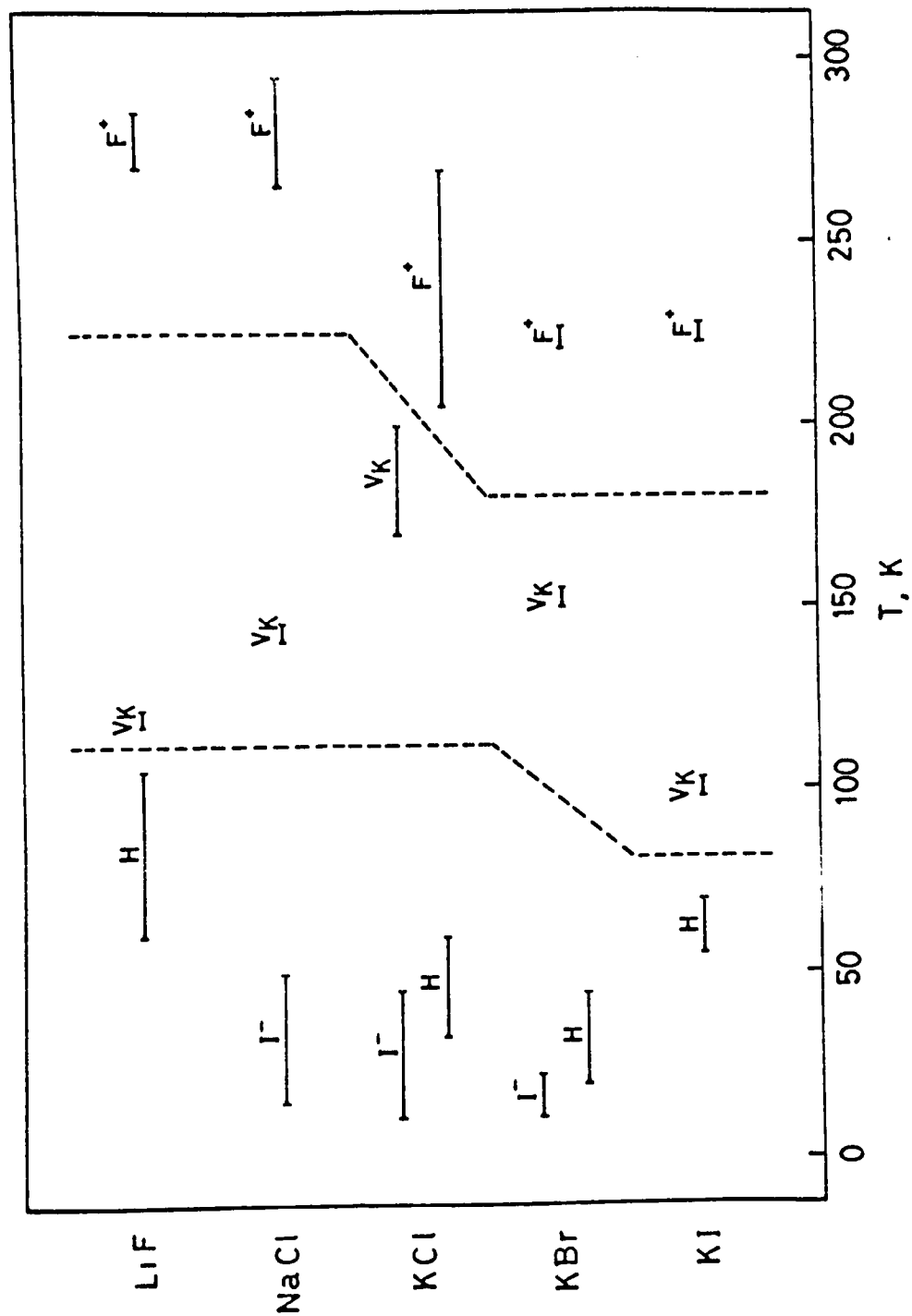


Fig. 2.14. Typical F centre saturation curve for 300 KeV proton irradiation of KCl from the data of Hughes and Pooley (1971). The energy deposition rate is indicated.

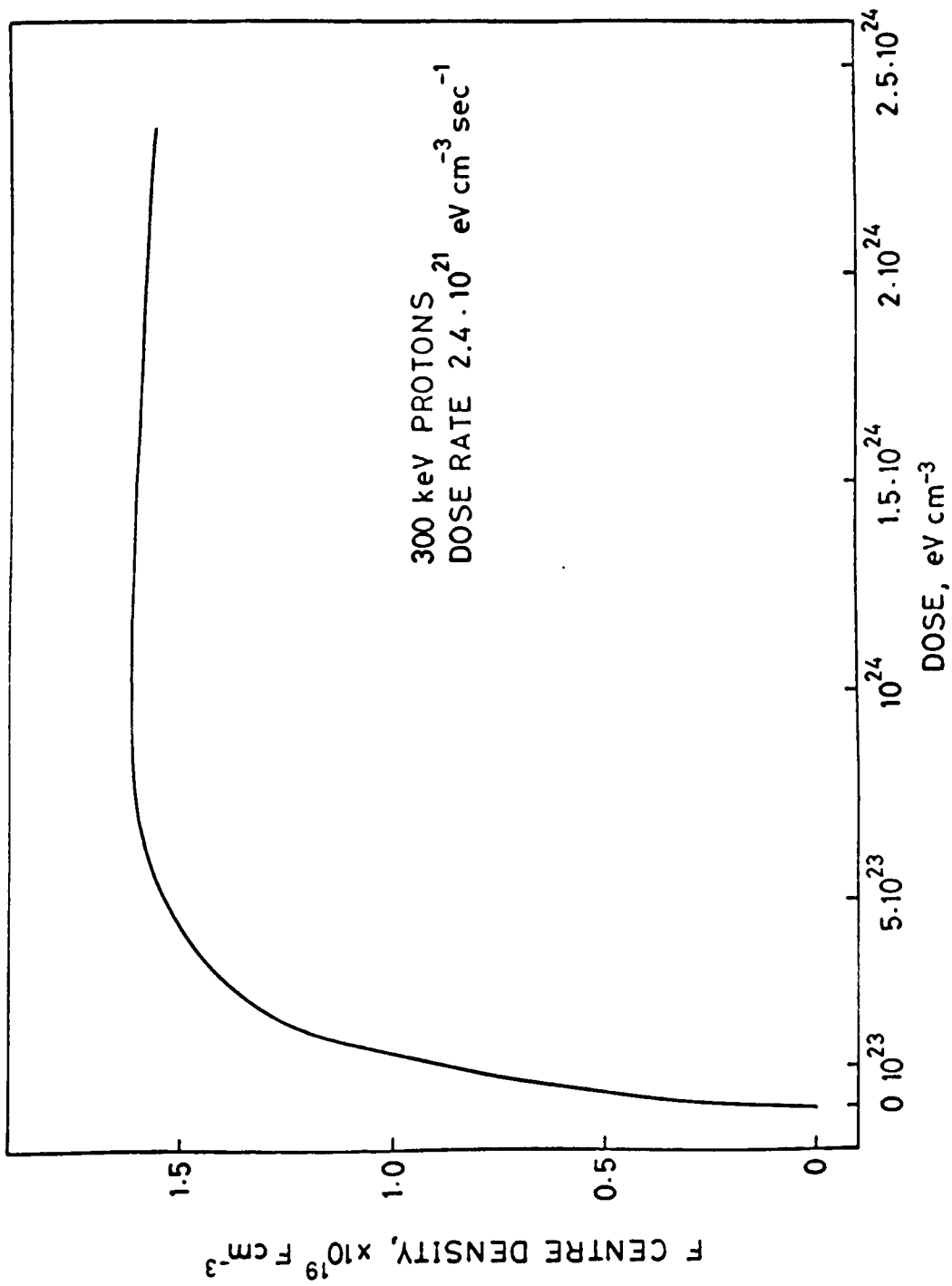
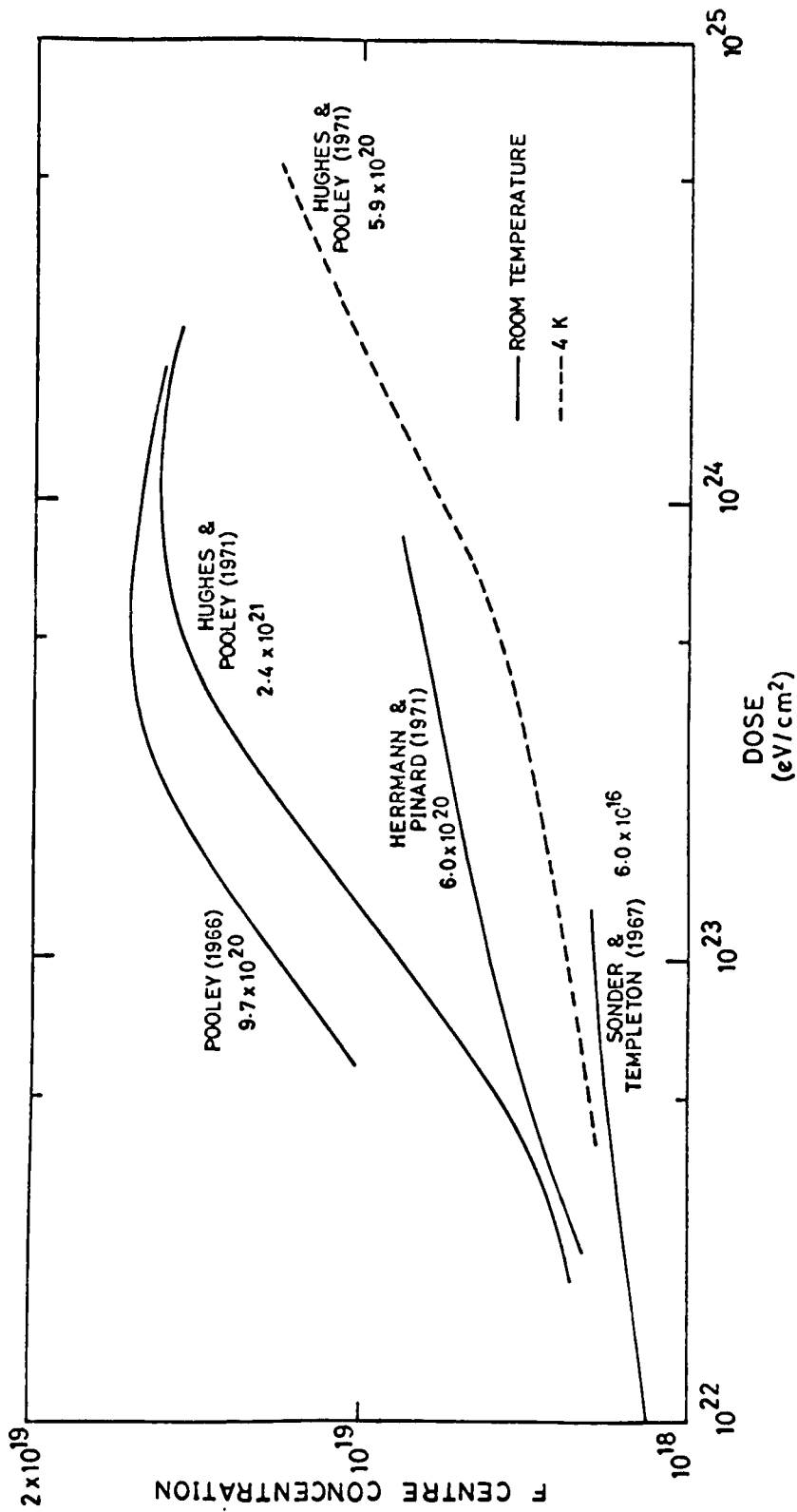


Fig. 2.15. Comparison of F centre saturation behaviour for five different dose rates and two temperatures. The slopes of room temperature curves increase monotonically with the irradiation dose rate indicated (in $\text{eV cm}^{-3} \text{sec}^{-1}$). The slope of the low temperature saturation curve begins much smaller than the corresponding room temperature slope, but at a critical defect density approaches room temperature behaviour.

F CENTRE SATURATION IN KCl



§3. Thin Foil Specimen Preparation and Examination

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3.1 Introduction

The basic requirement of transmission electron microscopy is a specimen foil thin enough (~ 100 - 500 nm) to be appreciably transparent to electrons with energies ~ 100 keV over a sufficient area to encompass interesting or significant features (typically $\sim$ tens of μm^2). The preparation process normally involves sectioning a starting slice of material to ~ 3 mm diameter and 1 mm thick from bulk material, followed by some thinning procedure for removing material until a foil is attained. Well-established techniques now exist for producing such foils for most metals and some semiconductors, but few have been successfully applied to dielectric materials.

The alkali halides are particularly resistant, in many ways, to the sorts of techniques normally employed. Because they are non-conducting, the enormously versatile spark-machining and electro-polishing techniques are not available. Because these crystals are extremely brittle, yet remarkably soft, the mechanical machining and thinning techniques used for semiconductors are not applicable. An extraordinary susceptibility to radiation damage precludes ion beam machining, often a successful recourse for otherwise intractable materials. Finally, rather pronounced chemical reactivity to many common solvents, particularly atmospheric moisture, makes application of chemical shaping techniques somewhat more difficult than in less reactive materials.

This chapter outlines successive techniques which were developed to produce consistently serviceable damage-free representative foils suitable for transmission electron microscopy from bulk alkali halide crystals. Problems peculiar to alkali halide foils (ease of

plastic deformation, moisture sensitivity, charge acquisition) are discussed and solutions detailed. Next, the various electron diffraction parameters necessary for establishing optimum conditions for alkali halide microscopy are derived, and an indication is given of the minimum electron absorption attainable with alkali halide foils operating in a standard microscope contrast mode, since this relates to the maximum usable transmitted electron intensity available for recording for a given permitted incident intensity. Finally, image recording statistics are discussed as they relate to the phosphor viewing screen and photographic emulsion response, and to the utilisation of the electron microscope under conditions of marginal illuminating intensity.

3.2 Sectioning

The first requirement for electron microscope specimen preparation is a technique for sectioning small sections suitable for further reduction from bulk crystal specimens, without introducing unacceptable mechanical damage to the section. By far the easiest way to accomplish this in alkali halides is by cleavage, but such a technique, used indiscriminately, can be shown to introduce unacceptable plastic deformation. An alternative technique is chemical sectioning, which is less severe and also not restricted to cleavage planes.

3.2.1 Cleavage

Single crystals of alkali halides cleave easily on certain crystallographic planes; this behaviour offers a convenient technique

for cutting large crystals to a desired smaller size or sectioning prior to polishing. The cleavage process is illustrated in fig. 3.1. A wedge is driven into the crystal along the trace of the cleavage plane, usually at or near a corner, initiating a crack which propagates with terminal velocities approaching the longitudinal sound velocity (Gilman, Knudsen and Walsh 1958). As the two separating sections of the crystal bend in a double cantilever mode and the crack advances, a portion of the strain energy in the two sections is converted into surface energy. As will be seen in §3.2.1.3 below, a large amount may also be dissipated in plastic strain.

3.2.1.1 Surface energies

The largest contribution to the cleavage energy in the absence of plastic strain is the creation of two free surfaces with their associated surface energy. The relative surface energies of different crystallographic faces appears to determine on which plane(s) cleavage is preferred (Gilman 1959). Surface energy calculations have been reviewed by Tosi (1964) in a discussion of cohesion in ionic solids on the Born model. The electrostatic contribution to specific surface energy may be obtained by assuming an inverse power ionic interaction and summarising interactions by the Madelung Method. Born and Stern (1919) also added a contribution from repulsive energy, and devised the Born-Stern Formulae for the NaCl structure.

$$\begin{aligned}\sigma(001) &= 0.1173 (Z e)^2/a^3 &&) \\ \sigma(011) &= 0.3150 (Z e)^2/a^3 &&) (3.1)\end{aligned}$$

where Z is the largest common factor in (Z^+, Z^-) . From (3.1), we surmise

that $\sigma(001)/(011) = 2.7$, i.e. (001) cleavage will be preferred to (011) cleavage in NaCl structure alkali halides, which is observed; (011) cleavage is possible in some NaCl structure alkali halides, but considerably more difficult. The Born-Stern Model may be improved by including van der Waal's contributions (Shuttleworth 1949; van Zeggeren and Benson 1957), surface distortion and polarisation (Benson, Balk and White 1959; Benson, Dempsey, and Balk 1961). Experiments of varying sophistication (Gilman 1960; Gutshell and Gross 1965; Westwood and Goldheim 1963; Burns and Webb 1970) have also been performed to directly determine surface energies. Table 3.1 lists and compares values obtained from the various methods. It is immediately evident that definitive values of surface energies are distinctly absent, and except for general trends one can pick a value nearly at random. All NaCl structure alkali halides and MgO will cleave on (001). LiF is about the only NaCl-type alkali halide which readily exhibits (011) cleavage. Although the CsCl structure indicates low (011) surfaces it is not experimentally possible to cleave these structures; this may have something to do with the dislocation processes needed to maintain cleavage crack propagation. Cleavage on other planes is possible in ionic crystals; the fluorite (CaF_2) structure cleaves easily on (111).

3.2.1.2 Cleavage mechanics

The mechanics of the cleavage process have been derived quasi-statically by Benbow and Roesler (1957); Gilman, Knudsen and Walsh (1958); Gilman (1959) and dynamically by Burns and Webb (1970).

Fig. 3.1 schematically represents a crystal of width w and two arms.

of thickness p_1 and p_2 undergoing cleavage. A reference frame moving with the cleavage crack tip is used, so that $x=0$ at the crack tip and $x=L$ at the opened end of the crystal. It is assumed that the wedge entering at $x=L$ is free to rotate so as to produce equal forces F acting on each cleavage arm. From an analysis of beam loading in the cantilver bending mode (Timoshenko and Goodier 1970), the displacements y of each arm relative to the cleavage plane are, neglecting shear components which are significant only for $p \leq L$,

$$\begin{aligned} y_1 &= \frac{6}{6YI_1} (3Lx^2 - x^3) \\ y_2 &= \frac{F}{6YI_2} (3Lx^2 - x^3) \end{aligned} \quad \left. \begin{array}{l}) \\) \\) \end{array} \right\} (3.2)$$

where Y is Young's modulus and I_1 and I_2 are the moments of inertia of each arm. Since $I = wp^3$, we immediately see that if $p_2 \gg p_1$, $y_2 \ll y_1$, and one arm must suffer all the displacement. This corresponds to the attempt to cleave thin sections from the end of a large crystal block. Since it is the reversible elastic displacement energy in the arms (which can be very much less than accompanying plastic deformation energy) which compensates for the increase in surface energy arising from the two cleaved faces, there will be correspondingly larger incidental deformation in the thinner arm. Therefore we will wherever possible choose to bisect the crystal instead, so that $p_1 = p_2 = p$. This bisection will always correspond to the minimum deformation in each arm. The separation of the arms at $x = L$ is then $2y$, where $y_0 = \frac{FL^3}{3YI}$ for each arm.

The reversible elastic energy U stored in each arm is

$$U = \frac{1}{2EI} \int_0^L M^2(x) dx = \frac{FL^3}{6YI} \quad (3.3)$$

where $M(x)$ is the bending moment at x ; for small angles of bending $M(x) \approx F(L - x)$. There will also be an energy component associated with the kinetic energy of each arm given by

$$T = \frac{1}{2} m \dot{y}^2 = \frac{Wp}{15} \left(\frac{\dot{L}}{v_s} \right)^2 \frac{F^2 L^5}{Y I^2} \quad (3.4)$$

where $\dot{y}$ is the arm separation velocity, $\dot{L}$ is the crack propagation velocity and $v_s = \sqrt{Y/\rho}$ is the longitudinal sound velocity. (3.4) may be rewritten in terms of U ,

$$T = \frac{24}{5} U \left(\frac{L}{p} \right)^2 \left(\frac{\dot{L}}{v_s} \right)^2, \quad (3.5)$$

and we see that for very fast cleavages, most of the compensatory energy comes from the kinetic energy of the separating arms rather than from deformation; therefore fast cleavages are to be preferred to slow ones. The limiting cleavage velocity appears to be $\approx 0.4 v_s$ (Roberts and Wells 1957; Gilman, Knudson and Walsh 1958), so that the limiting ratio is

$$\frac{T}{U} \sim 0.7 \left(\frac{L}{p} \right)^2. \quad (3.6)$$

In practice, it is not routinely practicable to achieve cleavage velocities $\dot{L} > 0.1 v_s$. In cleaving a finite section, for example $3 \times 3 \times 1$ mm, we are concerned with the stage of the crystal somewhere near the centre of the section and must have $p \sim L$ in the region of interest, in which case we can neglect T (since $T \approx 0.05U$).

The increase in surface area produced by cleavage is

$$S = \gamma w L, \quad (3.7)$$

and the work done by the applied force as the crack propagates is

$$F y_0 = \frac{FL^3}{3YI} = 2U. \quad (3.8)$$

We must then have an energy balance such that

$$S + T + U - Fy_0 = 0; \quad (3.9)$$

whence, neglecting T, we derive

$$F = \sqrt{(6YI\gamma_w/L)} = \frac{wP}{L} \sqrt{\left(\frac{Y_P\gamma}{2}\right)}. \quad (3.10)$$

This expression is valid up to the elastic limit of the material.

3.2.1.3 Plastic bending

We next consider the conditions under which permanent plastic bending deformation is likely to occur in the cantilever bending mode employed in cleavage. We shall use a quasi-static cleavage model such that if the shear stress from bending reaches the yield stress the crystal flows plastically, relieving all the elastic energy stored in bent cleavage arms. Plastic deformation continues until the work hardening of the crystal permits an elastic stress sufficient to maintain cleavage crack propagation. This quasi-static model, which thus neglects strain rate effects, is justified, at least for slow and moderately fast cleavages, because alkali halides are known to flow rapidly at stresses just above the yield stress. Slow or moderate dislocation velocities in alkali halides have been shown to follow the relation (Gilman and Johnston 1959; Evans and Pratt 1970)

$$v = \left(\frac{\tau}{\tau_0}\right)^m, \quad (3.11)$$

where τ_0 is the stress at unit velocity and $m \sim 15$, although deviations from (3.11) occur for high velocities where $m \rightarrow \frac{1}{2}$ (Cotner and Weertman 1964). Therefore the yield stress does not alter appreciably over large variations in the strain rate, and becomes a good criterion for onset of plastic flow. Attendant work hardening effects also saturate

quickly because of a facile cross slip mechanism for multiplication (Johnston and Gilman 1960; Mendelson 1963).

The outer fibre tensile stress in cantilever bending is given by

$$\sigma_{OF} = \frac{M(x) p}{2I} = \frac{6 M(x)}{wp^2} \quad (3.12)$$

where $M(x) = F(L-x)$. The maximum elastic tensile stress σ_m is related to the yield stress τ_y by Schmid relation

$$\tau_y = \sigma_m \sin \chi \cos \lambda, \quad (3.13)$$

where χ and λ are the angles between the tensile axis and either the glide plane or glide direction respectively. For {100} cleavage in alkali halides we have $\chi = \lambda = \pi/4$, and

$$\tau_y = \sigma_m / 2 = \frac{3F(L-x)}{wp^2} \quad (3.14)$$

From (3.14) we have for the maximum shear stress occurring at $x=0$, the maximum force consistent with elastic bending

$$F = \frac{wt^2 \tau_y}{3L}; \quad (3.15)$$

since we require that this force must be sufficient to propagate a crack, we derive from (3.10) the conclusion that

$$p > \frac{9 \gamma Y}{2 \tau_y^2}. \quad (3.16)$$

For alkali halides, where $\gamma \sim 200$ ergs cm^{-2} , $Y = 4 \times 10^{11}$ dynes cm^{-2} and $\tau_y = 50$ g $\text{mm}^{-2} = 5 \times 10^6$ dynes cm^{-2} we have that

$$p \geq 14 \text{ cm} \quad (3.17)$$

to avoid plastic bending. The unavoidable conclusion is that permanent bending deformation will always accompany realistic cleavage of alkali halide crystals.

We now consider the extent of this deformation. We have from (3.16) that the shear stress that must be maintained to sustain cleavage is

$$\tau^2 = \frac{9 \gamma Y}{2p} \quad (3.18)$$

This stress is independent of the crack length i.e. will be reached by every point along the cleavage plane at some time during the cleavage. For a $p = 1$ mm thick section, $\tau \sim 600 \text{ g mm}^{-2}$, which is well into Stage II of the work hardening curve. Both Hesse (1965, 1967) and Matucha, Franzbecker and Wilkens (1969) have shown that the dislocation density N for compression follows from the relation

$$\begin{aligned} \tau &= 0.37 G b N^{\frac{1}{2}} ; \\ N &\sim \frac{0.1}{G^2 b^2} \tau^2 , \end{aligned} \quad \left. \begin{array}{l}) \\) \\) \end{array} \right\} (3.19)$$

where G is the shear modulus $\sim 2 \times 10^{11} \text{ dynes cm}^{-2}$ and b the magnitude of the Burgers vector $\sim 0.3 \text{ nm}$, hence we obtain $N \sim 7 \times 10^8 \text{ cm}^{-3}$. If we denote by p' the distance from the neutral bending axis, the bending stresses increase as $2p'/p$. Therefore, we might expect N to increase as $(2p'/p)^2$. We may then calculate an average dislocation density $\bar{N}$ by

$$\bar{N} = \frac{2}{p} \int_0^{p/2} N (2p'/p)^2 dp' = \frac{1}{3} N \approx 2 \times 10^8 \text{ cm}^{-3} . \quad (3.20)$$

Another estimate for $\bar{N}$ can be obtained from the amount of energy absorbed by plastic deformation. If we assume that plastic flow occurs freely wherever the local shear stress exceeds the yield stress, we can use Gilman's (1959b) result that

$$\gamma_p = \frac{9 \gamma Y}{2 G} \ln \frac{G}{\pi \tau_y} \quad (3.21)$$

where γ_p is the apparent addition to the true surface energy γ contributed

by plastic deformation. For alkali halides this becomes $\gamma_p \sim 10^2 \gamma$, which illustrates that the largest proportion of the energy supplied to initiate and maintain cleavage goes into plastic deformation. For $\gamma \sim 200 \text{ ergs cm}^{-2}$, this amounts to $2 \times 10^4 \text{ ergs}$ for every cm^2 of cleavage surface. Each half of a $5 \times 5 \times 2 \text{ mm}$ crystal cleaved in two then absorbs $\sim 5 \times 10^3 \text{ ergs}$, or an energy density of $\sim 2 \times 10^5 \text{ ergs cm}^{-3}$. It has been estimated that approximately 5% of the energy contributed to plastic deformation is stored as dislocation strain energy, the rest going into heat (Nabarro 1967). Therefore, $\sim 10^4 \text{ ergs cm}^{-3}$ will be stored in dislocation strain fields. The strain energy of a dislocation is

$$W \sim \frac{Gb^2}{4\pi} \ln (r/r_c) \quad (3.22)$$

where r_c is the core radius $\sim 1 \text{ nm}$, and r is the crystal dimension $\sim 10 \text{ mm}$. Hence the energy associated with a dislocation line is $\sim 3 \times 10^{-4} \text{ ergs cm}^{-1}$ and the average dislocation density $\bar{N} \sim 4 \times 10^7 \text{ cm cm}^{-3}$.

Combining (3.19) and (3.20) leads to an average density

$$\bar{N} = \frac{11 \gamma \gamma_p}{G^2 b^2 p} ; \quad (3.23)$$

while combining (3.21) and (3.22) and setting $\tau \sim 50 \text{ g mm}^{-2}$ (yield stress) and the stored energy fraction $\sim 5\%$, leads to an average density

$$\bar{N} = \frac{2 \gamma \gamma_p}{G^2 b^2 p} . \quad (3.24)$$

In either case, a p^{-1} dependence applies, which suggests that there is little advantage in increasing the cleavage section by only a factor of 2 or 3, to 2 or 3 mm, except in reducing bending deformation from misalignment of the cleavage wedge.

So far as electron microscopy is concerned, an extraneous

dislocation density $\sim 10^8 \text{ cm cm}^{-3}$ is unacceptable. A typical $10 \text{ }\mu\text{m} \times 10 \text{ }\mu\text{m}$ area (the field of view at 10,000 times magnification) of a 500 nm foil will contain an average 50 μm of dislocation line; the density within a slip band may be considerably higher, and 10^8 cm cm^{-3} does correspond to well into Stage II deformation, implying possible rearrangement of existing dislocation structures during cleavage.

Fig. 3.2a, b illustrate direct transmission electron micrographs of KCl and NaCl foils prepared from initial (001) sections cleaved $\sim 1 \text{ mm}$ thick from high purity bulk crystals. The principal features are arrays of long straight screw dislocations of both signs lying along $\langle 110 \rangle$ directions in the foil. Dipole or multipole formations often appear, sometimes degenerating into strings of loops. One might expect screw segments to be retained, as it is well known that the edge component of nucleated loops propagates considerably faster than the screw component (Gilman and Johnston 1959; Pariiskii et al. 1966). The dislocation volume density involved is $2 \times 10^9 \text{ cm cm}^{-3}$ which is somewhat greater than predicted for homogeneous distribution, and undoubtedly reflects the inhomogeneity of slip.

It is possible to eliminate damage on this scale by sectioning sufficiently thick starting specimens for final polishing. Cleavage damage is also reduced in previously irradiated specimens in which the flow stress is raised considerably. However, a much safer alternative is the chemical sectioning technique described below.

3.2.2. Chemical sectioning

The most satisfactory way to produce sections of arbitrary orientation and thickness with little incidental deformation is by chemical sectioning. Fig. 3.3 illustrates the chemical slicing saw

built to perform this sort of sectioning. Solvent from bottle B is drip-fed via adjustable needle valves and capillary tubes F onto a reciprocating string S against which the specimen is cantilevered by means of the counterbalance system C. The string drive system, adapted from a Metallurgical Services "Metaserve" chemical saw, incorporates both the continuous translation principle of Armstrong and Rapp (1958) and the reciprocating action used by Young and Wilson (1961). The rotating arm A provides a simple harmonic reciprocation of the string through the pulleys P and translates the string by a few centimetres every rotation by advancing the spool G. A weight W provides an approximately constant (its restraining force varies slightly with acceleration) string tension while the oil-filled dash-pot damper smooths out specimen bounce during the reciprocating cutting process. The delicate counterbalance system at C is attained with ball-race pivots; a specimen cutting pressure of less than one gram across the string width, corresponding to a normal stress $< 1/20$ the yield stress in undeformed crystals can be easily attained. The best string for use is two-strand fly-tying silk with a diameter of 0.1 mm, running through precision grooved stainless steel ball race pulleys P. This string material is available in convenient 50 m lengths (about 1 hr running time) and is resistant to creep, even when wet, under load W of 200 g. Monofilament line (nylon) was found not to carry solution adequately nor remove dissolution products, whereas the double twist line is very efficient in this respect.

The motor driving arm A is fitted with an automatic reversing system to provide for unattended operation over the several hour periods needed to make cuts of several mm depth in bulk crystals. The motor

shaft drives through a two-stage 1000:1 gear reduction box to a cam operating a reversing switch which changes the phase of the motor field with respect to the motor armature. To prevent the motor from driving through reversal and continuing its forward rotation in anti-phase, a condition achieved with alarming frequency, a capacitor bank was arranged to discharge through DC relay upon activation of the reversing switch. The contacts of the relay are wired to interrupt the motor mains supply while the relay remains momentarily energised (about 2 sec); this delay ensures positive motor reversal. The capacitor bank acquires sufficient charge for reactivation of the relay in about five minutes, adequate for the time between reversals (about 1 hour).

The specimen is mounted on a goniometric platform with polyester resin or mounting wax. Sections of varying orientation may be cut with accuracy of 1° . The solvents employed for sectioning are normally those used for subsequent polishing and are listed in Table 3.2. To prevent a solvent layer accumulating on the crystal surfaces, an extractor fan is mounted in the housing enclosure and quickly evaporates solution diffusing from the cut groove onto the crystal faces. With drip feed rates about five drops per minute, solvent consumption is low ($<50 \text{ cm}^3$ per hour). No incidental deformation could be detected in the microscope in previously undeformed sections cut $>500 \text{ }\mu\text{m}$ thick and subsequently polished to a foil, indicating an introduced dislocation density $<10^6 \text{ cm}^{-2}$. X-ray topographs indicate no apparent gross damage. Although sections as thin as $100 \text{ }\mu\text{m}$ could be successfully cut, sectioning is normally carried out to 1 mm thickness to preclude accidental deformation during subsequent handling and mounting.

3.2.4 Prethinning

Surface damage and surface recrystallisation that may be introduced during sectioning is removed from the specimen section prior to mounting by agitated dissolution in static solvent baths. The polishing and washing solvents used in prethinning each alkali halide are listed in Table 3.2. Specimens are either held by one corner with tweezers or cemented to a glass rod with perspex in chloroform during these operations. A two-step wash, first in a dilute polishing solvent, then in an inert washing solvent was found necessary to remove all polishing solution and prevent etching. One of the purposes of the prethinning procedure is to produce transparent specimens so that specimens may be accurately positioned over polishing jets viewed from above through the specimen; an opaque recrystallised surface layer defeats this aim. Any ridges produced in sectioning are also smoothed during prethinning. Agitation in the polishing bath is usually for a few minutes followed by a few seconds' vigorous agitation in both washing baths. The washing solution must be quickly evaporated from the specimen after washing, preferably on absorbent tissue under a draught of hot air, to prevent surface recrystallisation due to atmospheric water condensing on a specimen surface cooled by solvent evaporation. Prethinned specimens are typically 300-500 μm thick and a few mm square.

3.3 Foil Thinning

Several thickness reduction techniques exist for producing thin foil areas in alkali halide sections suitable for transmission of 100 keV

electrons. We shall discuss each approach together with examples of the end product, illustrating the limitations imposed by each technique.

3.3.1 Edge polishing

The simplest technique amounts to immersing the specimen in a polishing solution until regions of the specimen become thin enough for transmission. Since its periphery dissolves more quickly than its centre the specimen tends to assume a lenticular profile, the specimen edges being thin enough in some instances for microscopy. This technique has been used by Kawamata and Hibi (1965), and a modification (dropping solvent in the centre of a section with an eye dropper until a hole appeared) by Smiser and McGee (1969).

Several points should be made in connection with the quality afforded by this procedure. First, the section so produced is thin over only a small region, typically on a few μm from the edge, with a large wedge angle; the latter obtains because the regions of sharpest curvature always polish most quickly, so very thin regions of small wedge angle can never be sustained. Second, the evaporation of washing solutions in atmosphere can lead to appreciable condensation of atmospheric water vapour onto the cooled specimen surfaces leading to etching effects; moreover the technique is not at all applicable to the more hygroscopic alkali halides (such as KI, NaBr etc.) because of the attack of thin foils by water vapour during atmospheric exposure. Third, the technique is not applicable to other than (100) sections because static polishing results in preferential removal along $\langle 100 \rangle$ and produces

etched furrows in other sections along $\langle 100 \rangle$; this point will be discussed below in connection with static polishing. Fourth, the specimens so produced are most unsuitable for mounting and particularly for subsequent cooling to low temperatures; the only really practicable method of mounting is clamping between folding copper grids, which provides poor thermal and electrical paths.

3.3.2 Beam flashing

A slightly more useful technique has been developed by Yagi and Honjo (1964, 1967) for calcium-doped NaCl and subsequently utilised by Izumi (1969) for pure NaCl and KCl. To produce large thin areas in the absence of atmospheric moisture, which is especially deleterious to calcium-doped crystals, 2-10 μm -thick platelets prepared by cleavage and water-alcohol thinning were irradiated over large areas with a sudden increase in electron beam current from $5 \times 10^{-5} \text{ A cm}^{-2}$ to $10^{-2} \text{ A cm}^{-2}$. The presumably very large thermal and/or electrical forces generated from the large gradients produced in such thin plates resulted in widespread cleavage of the crystal slice, leaving transparent foil areas exposed.

The extreme thermal, mechanical and irradiative conditions under which the foils are produced justify concern for the introduction of extraneous defects into the specimen; it is doubtful whether such foils can be considered in any way representative of the irradiative or deformation state of the bulk platelet before beam flashing. The method clearly involves irradiation at levels guaranteed to produce irradiation defects near saturation in pure alkali halide crystals. Stresses

large enough to generate cleavage cannot be trusted to preserve the form of defect configurations existing in the unthinned platelet; indeed, Yagi and Honjo (1964) reported many "grown-in" dislocations which suspiciously resemble dislocations introduced by bending and/or cleavage. Moreover, significant heating can occur during beam flashing, in some cases sufficient to initiate annealing processes.

We shall content ourselves with demonstrating that the beam flashing technique introduces, besides severe irradiation damage, unacceptable thermal stress levels. Over a thickness of 10 μm the Bethe energy loss (§2.4) will not remain constant and will give rise to differential heating throughout the platelet and to a differential temperature distribution. The Bethe loss is of the form

$$\frac{dE}{dz} = -\frac{C}{E} \ln \frac{4E}{I}; \quad (3.25)$$

if E does not alter appreciably throughout the slice, the logarithmic term will remain essentially constant and

$$\frac{dE}{dz} = -\frac{B}{E}. \quad (3.26)$$

For alkali halides $B \sim 7 \times 10^{11} \text{ eV}^2 \text{ cm}^{-1}$. To express $dE/dz(E)$ as a function of depth z from the top of the slice at $z = 0$ to the bottom at $z = p$, we integrate (3.26) between E_0 and $E(z)$ for $0 \leq z \leq p$ and obtain

$$\begin{aligned} E &= \sqrt{E_0^2 - 2Bz}; \\ \frac{dE}{dz}(z) &= -B/\sqrt{E_0^2 - 2Bz}. \end{aligned} \quad (3.27)$$

It can be seen from (3.27) that more energy is lost at the bottom of the foil than at the top, and therefore a temperature gradient will be

established across the slice. Although this energy loss differential amounts to only 7% for 100 keV electrons in a 10 μm thick foil, we can show this difference alone lends to appreciable thermal stresses; there will be in addition appreciable buckling stresses arising from thermal expansion of the irradiated area with respect to the unirradiated area, which are critically time dependent and whose analysis is beyond the scope of this treatment. We shall consider only the eventual steady state temperature differential established across the specimen thickness.

If we assume that the thermal conduction path away from the specimen is considerably poorer than that within the specimen (a good assumption for a specimen lightly held between grids, for example), we can neglect the sink and consider only the flow of heat in the specimen itself which establishes a steady state temperature distribution across the slice. The steady state heat conduction equation to be satisfied is

$$\frac{\partial}{\partial z} \left\{ \frac{\partial T}{\partial z} \right\} + \frac{1}{\kappa} H(z) = 0, \quad (3.28)$$

where κ is the alkali halide thermal conductivity and $H(z)$ is the heat source distribution per unit volume,

$$H(z) = j \left\{ \frac{dE}{dz} \right\} = jB/\sqrt{\{E_o^2 - 2Bz\}}. \quad (3.29)$$

Solving (3.28) and using the approximation $\sqrt{\{E_o^2 - 2Bz\}} \approx E_o \{1 - Bz/E_o^2\}$ because $Bz \ll E_o^2$, we obtain

$$T(z) - T(o) = \frac{jBz^2}{2\kappa E_o^2} = \frac{j}{2\kappa} \left\{ \frac{dE}{dz} \right\}_o z^2. \quad (3.30)$$

This difference amounts to 8 K for a 10 μm thick slice, or a thermal gradient of 8000 K cm^{-1} .

To evaluate the thermal stresses introduced by this gradient, it is convenient to change the coordinate system to one where the x-y plane passes through the centre specimen plane. Letting $z'=c$ at the top of the specimen and $z'=-c$ at the bottom, we have

$$z = c - z' ; \quad c = p/2$$

and

$$T(z') - T(c) = \frac{j \left\{ \frac{dE}{dz} \right\}_0}{2\kappa} (c - z')^2. \quad (3.31)$$

For a temperature gradient in z' and $T(c) \equiv 0$, the normal stresses are (Timoshenko and Goodier 1970)

$$\begin{aligned} \sigma_x = \sigma_y = \sigma(z) = \frac{\alpha Y}{(1-\nu)} & \left\{ -T(z') + \frac{1}{2c} \int_{-c}^c T(z') dz' + \right. \\ & \left. \frac{3z'}{2c^3} \int_{-c}^c T(z') z' dz' \right\} \\ \sigma_z = \sigma_{xy} = \sigma_{xz} = \sigma_{yz} & = 0. \end{aligned} \quad (3.32)$$

Performing the integration in (3.32) we find

$$\sigma = \frac{\alpha Y j \left\{ \frac{dE}{dz} \right\}_0}{2\kappa (1-\nu)} \left(\frac{c^2}{3} - z'^2 \right). \quad (3.33)$$

The normal stresses are compressive at top and bottom and tensile in the specimen centre; also

$$\sigma(0) = 2\sigma(\pm c), \quad (3.34)$$

with zero stress at $z' = \pm 0.58 c$. The maximum tensile stress in the centre is

$$\sigma = 3 \times 10^7 \text{ dynes cm}^{-2} = 300 \text{ g mm}^{-2} \quad (3.35)$$

or about ten times the yield stress in pure undeformed crystals, certainly ample to effect some rearrangement of existing defects and to nucleate unacceptable plastic deformation.

3.3.3 Ion beam thinning

Hirth, Melville and Wackman (1967) have shown that thin foils of ionic crystals such as rutile (TiO_2) can be successfully thinned by argon ion bombardment. In a typical ion bombardment apparatus, argon ions accelerated through 3-6 kV are directed at a bulk specimen several μm thick, sputtering off surface ions until thin regions are produced. Typical thinning rates are $\sim 1 \mu\text{m hr}^{-1}$ for currents of 25-100 μA . To investigate whether ion beam thinning would introduce unacceptable damage, a (101) KCl foil, previously sectioned and dish-polished to a hole (see §3.3.4) was ion bombarded in an Edwards IBMA-1 ion thinning machine with 6kV argon ions at 15° incidence from both sides, at a total ion current of 25 μA for 6 hr until the hole could be seen to have opened from 50 μm to 100 μm diameter. The specimen was then examined in the electron microscope at 10 K (see §5.4) for evidence of ion damage. Fig. 3.4a, b illustrate the form and extent of the damage introduced. In particular, fig. 3.4a indicates that as the foil thickness increases the projected damage density also increases to a point, indicating either that appreciable diffusion of damage has taken place into the foil or that damage is being produced at significant depths ($\sim 100 \text{ nm}$) in the foil. However, in much thicker regions ($\sim 300 \text{ nm}$), fig. 3.4b, dislocations could be observed through the dense damage, indicating that the damaged layer

probably did not extend completely through the foil. The damage in this (101) section appears in the form of very small loops of the sort observed in electron-irradiated KCl, a distinct $|010|$ orientation occurring for many loops (see §5.5 for a comparison with electron irradiation damage loops in (101) sections).

Argon ions of 6 keV may introduce two sorts of damage into the lattice: knock-on displacement damage, which is expected to predominate; and ionisation damage, which may be several orders of magnitude less likely. We must calculate the respective cross sections and range for each of these displacement mechanisms in order to investigate the source of the damage.

3.3.3.1 Knock-on displacement damage

For a collision of a moderately energetic heavy ion of energy E , mass M , and atomic number Z , with a lattice ion nucleus of mass M_2 , atomic number Z_2 , and displacement threshold E_d , we may use an inverse square potential and show that the cross section for damage from nuclear stopping (Thompson 1969) is

$$\sigma_{d,n} = \frac{\pi^2 a_H^2 E_R (Z_1 Z_2)^{5/6} \sqrt{(M_1 M_2)}}{2.72 \sqrt{(E E_d)} M_2 (M_1 + M_2)} \quad (3.36)$$

where a_H is the Bohr radius and E_R the Rydberg energy, 13.6 eV. The displacement threshold E_d is typically ~ 25 eV (Torrens and Chadderton 1967). For 6 keV argon ions $|^{40}\text{Ar}^+|$ colliding with a $^{39}\text{K}^+ \text{ } ^{35}\text{Cl}^-$ lattice we find

$$\sigma_{d,n} \sim 4 \times 10^{-16} \text{ cm}^2,$$

an immense cross section. The average energy transferred per collision,

$\bar{E}$, is given by

$$\bar{E} = \sqrt{4EE_d M_1 M_2 / (M_1 + M_2)} \sim 388 \text{ eV.} \quad (3.37)$$

Since $\bar{E} \gg E_d$, the primary knock-on ions produced may have sufficient energy to produce further displacements. We therefore use the treatment of Kinchin and Pease (1955) to derive that the total number of displaced lattice ions per incident ion due to both the primary ion and the primary knock-on ions,

$$n_{d,n} = \sigma_{d,n} \sqrt{(M_1 M_2 E / E_d) / (M_1 + M_2)} \sim 77. \quad (3.38)$$

The total damage rate $\dot{N}_d$ is found by multiplying by the flux ϕ which for 25 μA amounts to $\phi = 2.3 \times 10^{16} \text{ ions cm}^{-2} \text{ sec}^{-1}$ each side. We then calculate

$$\dot{N}_{d,n} = \phi n_{d,n} \sim 1.2 \times 10^{24} \text{ cm}^{-3} \text{ sec}^{-1} \text{ side}^{-1}. \quad (3.39)$$

Since the lattice density is $N_0 \sim 2 \times 10^{22} \text{ cm}^{-3}$ each lattice ion is displaced 50 times per second and we may well expect an amorphous layer at each surface.

(3.38) implicitly embodies the range of the incident ions and the primary knock-ons. To extract this information explicitly we will first assume an amorphous solid and use the result of Nielsen (1956) for the total accumulated path length of the primary ion, called the linear range,

$$R_L(E) = 0.6 \frac{(Z_1^{2/3} + Z_2^{2/3})^{1/2}}{Z_1 Z_2} \frac{(M_1 + M_2) M_2 E}{M_1 \rho} \sim 14.6 \text{ nm}, \quad (3.40)$$

where ρ is the lattice density and E is expressed in keV. The penetration depth or projected range R_Z can be obtained via the result of Lindhard and Scharff (1961) who calculated that the ratio of linear

range R_L to projected range R_Z on the inverse square potential is

$$\frac{R_L}{R_Z} \sim 1 + \frac{1}{3} \frac{M_2}{M_1} \sim 1.3 ; \quad (3.41)$$

thus we calculate that $R_Z \sim 11$ nm.

R_Z is of course a most probable range and we must consider straggling (the statistical uncertainty in range) particularly because of the catastrophic damage induced by each ion. We define the width of the range distribution at half maximum as ΔR_Z and use the estimate of Bohr (1948) that

$$\frac{\Delta R_Z}{R_Z} = \frac{4}{3} \frac{M_1 M_2}{(M_1 + M_2)^2} \sim \frac{1}{3} \quad (3.42)$$

However, Lindhard, Scharff and Schiott (1963), using a Thomas-Fermi potential, conclude $\Delta R_Z \sim 0.14$ in the above case and reduces to $\Delta R_Z \sim 0.06$ if electronic stopping is included. We may therefore expect that there is little damage production from primary ions beyond the range calculated in (3.41) for an amorphous material. The range R_Z of the primary knock-ons produced at the end of the primary range can be estimated by using the average knock-on energy $\bar{E}$ from (3.38) in (3.40) and (3.41) yielding $R_Z \sim 1.5$ nm which does not measurably increase the damage depth.

In a crystal lattice, however, rather than an amorphous scatterer, open lattice paths in certain directions can lead to extensive channelling of the incident ions. Whitton and Matzke (1966) have found for 40 keV Xe^+ ions channelled in $\langle 100 \rangle$ in single crystals of NaCl, KBr, and MgO a range increase of an order of magnitude or more over the range observed for the same materials in an amorphous

state. Lehmann and Leibfried (1963) have derived an E^{-1} dependence on the stopping cross section σ_c for perfectly channelled particles. Since we know from (3.36) that the collision cross section σ_n for nonchannelled particles has a $E^{-1/2}$ dependence, we can write

$$\frac{\sigma_c/\sigma_n(E_1)}{\sigma_c/\sigma_n(E_2)} = \frac{\sqrt{E_2}}{\sqrt{E_1}} ; \quad (3.43)$$

and, using the fact that $R_Z \propto \sigma^{-2}$ from comparison of (3.36) and (3.39) and the result of Whitton and Matzke, estimate that for 6 keV ions

$$\frac{R_{Z,c}}{R_{Z,n}} (6 \text{ keV}) = \frac{R_{Z,c}}{R_{Z,n}} (40 \text{ keV}) \frac{\sqrt{6}}{\sqrt{40}} = 3.8 \quad (3.44)$$

We thus calculate the channelled ranged $R_Z \sim 42 \text{ nm}$. It is still unlikely that even channelled primaries can fully account for the damage observed, since channelling is apt to be diminished by two polishing conditions: first, rotating (101) foil inclined 75° to the ion beam will never present a $\langle 100 \rangle$ channel less than 15° off axis, considerably above the critical channelling angle (Lindhard 1965); second, by the time the ion beam has polished to the depth of the region which will be observed in the microscope, a fully amorphous surface layer will presumably have formed which would decollimate the incoming ion beam and further reduce channelling probability.

3.3.3.2 Ionisation damage

The range calculations of §3.3.3.1 neglect energy loss due to ionisation of the lattice by the incident or knock on ions; this will be shown to be small in comparison with nuclear stopping, but

could contribute a disproportionate share of the damage production at far greater depths because of the recombination mechanism for damage production in alkali halides.

Strong excitation, corresponding to complete ionisation of valence electrons of the conduction band will only occur for incident ion energies greater than

$$E_{\text{ex}} \sim \frac{M E_g^2}{4 m E_R} \sim 66 \text{ keV} , \quad (3.45)$$

where m is the electron mass and M the ion mass. Thus 6 keV A^+ will only transfer a fraction of the ionisation threshold energy, in fact, only

$$E_{\text{max}} = \sqrt{\left\{ \frac{4m}{M} E E_R \right\}} \sim 2 \text{ eV} \quad (3.46)$$

There are, of course, no electron states 2 eV above the valence band in a wide-gap insulator like an alkali halide, although quantum mechanically there is a finite possibility of transferring more than the 2 eV calculated classically in (3.46) to an electron. Thus a classical calculation of electronic stopping is not valid in this case.

It is of interest, nevertheless, to calculate the latter on a classical continuum method for comparison with nuclear stopping. Since A^+ in KCl is sufficiently like a lattice ion, we can utilise the result of Lindhard and Thomsen (1962) for recoil atoms in their own solid that

$$\left(\frac{dE}{dz} \right)_e \sim 3\pi a_o^2 n Z^{7/6} \sqrt{\left\{ \frac{m}{M} E_R E \right\}} \sim 2.5 \times 10^8 \text{ eV cm}^{-1} \text{ ion}^{-1} , \quad (3.47)$$

where for n we use the number of valence electrons = N_o . Since the cross section for nuclear stopping is

$$\sigma_n \propto 1/\sqrt{E} \quad \text{and} \quad \left(\frac{dE}{dz}\right)_n = N_o \int_0^{\infty} \frac{4M_1 M_2 E}{(M_1 + M_2)^2} E d\sigma \quad (3.48)$$

we have

$$\left(\frac{dE}{dz}\right)_n \approx N_o \sigma E \sim 5 \times 10^{10} \text{ eV cm}^{-1} \text{ ion}^{-1} . \quad (3.49)$$

The ratio of nuclear to electronic stopping power is then

$$\frac{(dE/dz)_n}{(dE/dz)_e} \sim 200 , \quad (3.50)$$

and even on the classical model electron stopping plays a negligible role in determining the primary range. It is reasonable to suppose that the quantum mechanical probability of electron excitation would result in an electronic stopping component considerably less than that calculated classically, and that electronic stopping is not likely to contribute significantly to either ion energy loss or damage production by an ionisation mechanism.

3.3.3.3 Source of observable ion damage

In reconciling the results of §3.3.3.1 and §3.3.3.2 with the observations of fig. 3.4, we are left with essentially two alternatives for the source of observable damage loops at appreciable depths in the foil (i) interstitial migration and (ii) absence of amorphous layer. We consider the arguments for each:

(i) Interstitial migration

The interstitial is sufficiently mobile and certainly adequate numbers are produced within the primary range to more than account for

the observed damage production if in fact the interstitial does manage to diffuse beyond the primary range. It will be shown in §5 that observable radiation damage clusters in alkali halides are of interstitial type and account for the form of the damage produced from other irradiation types. Bowden and Brandon (1963) reported dislocation loops which were thought to be interstitial in gold and copper foils irradiated with 100 eV A^+ ions to doses $\sim 10^{17}$ ions cm^{-2} which is near the ion thinning dose. Considering the short range of the A^+ ions, it was suggested that damage was formed by agglomeration of interstitials that had diffused into the foil via replacement collision sequences. Diehl, Diepers and Hertel (1968) investigated damage produced by 1-5 keV A^+ ions in single crystal foils of copper and gold irradiated to doses between 10^{13} and 10^{16} ions cm^{-2} ; stereomicroscopy showed the damage lay about 20 nm below the foil surface (i.e., just beyond the primary ion range) and consisted of interstitial Frank sessile loops. Certainly, with no vacancies produced in regions beyond the primary ion range, interstitials that do propagate into these regions have a high survival probability; therefore the approach to saturation is linear rather than logarithmic and saturation is determined not by eventual athermal bulk recombination but by unavailability of interstitial sites.

(ii) Absence of amorphous layer

It may be that the ionic nature of the alkali halide lattice precludes an amorphous layer forming, and that even massive damage is stabilised by stable saturation defect concentration and

continuous defect recombinations. In this case, it is possible that displacement damage alone within the primary ion range can account for the damage observed. There is also the possibility that the A^+ ion is incorporated stably in the ionic lattice, and that some defect clusters arise from the presence of this implanted ion.

3.3.4 Chemical dish polishing

3.3.4.1 Principle of dish polishing

The most effective technique to prepare thin foils of alkali halide crystals suitable for transmission electron microscopy is dissolution by a chemical jet providing a dish polishing profile. The principle of the technique, used extensively by Booker and Stickler (1962) on silicon, is illustrated in fig. 3.5. One or both sides of a section of crystal are subjected in turn to a jet of chemical solvent from the underside until a hole appears in the centre; the profile becomes a shallow dish because of the distribution of fluid velocity in the jet which is highest in the centre. Generally the full diameter of the dish will be about twice the jet diameter. One distinct advantage of this technique is that if a small enough jet diameter is chosen the final hole and associated thin area at the hole edge can be selectively positioned in the specimen, for example, directly in the centre. A particular advantage accrues from positioning accuracy in low temperature microscopy work where contamination rates necessitate use of small apertures above and below the specimen plane. The greatest dis-

advantage is that the polishing must be relatively rapid to reduce thick starting sections in a finite time and must be stopped immediately at perforation of the foil to preserve the thin area round the hole produced.

Because of the comparatively higher solvent fluid velocities in dynamical polishing (as distinct from static polishing) considerably less reactive polishing solvents can be utilised than would normally be expected to produce appreciable solubility, as indicated, say, by solubility tables. For example previous workers (Kawamata and Hibi 1965; Tanaka, Mannami and Izumi 1963) have used water-alcohol mixtures to statically polish NaCl and KCl, whereas the same crystals immersed in pure methanol exhibit virtually no observable dissolution. However, methanol is an extremely efficient solvent in the jet polishing mode and will perforate a 500 μm section of NaCl or KCl in under 5 minutes.

3.3.4.2 Polishing and washing reagents

Table 3.3 lists those reagents useful for chemical dish polishing of alkali halides together with the salt solubility in $\text{cm}^3/100 \text{ cm}^3$ (this is more meaningful for dynamic polishing than the normally quoted solubility in g solute/100 g solvent and enables direct comparison of solubilities in the jetting mode for different alkali halides in different solvents). It is seen that polar solvents, principally the alcohols, are the useful reagents; the more reactive the alkali halide, the less

polar a solvent must be employed to maintain controllable polishing rates. The ideal range of solubility is found to be between 0.2 and 1.5 cm³/100 cm³, although foils have been prepared with solubilities as low as 0.1 cm³/100 cm³ (KBr in EtOH). The very high dissolution rates of the reactive alkali halides make polishing difficult in pure reagents and considerably diluted (~1:10) solvents must be used; the iodides are also nucleophilic with most suitable washing fluids (for example, diethyl ether) which exacerbates difficulties of solvent dilution and specimen washing. Rapid and efficient removal of the polishing solution is of paramount importance to the extent of the thin area produced and the quality of the foil surface. Diethyl ether is suitable for washing all but the most reactive alkali halides; acetone is appropriate for the least reactive where water is used as a polish solvent, diethyl ether being immiscible with water.

3.3.4.3 Solvent drying

Analytical grade reagents almost invariably contain up to 1% dissolved water; this is particularly true of the hygroscopic alcohols and ketones if they have been exposed to atmosphere for any appreciable period and even true of ethers which exhibit little miscibility with water. This water content can represent a significant contribution to crystal solubility and, given the preferential affinity of the more reactive alkali halides for the polar water molecule can lead to undesired

etching effects. It is particularly important that water be removed from the washing reagent as this solution is chosen to evaporate quickly and any water present and left behind preferentially will collect in higher concentration.

The most convenient way to remove water from polar solvents is by preferential adsorption using "molecular sieve" compounds (British Drug Houses 1965). These are complex aluminosilicates (zeolites) of the sort used in water softening applications, and crystallise in a very open lattice containing pores or channels from 0.3-1 nm diameter depending on the compound. Because a specific channel size is associated with a particular zeolite, choice of any one zeolite can lead to selective adsorption of those molecules with molecular diameters smaller than the channel size. Union Carbide type 4A XW (channel size 0.4 nm) is most effective for adsorbing water, and can adsorb up to 1/10 its weight in water even in the presence of other polar liquids. The following adsorption efficiencies apply to static drying of the solvents use for polish and water operations with 4A XW

<u>Liquid</u>	<u>Wt% water adsorbed</u>
Methanol	2.5
Ethanol	7.0
Diethyl ether	9.5
Amyl acetates	9.3

The zeolite is available in powder form which is very efficient for static drying of liquids. A quantity of powder sufficient to adsorb the residual water content is thoroughly shaken together with the reagent liquid and allowed to settle (~1 day) before

siphoning off the dried reagent.

3.3.4.4 Dish polishing head

An effective design for ensuring both rapid solvent removal and also polish dilution in the later stages of polishing has been described by this author (Hobbs 1970a) and is illustrated in fig. 3.6. Polishing solvent and washing solution are gravity fed from a height of about 1 m via separate magnetic solenoid valves and adjustable needle valves to the dish polishing head, shown in both exploded and assembled views. The two solutions are fed respectively to concentric jets spark-machined from fine stainless steel hypodermic needles; the diameter of the inner jet, used for polishing solvent is 200 μm ; the outer used for washing solution is 1 mm. Both jets are cemented in the centres of glass discs with epoxy resin (CIBA Araldite) and are easily replaced in the event of accidental clogging. Seals to their respective chambers are made with PTFE washers. All other parts of the head are made of stainless steel to resist corrosion from the salts. The grooved body mounts in a micrometer stage for proper alignment under the specimen. Light for observation, supplied by a 100 w quartz-iodine bulb, is transmitted through the glass windows concentric with the jets. The course of polishing is followed with a binocular stereo microscope situated above the specimen; the magnification of the viewing microscope is so arranged that the field of view just encompasses the specimen, which occurs at about x 100 magnification. As alkali halide specimens are transparent, the

stereo microscope provides a three dimensional impression that a definite polishing contour is developing on the underside; this certainty is essential to gauge successfully the point at which perforation will likely occur. (Crystals previously coloured by irradiation in bulk are quite useful in this latter respect as the change in colour density with thickness is a fair indication of polishing progress). The polishing control system consists of solenoid valves in the polish and wash lines controlled from the same double pole centre-off toggle switch, providing fast (~ 0.1 sec), positive control of both operations. Needle valves in each line permit initial adjustment of the respective flow rates. The specimen section is normally positioned 5 mm above the jets, with a polish jet flow rate sufficient to just reach the specimen and a wash flow rate to amply flood the specimen region. An additional solenoid valve (and needle valve) are placed in parallel with the valve in the wash line and can be arranged to energise in the polishing mode to provide dilution of the polishing solvent; a dilution rate of 5 wash: 1 polish is quite convenient for the later stages of polishing and ensures that the hole produced at perforation will not have grown large during the operator's reaction time before the wash switch is thrown. Also, dilution from the larger wash jet increases the diameter of the diluted polish jet and provides a broader polishing profile (leading to smaller wedge angle in the thin area produced at perforation) than the initial narrow jetting at full polish strength, which precisely selects the point at which perforation will subsequently occur. Holes have been successfully positioned

in the gauge length of a crystal mounted on an in situ tensile testing holder, the separation of whose grips was 200 μm . (This accuracy in positioning allows small apertures to be used above and below the specimen in low temperature stages, as mentioned previously, to reduce contamination.) The moment of perforation is easily detected when polishing solution is seen emerging above the top surface of the specimen. Typical polishing times are ~ 1 min each side of full strength jetting and ~ 5 min of dilute polishing to perforation, both operations followed immediately by a 2 min wash. Hole sizes at perforation are typically 50-100 μm diameter with suitable thin area often extending 30-50 μm from the periphery into the interior.

3.4 Foil Preservation

If those alkali halides with appreciable water solubility (viz. all except LiF and NaF) are polished and washed in normal atmosphere, the evaporation of polishing and washing solvents from the foil produced cools the foil sufficiently for appreciable water condensation to take place on the foil surface. This condensation leads to etching, dissolution and recrystallisation of those thin areas intended for microscopy, as well as appreciable water absorption in the more reactive alkali halides. The effect is illustrated by fig. 3.7a for a KCl foil prepared in atmosphere with the dish polishing apparatus described above. It is therefore necessary to provide for solvent evaporation in dry atmosphere

or vacuum. Moreover, it has been found that even properly dried foils of the more reactive alkali halides cannot tolerate incidental atmospheric exposure without appreciable degradation.

Fig. 3.7b illustrates a NaBr foil prepared in dry inert atmosphere and afterwards exposed to atmosphere for 20 sec; both recrystallisation and etching effects are prominent. There is, therefore, the further necessity for transfer in dry atmosphere.

That atmospheric water vapour content should constitute an annoyance is not really surprising where a polar affinity exists for those water molecules adsorbed on a surface. The water vapour content of the atmosphere in the U.K. is often close to saturation, ~ 3.4 mol %. The concentration of water molecules under these conditions is $9 \times 10^{17} \text{ cm}^{-3}$ with a flux of $1.4 \times 10^{21} \text{ cm}^{-2} \text{ sec}^{-1}$ striking any exposed surface (molecular incidence is discussed in §4.6 where condensation on cryosurfaces is considered). The subsequent absorption and occlusion of water have been discussed by a number of workers (Gründing and Rllhenbeck 1965; Rllhenbeck 1967; Green and Bauer 1968), as well as the deleterious effect of surface moisture attack on mechanical properties, particularly atmospheric embrittlement (Stokes, Johnston and Li 1960; Lad, Stearns and Del Duca 1958; Lad 1968), and on epitaxial growth on alkali halide substrates (e.g. Matthews 1966). The relative sensitivity of various alkali halides to atmospheric moisture is directly related to their sensitivity to polar solvents and can be predicted from Table 3.3. Those alkali halides for which water can be used as a dish polishing solvent are fairly insensitive to incidental

moisture contact; those soluble in MeOH are moderately sensitive, those soluble in EtOH are very sensitive, and those soluble in the ketones are severely affected by any incidental moisture, so much so that successful handling of even comparatively bulk crystals can be accomplished only under protected conditions, e.g. dry, inert atmosphere or vacuum.

3.4.1 Inert atmosphere chamber

To enable foil preparation to proceed in dry atmosphere, a chamber was constructed to house the dish polishing head. A photograph of the chamber is shown in fig. 3.8. The apparatus was originally designed for polishing specimen sections mounted directly in a Siemens electron microscope cartridge. This cartridge fits into an adjustable seating S riding in a ball-bearing race mounted in a pivoted arm A; this arrangement enables the cartridge to be rotated by means of a belt drive and swung around out of the way when polishing is complete, to be withdrawn and loaded into a vacuum lock L below by means of the push rod assembly at P. A single drive system fed through a rotary vacuum seal controls both specimen rotation, through bevel gears and a rubber belt pulley drive, and arm rotation through a second set of bevel gears. An inward thrust on the drive shaft D engages the latter while disengaging the former.

The drive system and polishing head are both integral to a large stainless steel block which houses the light assembly and serves as a catch-all basin for used polish and wash solutions.

Used solutions drain from the block into a long stainless steel cold trap cooled by liquid nitrogen and are immediately frozen out to prevent recondensation onto the specimen and fogging of the observation port. The entire top plate of the chamber is removable, as is also a smaller plate glass viewing port through which specimen cartridge loading and polishing head adjustments are accomplished. A glass shield attached to the arm A can be swung over the polishing head when initial flow rate adjustments are made to avoid obscuring the viewing port.

When it became evident (see §3.4.3) that both sides of the specimen had to be dynamically polished to avoid etching effects, the specimen was at first polished halfway through on one side, then removed via the vacuum lock, inverted in the cartridge, replaced in the chamber and polished to perforation from the other side. Less reactive alkali halides (e.g. KCl, NaCl, etc.) could be briefly exposed to atmosphere during this operation, provided all solvents had been previously evaporated from the specimen in the vacuum lock; more reactive crystals (e.g. KI, NaBr, etc.) had to be transferred to an inert atmosphere glove box, described below, for inversion. A later modification provided for inversion of the specimen without removal from the chamber.

The inert gas purge and solution feed systems used are illustrated in fig. 3.9. Polish and wash solutions are contained in 2 litre bottles fitted with o-ring seal caps and feed-through pipes. Helium gas of mineral purity, is fed through a molecular sieve trap containing Union Carbide type 4A XW molecular sieve

pellets to remove ambient water content. It was necessary to use helium gas, as this is the only convenient gas that does not liquefy when using the liquid nitrogen cooled solvent trap. The chamber is first evacuated to rough vacuum (~ 0.1 torr), then filled to a slight overpressure of helium gas; the space above the polishing solution is then opened to the chamber to equalise the pressure and provide only a constant gravity pressure head. After transfer of the specimen to the vacuum lock, the lock is sealed off from the chamber and evacuated to remove all solvents adhering to the polished foil.

3.4.2 Vacuum lock

The vacuum lock used for both solvent evaporation and specimen transfer is shown in fig. 3.10. The sliding plug and pivoted yoke assembly attach to the specimen cartridge by means of a threaded collar, and slide down the inside of the tube to a stop near the middle. The specimen cartridge then rests in an evacuable volume serviced through a cutout in the tube by a vacuum valve. The sliding tube itself is made of polished stainless steel tubing and slides through o-ring seals at either end of the lock body. A collet fitted at one end enables the sliding tube to be locked in any position.

The vacuum lock is mounted on the underside of the polishing chamber with the open end of the sliding tube upwards. The opposite end of the lock to that which fits the polishing chamber is designed to fit into a Ward type specimen chamber (Ward 1967)

for the electron microscope. When this chamber has been evacuated, the sliding tube is passed through the lock body into the chamber, exposing the specimen cartridge and allowing it to pivot on the attached yoke and drop out of the sliding tube. A knob at the end of the tube limits sliding travel and enables easy rotation. Similarly, a keyed rod passed through the open end of the tube into the sliding plug enables rotation of the yoke to the proper position to pivot out of the tube. The split spring-loaded collar in the photograph keeps the pivoted yoke rigid when extracting the polishing cartridge from the polishing chamber.

A similar arrangement fitted to an inert atmosphere glove box enables the specimen to be transferred from the polishing specimen holder to a proper microscope tilting cartridge and back into the lock again in dry atmosphere. The glove box is continually purged with dry argon, and any incidental water content is removed with open trays of phosphorous pentoxide.

3.4.3 Mounting procedures

Polar solvents are known to etch selectively along certain crystallographic directions in the static mode; in fact, this property provides a basis for etch pitting techniques in alkali halides (Johnston 1961). Fig. 3.7c illustrates selective etching in a (101) foil of KCl where polishing was allowed to proceed statically on one foil surface. Severe etching is evident along the cubic $\langle 010 \rangle$ direction. In fact, sections other than (001) in

the less reactive alkali halides and any section in more reactive crystals could not be prepared successfully unless scrupulous attention was paid to ensuring dynamic dish polishing at all times, followed by rapid removal of solvent after perforation. In practice, this means ensuring that the specimen is sealed from the solvent at its periphery so that no solvent can creep around to the top surface during dish polishing from the underside.

Several procedures were developed for mounting specimens in such a sealed manner prior to polishing as the polishing technique progressed, culminating in the last of the procedures outlined below, which was judged to be the best so far. The others are described as a matter of historical interest to illustrate some of the difficulties involved.

3.4.3.1 Direct ring mounting to specimen cartridge

This was the first technique tried, and it has been used with non-tilting holders and both the Ward (1965) and Valdrè (1962) double tilting holders. It is suitable only for (001) sections of less reactive alkali halides observed at room temperature, i.e. without any specimen cooling in the microscope. Rectangular sections were cut and prethinned to 200-500 μm thickness; these were mounted on a threaded phosphor-bronze ring 2.3 mm diameter with, at first, "Qwikfill" polyester resin and, later, a CIBA "Araldite" 750/951 epoxy resin hardener combination. The curing time of the polyester resin was ~ 15 min, while that of the Araldite was about 1 hr; however, the polyester resin often developed a tacky uncured surface which subsequently dissolved in alcohol/ether polishing/washing solvents and left contamination residues

on the specimen. No such difficulty was experienced with epoxy resins. The threaded mounting ring was easily manipulated by a threaded rod screwed into it, without the necessity of further manipulating the specimen itself. After curing, the corners of the rectangular specimen section were carefully dissolved away with a polishing cloth dampened with a suitable solvent (water, water/alcohol, methanol, ethanol, depending on the reactivity of the alkali halide); this treatment was followed by a thorough wash (usually propanol, then ether) and rapid drying in a warm air draught to preserve the transparency of the section. Sections fogged over with a recrystallised layer were difficult to centre over the polishing jets. A layer of conducting paint (suspension of colloidal silver in xylol, "Ag dag") was applied between the specimen edges and mounting ring to preserve electrical continuity to a conducting layer that would be evaporated later onto the thinned specimen (see §3.5). This composite was then glued into the respective specimen cartridge tip with, at first, polyester resin and later, conducting paint, both of which sufficiently soften in acetone to enable subsequent removable. In polishing, the cartridge tip was first doused with polishing solution from one side to dissolve away enough of the top specimen surface to remove the contaminated surface layer. The Ward open platform cartridge was eminently suited to this approach, but both the non-tilting and the Valdrè cartridges required holes to be spark machined above the specimen level to allow solvent entry, and capillary action then made subsequent dish polishing from only the underside difficult. Next the area was thoroughly washed with washing solution to remove the static polishing layer above the

specimen, and polishing was continued from the underside until perforation. The technique produced perfectly usable (001) foils of NaCl and KCl, but was hopeless (because of etching from the static polish) both for other crystallographic sections of these crystals and for the more reactive alkali halides. Nor was the technique suited to cryomicroscopy because of the differential thermal contraction of the specimen and its mounting ring, which is discussed later in detail in §5.11, and because the Ward tilting cartridge was not easily adapted to cryomicroscopy. An attempt to solve both problems resulted in the next approach.

3.4.3.2 Reversible ring mounting

In this approach, the phosphor-bronze mounting ring was replaced by a zinc ring, which produced a closer match to the alkali halides in thermal contraction rate (see §4.11). Mounting proceeded as before, except that the final composite was mounted into a special PTFE cartridge tip with Araldite; the PTFE-Araldite interface provided a leak-tight but non-adhesive seal, so that after dish polishing one side of the specimen, the composite could be easily dislodged, inverted and remounted with conducting paint into the Valdrè cartridge, utilised in cryomicroscopy (see §5.10), specimen side upwards to maintain the specimen in the diametral plane of the tilting ball. Use of this cartridge necessitated an additional PTFE shield to prevent capillary seepage around the tilting ball to the top specimen surface during polishing of the second surface; this shield easily dislodged upon removal of the cartridge from its seating in the polishing apparatus.

Considerable difficulty was experienced in maintaining an adequate electrical path between a conducting film subsequently evaporated onto the bottom specimen surface which had received no conducting paint coating. This problem was most easily solved by altering the shape of the mounting ring to a tall "top hat" with very thin "brim" (so as not to displace the specimen appreciably from the diametral plane), the "top hat" portion mounting deep into the bore of the tilting ball, the specimen mounting on the wider brim with Araldite and conducting paint and facing downwards. A later modification dispensed with the inconvenient PTFE shield in the Valdrè holder and polished both sides of the specimen in the special PTFE cartridge tip, the specimen being transferred to the Valdrè cartridge prior to conducting film deposition. Quality foils in all orientations from even reactive crystals were prepared with these techniques. However, the zinc ring did not completely solve the differential contraction problem in cryomicroscopy. Therefore, a third approach was adopted.

3.4.3.3 PTFE mounting

Since the mounting rings were to be dispensed with, rectangular specimen sections were instead mounted on the flat end of a 2.3 mm solid rod with an easily soluble cement, such as "Durofix" or polymethyl methacrylate ("perspex") dissolved in chloroform, so that the specimen corners could be rounded as before. The resulting discs were separated from the rod by dissolving the cement, and were mounted over a hole in a flattened PTFE rod, with a thin layer of either "Lacomit" stopping-off lacquer or Araldite around the disc edges only.

This rod push fits horizontally into a suitably bored hole in a special PTFE tip designed for a standard specimen cartridge used in the polishing chamber. It can be rotated with the cartridge in place in the chamber to invert the specimen. After polishing, the polished specimen is transferred to the glove box (or to atmosphere in the case of less reactive alkali halides), and the cement is carefully peeled away from the PTFE rod with a razor blade to free the specimen. This operation is easily accomplished with little risk to the specimen, since adhesion to the PTFE is so poor. The separated specimen disc is then carefully mounted into the Valdrè cartridge tilting ball with vacuum tweezers and secured with a single drop of conducting paint at its periphery. Conducting film deposition is carried out with the specimen mounted in the Valdrè cartridge. This technique is equally effective for foil production and is considerably less tedious overall, if more exacting in the final cartridge mounting. Provided the initial Lacomit or Araldite layer is kept thin enough, the specimen is also free to contract independent of its surroundings during cryomicroscopy.

3.5 Charge Acquisition

Thin foils of dielectric materials acquire an electric charge when examined in the electron beam of an electron microscope. Charge effects in thin carbon films supported on copper grids have been investigated by Dove (1964) and Curtis and Ferrier (1969), but these investigations are not generally applicable to bulk mounted dielectric foils of high inherent resistivity. The electrical volume conductivity

of alkali halides is in the region 10^{-8} (ohm cm) $^{-1}$ at 300 K and decreases exponentially with decreasing temperature (§1.6; Lidiard 1957), introducing problems of an altogether different magnitude. The observable effect is a pronounced deflection of the incident electron beam as soon as the beam intercepts the specimen, rendering microscopy useless. Previous workers (Hibi et al. 1960, 1965; Groves and Kelly 1963; see §5.1), in studies conducted only at or above room temperature, have used fine mesh copper grids to mount specimen flakes. Provided the mesh used is fine enough (<200 mesh), this method apparently affords some measure of protection. However, for bulk mounted specimens and especially in cryoexamination, further measures must be applied. For example in the present experiments a thin film of aluminium evaporated onto the lower (exit) specimen surface prior to observation eliminated charging effects down to 5 K. To the author's knowledge, no investigation has been made of the phenomenon of charge acquisition in thin dielectric foils or its remedy, so the following theory was developed to account for the charging behaviour observed in alkali halide foils and to indicate how best this problem might be eliminated.

3.5.1 Charging mechanism

The process by which thin insulating materials subjected to bombardment by electrons >10 eV acquire a static charge is almost certainly that of secondary electron emission. In bulk insulating materials the number of primary incident electrons absorbed and the number of electrons back-reflected or emitted as secondaries will,

in general, be unequal, so that the insulator surface tends to acquire a charge of either sign depending on the secondary emission and back-reflection coefficients. In thin foils whose thickness $p \ll z_p$, the range of primary electrons, essentially all primaries leave the foil, so that any secondary electrons produced by interaction of the primary beam and electrons in the lattice near enough to the foil surface to escape will leave behind a net positive surface charge. For a thin foil of an imperfect insulator such as an ionic crystal when fixed at its periphery to a conducting medium, the continuously increasing positive charge gives rise to a potential difference $+V$ with respect to the surrounding conducting medium, which will initiate charge flow across the foil by conduction until some potential V' is reached at which the conduction current I_c is equal to the secondary emission current I_s . The secondary emission current I_s consists of all emitted secondary electrons of energy $W > W' = V'e$, since all secondary electrons of energy $W < W'$ will encounter a potential barrier at the surface. Thus V' (or W') will be a function both of the conductivity σ_c of the foil and of the energy distribution of secondary electron emission, both of which we must investigate. At V' the electric field strength E might exceed that for which an ionic material obeys Ohm's Law, or indeed even the dielectric strength of the material.

3.5.2 Secondary electron emission

The processes of secondary electron emission have been reviewed by Dekker (1958). We are concerned with both the production of secondary

electrons by interaction of a beam of energetic incident electrons, i.e. the cross section for production of secondary electrons of energy W ; and the escape of secondary electrons from the surface which is a function of their energy distribution and absorption processes occurring in the solid.

3.5.2.1 General energy distribution and range

Typical secondary electron energy distributions for metals and insulators peak at between 5 and 10 eV. The total integrated area under the distribution curve is called the secondary yield δ and expresses the flux ratio of secondary electron emission to primary electron incidence. In metals, the maximum secondary yield of $\delta \sim 1$ occurs at a primary energy $E_p \sim 500$ eV; in insulators, such as ionic crystals, secondary yield is very much higher, reaching a maximum $\delta \sim 5-10$ for $E_p \sim 1-2$ keV. For both metals and insulators the yield decreases with increasing primary energy approximately as $1/E_p$ so that at very high incident energies, $E_p \sim 100$ keV, the total secondary yield has levelled off to $\delta \sim 0.1$. The general shape of the energy distribution curve is maintained, however, with the most probable secondary energies $W < 50$ eV.

The disparity in δ for conducting and non-conducting media can be attributed to the differing escape thresholds: in conductors the energy for escape from the surface is $(\phi + E_f)$, the sum of the work function ϕ and the Fermi energy E_f , where $(\phi + E_f) \sim 5-10$ eV; in insulators the threshold is $\sim \chi$, the electron affinity. In alkali

halides $\chi \sim 0.5$ eV. The difference in escape thresholds also explains the shift of most probable secondary emission energy in metals to higher energies than insulators.

A rapid decrease in secondary energy distribution at above 7 eV in insulators and above 15 eV in metals may be explained by the absorption processes affecting the passage of secondary electrons through the material. The first exciton state in alkali halides at ~ 5 eV is followed by a succession of energy loss peaks lying at higher energies (Philipp and Ehrenreich 1963). In metals the first plasmon loss is much higher, ~ 15 eV. Below these loss thresholds, secondary electrons will suffer interaction with lattice phonons, these collisions determining the effective range of those secondary electrons of most probable energy. Secondary electrons in alkali halides can additionally suffer energy loss due to excitation of existing radiation defects, for example $F \rightarrow F^*$.

Dekker (1954) has shown that the mean free path for phonon excitation in ionic crystals is given by

$$\lambda_p = \lambda_0 W / (2 n_\nu + 1) \quad (3.51)$$

where λ_0 is a constant ~ 1.5 nm for alkali halides, W the secondary energy in eV and

$$n_\nu = \{ \exp h\nu/kT - 1 \}^{-1}, \quad (3.52)$$

where ν is the frequency of the first optical longitudinal vibrational mode of the crystal ($\nu \sim 3 \times 10^{13} \text{ sec}^{-1}$ for alkali halides). Therefore $h\nu \sim 10^3 k$, $n_\nu \sim 10^{-1}$ and $\lambda_p \sim 10$ nm for 5 eV secondaries. The average energy loss suffered in each collision is given by

$$\alpha(T) = h\nu / (2n_\nu + 1) \sim 0.1 \text{ eV for } T = 300 \text{ K} \quad (3.53)$$

A 5 eV secondary can then suffer up to about 50 collisions with the lattice and still escape with an energy $\chi \sim 0.5$ eV. If we assume an isotropic scattering distribution (which is reasonable since the ion mass is $\gg$ the electron mass), the range of these secondaries is determined by a p-dimensional (p=3) random walk process for n events each a distance a apart. The probability that a range less than z is achieved is then given by (Rayleigh 1919)

$$P(z, n, a) = \frac{1}{\Gamma(\frac{1}{2}p+1)} \left\{ \frac{z^{\frac{1}{2}p}}{2na^2} \right\} \times {}_1F_1\left(\frac{1}{2}p; \frac{1}{2}p+1; \frac{-z^{\frac{1}{2}p}}{2na^2}\right) \quad (3.54)$$

where Γ is the Gamma function, ${}_1F_1$ is the hypergeometric series

$${}_1F_1(u, v, w) = \sum_{n=0}^{\infty} \frac{(u)_n}{n! (v)_n} w^n, \quad (3.55)$$

$$\text{where } (u)_n = u(u+1)(u+2) \dots (u+n-1); u_0 = 1.$$

Evaluating (3.54) for p=3, a=10 nm and n=50, we find that P=1.0 at $z \sim 90$ nm and P=0.5 at $z \sim 50$ nm. Therefore we can assume a mean range of at least 50 nm for the most probable secondary production, or equally that the probability of escape from a 100 nm thick foil is approaching unity. This will also be the minimum range for secondary electrons of higher energy.

In a review of secondary electron emission, Seiler (1967) tabulates measured values of mean free path and maximum escape depth from recent Soviet work. For NaCl, KBr and KCl measured values of λ , the mean free path for phonon excitation, lie between 8 nm and 20 nm and for maximum escape depth between 80 nm and 100 nm, confirming

the magnitude estimated by phonon scattering calculations. Practically, these escape depths imply that, in most of the foils we shall be concerned with, secondary emission will vary approximately linearly with foil thickness.

3.5.2.2 Energy distribution of higher energy secondary electrons

For a specimen that has charged to some positive potential $V' = W'/e$, we are concerned only with those secondary electrons of energy $W > W'$, which in general will lie above the most probable energy. We must therefore calculate the energy distribution of secondary electrons of energies > 10 eV. If the incident electrons are energetic (the condition is $e^2/h\nu \ll 1$) and the secondary energy is significantly larger than the binding energy (~ 10 eV), we may approximate the lattice electron distribution by an electron gas of valence electrons (for which the scattering cross sections are largest) and use an expression for the differential cross section for free electron-electron scattering to estimate the energy distribution of secondary production.

Mott (Mott and Massey 1965) has derived the quantum mechanical angular distribution of electron-electron collisions, arriving at essentially the differential cross section $d\sigma_{\theta}$ for scattering into an angle $\theta + d\theta$,

$$d\sigma_{\theta} = \frac{\pi e^4}{E_p} \{ \operatorname{cosec}^4 \theta + \sec^4 \theta \} \cos \theta d\theta . \quad (3.56)$$

This may be transformed into differential cross section in energy W (Birkhoff 1958)

$$d\sigma_W = \frac{\pi e^4}{E_p} \left\{ \frac{1}{W^2} + \frac{1}{W(E_p - W)} \right\} dW . \quad (3.57)$$

We observe that E_p , the incident electron energy, must be replaced by $E_a + W'$, where $V_a = E_a/e$ is the accelerating potential, for a foil charging to potential $V' = W'/e$. Integrating (3.57) between W' and $E_a + W'$ we obtain

$$\begin{aligned} \sigma_W &= \frac{\pi e^4}{E_a + W'} \int_{W'}^{E_a + W'} \left\{ \frac{1}{W^2} - \frac{1}{W(E_a + W' - W)} \right\} dW \\ &= \frac{\pi e^4}{W} \frac{E_a - W'}{(E_a + W')^2} \end{aligned} \quad (3.58)$$

which is the required distribution. For small W , (3.58) reduces to the classical result

$$\sigma_W = \frac{\pi e^4}{WE_p} \quad (3.59)$$

which is the behaviour reflected in secondary yield curves. It will be noted that although no limits have been placed upon W' the cross section vanishes for $W' = E_a$. This is no disadvantage, as this value for W' leads to an electric field strength in the foil greater than the dielectric breakdown strength of the material ($\sim 10^6 - 10^7$ v cm⁻¹) and will never actually be attained.

3.5.4 Internal electric field

We now seek the magnitude and distribution of the electric field set up in the specimen foil; in this treatment, we shall utilise the ionic conductivity relations derived in §1.6.

We consider a thin dish polished alkali halide foil tapering from thickness $p = 200$ μ m at the outside edge to $p = 0$ at a small hole in the centre. The polishing profile is of constant 1 cm radius and the periphery is firmly anchored to an electrically conducting sink. We

irradiate in the centre at the edge of the hole a region of radius $b \sim 5 \mu\text{m}$ with a 100 keV electron beam current of $5 \times 10^{-10} \text{ A}$.

The resistance R of this foil at the irradiated area will be given by

$$R = \int_r^s \frac{dr}{2\pi r p \sigma_c} \approx \frac{p}{4\pi \sigma_c r^2} \text{ for } s \gg r, \quad (3.60)$$

where r is the radial distance from the foil edge, extending to s at the periphery, and p is the radius of the profile curvature. We note that for s appreciably larger than the distance of the irradiated area from the edge, there is no s dependence of the resistance; this implies that a fine mesh mounting grid (200 mesh $\approx 100 \mu\text{m}$ grid squares) will appreciably reduce the resistive path only when the area examined is very near a grid bar. Substituting the appropriate dimensions we find near the edge of the foil ($r \sim b$) that

$$R \sim \frac{3.4 \times 10^5}{\sigma_c}. \quad (3.61)$$

Since at 300 K, $\sigma_c \sim 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ from (1.12), $R_{300} \sim 2 \times 10^{13} \text{ ohm}$. At 100 K, $\sigma_c < 10^{-24} \text{ ohm}^{-1} \text{ cm}^{-1}$ and $R_{100} \sim 2 \times 10^{29} \text{ ohm}$.

At equilibrium the secondary current I_s will be equal to the foil conduction current I_c . For a given primary irradiating current I_p , I_s is given by

$$I_s = 2N_o p' I_p \alpha_W, \quad (3.62)$$

where N_o is the number of valence electrons and p' the maximum secondary escape distance. It is assumed that $p' = p/2$ for foil thickness $<$ twice the maximum escape distance. For the parameters of our irradiation and α_W from (3.59) we have

$$I_s = \frac{1.1 \times 10^{11} I_p p'}{WE} \quad \text{for } W \ll E. \quad (3.63)$$

If the conduction is ohmic, we have at equilibrium

$$V' = W'/e = I_s R = \frac{7 \times 10^{10} I_p p' \rho}{8 WE \sigma_c r^2} \quad (3.64)$$

If we investigate conditions at the foil edge, $p \sim 10$ nm and solve for W' at 300 K, we find $W' \sim 7$ eV and $I_s \sim 10^{-12}$ A; thus the $W \ll E$ approximation is justified. Since 7 eV lies near the middle of the secondary emission peak for which we know $I_s \sim 0.1 I_p \sim 5 \times 10^{-11}$ A and where the scattering cross section alone is not adequate to describe emission, we expect that the actual potential will shift past the emission peak to higher energies, probably ~ 10 eV ($V' \sim 10$ V). The corresponding maximum field strength E' at b will be $E' \sim 4 \times 10^4$ V cm $^{-1}$.

According to (1.14) the conduction will become non-ohmic (exponential with E) for fields $E' \sim 3 \times 10^6$ V cm $^{-1}$. In this region

$$E' = \frac{2kT}{ae} \ln \frac{Jae}{\sigma_W kT}, \quad (3.65)$$

and from the full definition of σ_c implied in (1.14) we expect to lose all T and σ_W dependence of E ; i.e. E' will level out at some value

$$E^* = \text{constant} \times \ln J^* + \text{constant},$$

where J^* is the maximum current density when conduction becomes non-ohmic, or equivalently

$$E^* = J^*/\sigma_c^*. \quad (3.66)$$

J^* is given by

$$J^* = \frac{I_s^*}{2\pi b p} = \frac{I_s^*}{2\pi b r^2} \quad \text{since } p \sim \frac{r^2}{\rho}, \quad (3.67)$$

$$\text{and} \quad \sigma_c^* = \frac{I_s^*}{W^*} \frac{\rho}{4\pi r^2}, \quad (3.68)$$

$$\text{leading to} \quad E^* = \frac{2W^*}{b}, \quad (3.69)$$

Setting $E^* \sim 3 \times 10^6 \text{ V cm}^{-1}$ and solving (3.69) for W^* we obtain

$$W^* \sim 750 \text{ eV}; V^* = 750 \text{ V}. \quad (3.70)$$

This potential will be attained for $\sigma_c^* \sim 5 \times 10^{-13} \text{ (ohm cm)}^{-1}$, corresponding to a temperature $T \sim 200 \text{ K}$ and will be maintained for all temperatures below 200 K . This is, in fact, just the temperature for which uncontrollable charging effects set in during observation of alkali halide foils.

Several points should be noted about the E^* dependence in (3.69). Since $W^* \propto (p'\rho I_p)^{1/2} / r$ from (3.64) we have from (3.69) that

$$E \propto \frac{(p'\rho I_p)^{1/2}}{br}. \quad (3.71)$$

At higher temperatures, when W (or V) is small we have that the thickness over which the lowest energy secondaries are produced, p' , is constant $\sim 50 \text{ nm}$ and independent of foil thickness above $p \sim 100 \text{ nm}$ (i.e. in normally viewed regions). Therefore, we see that if we increase the irradiating current or broaden the polishing profile we will have increased charging behaviour. Conversely, if we decrease the irradiated area (keeping the beam current constant), or move further into the foil or use specimens with a larger wedge angle, charging behaviour decreases. The ρ dependence probably explains why previous workers using edge polished specimens of considerably greater wedge angle than carefully dish polished foils experienced less difficulty with charging behaviour; the r dependence indicates that charging will always be more severe near

foil edges and less so in the specimen interior.

At low temperatures, since W (or V) increases to a large value and those secondaries which do escape are of much higher energies, the escape path increases, so that $p \sim p'$ for all thicknesses p which are likely to be encountered in transmission microscopy. Since $p = \rho/r^2$, we may remove the ρ and r dependence, indicating that there is little benefit in staying away from foil edges, and charging is nearly everywhere severe.

3.5.4 External electric field

Calculation of the three dimensional distribution of electric field strength in vacuum surrounding a charged specimen presents an intractable analysis problem. This field will depend on the asymmetry of the specimen surroundings, the hole position in the foil and the foil tilt with respect to the microscope symmetry axis. A good estimate can be obtained, however, from empirical planar field mapping. A 1000:1 scale representation of the specimen and its surroundings was made on graphitised paper. The irradiated area of the specimen was metallised, as were all surrounding conducting surfaces, and was located the equivalent of 50 μm from the symmetry axis to approximate a region at the edge of a central 100 μm hole. No attempt was made to simulate the permittivity of the specimen, the difference between ϵ and ϵ_0 being small compared with that between ϵ_0 and the conducting surroundings. A potential difference V_0 was established between the irradiated area representation and the surrounding surfaces, and the axial and transverse fields were plotted by taking small axial or transverse distance increments

and measuring the differential potential across them ($E_z \approx -\Delta V/\Delta z$).

The high field strengths very near to the specimen were established by extrapolation from adjacent regions. The distribution of net transverse field along the axis is plotted in fig. 3.11. It will be noted that quite substantial net transverse fields, $\sim 100V_0 \text{ V cm}^{-1}$, still exist at distances $\sim 10 \text{ }\mu\text{m}$ above and below the specimen.

3.5.5 Beam deflection

The observable effect of the transverse electric field set up external to the specimen will be to deflect the electron beam in a direction opposite to the sense of the field. Thus if the electron beam passing through the central hole of a specimen is brought up to the edge of the foil, the transverse field will tend to bend the beam away from its normal incidence on the specimen, i.e. usually away from the hole. Estimating the magnitude of beam deflection is a complex problem because the incident beam, wherever it is incident on the specimen, generates its own deflection field. We will content ourselves with calculating the deflection of an electron beam in free space induced by the field established at the specimen; this should provide a sort of minimum estimate.

The transverse force $F_T(z)$ arising from an electron field strength $E_T(z)$ acting at each point z on the z -axis on a beam of electrons propagating in the z direction is given by

$$F_T(z) = eE_T(z) . \quad (3.72)$$

This force produces a transverse acceleration $a_T(z)$ of the beam given by

$$a_T(z) = e\Xi_T(z)/m^* \quad (3.73)$$

where m^* is the relativistic electron mass. The transverse velocity component $v_T(z)$ induced at z during the time dt the electron spends traversing a distance dz will be given by

$$v_T = a_T dt = \frac{e\Xi_T(z) dz}{m^*v} \quad (3.74)$$

where v is the incident electron velocity. The angular deflection $\alpha_T(z)$ of the beam arising at each point z is then given by

$$\alpha_T(z) = \tan^{-1} \frac{v_T}{v} = \tan^{-1} \frac{e\Xi_T(z)dz}{m^*v^2} \approx \frac{\Xi_T(z)dz}{2E_a} \quad (3.75)$$

for small deviations, where E_a is the incident electron beam energy in electron volts. Integrating (3.75) over all z for which a significant field exists, we have the total deviation

$$\alpha_T = \frac{1}{2E_a} \int_{\Xi \gg 0} \Xi_T(z) dz \quad (3.76)$$

If we choose $z = 0$ at the centre of the specimen, and assume z -axial symmetry, we have

$$\alpha_T = \frac{1}{E_a} \int_{z=0}^{\infty} \Xi_T(z) dz. \quad (3.77)$$

We may approximate the $\Xi(z)$ distribution with the following function, by reference to fig. 3.11,

$$\begin{aligned} \Xi(z) &= 4 \times 10^3 V' & 0 \leq z \leq p/2, \\ \Xi(z) &= \frac{10^{-4} V'}{(z+c)^2} & \frac{p}{2} \leq z < \infty, \end{aligned} \quad (3.78)$$

where $c = 1.6 \times 10^{-4}$.

$$\text{Then, } \alpha_T = \frac{1}{E_a} \{2 \times 10^{-3} V' + 6 \times 10^{-1} V'\} \approx 6 \times 10^{-6} V', \quad (3.79)$$

and we notice that the external field predominates over the internal one.

The magnitude of these deflections can be gauged in comparison with the angle subtended by the objective aperture, $\alpha_o \sim 2 \times 10^{-3}$ rad for a 20 μ m aperture. We then have the following deviations:

	<u>T = 300 K</u>	<u>T < 200 K</u>	)
α_T	6×10^{-5} radians	5×10^{-3} radians	)
α_T/α_o	0.03	2.5	)

(3.80)

Microscopy is then possible at 300 K, but charging effects near the edge can be clearly annoying, particularly at sharp corners. Below 200 K it is virtually impossible to keep the beam within the objective aperture; the shift, in fact, corresponds to nearly a whole Bragg angle. Furthermore, the deviations calculated represent conditions of highest symmetry, minimum beam current density, etc. Deflections several Bragg angles are frequently observed.

From (3.74) we can clearly see the effect of a fine mesh grid which decreases the spatial extent of the field above and below the specimen, and thus minimises the distance over which this field can deflect the beam. The external field is then nearly coincident with the specimen surface, in which case beam deflection occurs only over a path equivalent to the specimen thickness and

$$\alpha_T (< 200 \text{ K}) \sim 2 \times 10^{-5} \text{ radians} \quad (3.81)$$

with perfect grid-foil intimacy.

3.5.6 Evaporated conducting films

The logical solution to charging behaviour is to evaporate a thin conducting amorphous or polycrystalline layer on either or both foil surfaces. This film will achieve far better intimacy with the

specimen than any mesh grid. Such a layer on the upper foil surface is best avoided to prevent contrast degradation; a layer on the lower surface will contribute only to the overall absorption. Since this absorption will be roughly proportional to atomic number, one seeks the lightest possible elements that evaporate easily and conduct well; these are carbon ($Z = 4$) and aluminium ($Z = 13$). Be ($Z = 4$) and Mg ($Z = 12$) do not evaporate easily; Li ($Z = 3$) and Na ($Z = 11$) introduce their own special problems. The maximum permissible layer thickness is several tens of nm if excessive absorption is not to be introduced. For a metallic conductor it can be shown that (Dekker 1965)

$$\sigma = ne^2 \Lambda_F / mv_F \quad (3.82)$$

where n is the number of conduction electrons, Λ_F the mean free path between collisions for electrons at the Fermi level, m the electron mass and v_F the velocity of an electron with the Fermi energy E_F . From a knowledge of E_F and σ , we can deduce $\Lambda_F \sim 35$ nm for aluminium. We must therefore investigate the mechanism of electrical conduction in a film of thickness $p \lesssim \Lambda_F$. If the film is polycrystalline and deposited on a non-atomically-smooth surface, we can assume electrons are diffusely reflected at the boundary. Defining $k = p/\Lambda_F$, the ratio of film conductivity to bulk conductivity σ/σ_0 for diffuse reflection is given by (Sondheimer 1952)

$$\sigma/\sigma_0 = \frac{3k}{4} \left(\ln \frac{1}{k} + 0.43 \right). \quad (3.83)$$

Chopra, Bobb and Francombe (1963) and Chopra and Bobb (1964) have conducted extensive studies of the resistivities of evaporated single crystal and polycrystalline gold films in various substrates. They find significant deviations from (3.83) only at very small thicknesses

($p \sim 20 \text{ nm}$) where it is difficult to maintain a uniform evaporated film thickness. Instead, islands nucleate and grow until their boundaries touch; at this point the resistance is still higher than average film thickness would indicate because only a few conduction paths are available. The extrapolated result for aluminium correlates well with the experimental observation that aluminium film thicknesses $< 10 \text{ nm}$ are not sufficient to preclude completely charging behaviour in alkali halide foils at low temperatures. However, for films $> 20 \text{ nm}$ thick there is little difference between film and bulk conductivity. The conductivity of bulk aluminium is $\sim 4 \times 10^5 \text{ (ohm cm)}^{-1}$ and, at worst, we can expect $\sigma > 2 \times 10^5 \text{ (ohm cm)}^{-1}$ for films $> 20 \text{ nm}$ thick. If this film has a radius $s \sim 1 \text{ mm}$ and thickness $p \sim 20 \text{ nm}$ and is irradiated over any area radius $b \sim 5 \text{ }\mu\text{m}$, resistance R at b is

$$R = \frac{1}{2\pi p\sigma} \int_b^s \frac{dr}{r} = \frac{1}{2\pi p\sigma} \ln \frac{s}{b} \sim 21 \text{ ohm} . \quad (3.84)$$

The maximum potential difference across the foil V_m is then given by the maximum secondary emission current I_m

$$V_m = I_m R \sim 10^{-8} \text{ V}, \quad (3.85)$$

which is negligible.

Evaporation is carried out in a special chamber fitted onto an Edwards evaporator unit (fig. 3.12) which accepts the vacuum lock used for specimen transfer. The chamber is similar to the specimen chamber used in the microscope but utilised in an inverted sense which enables the specimen cartridge to pivot from the transfer lock into a collar positioned centrally in the chamber. A shutter is incorporated just below the specimen position to eliminate the initial surge of oxide

impurities found with aluminium evaporation; and beneath this, the evaporation source. Either a tungsten hairpin filament for evaporating aluminium or a pair of spring-loaded carbon rods for carbon evaporation can be used; these units can be removed from the chamber for maintenance or replacement of the evaporation sources.

Film thickness is monitored with cover glass discs positioned at the specimen level, centrally drilled to pass a 3 mm diameter evaporation beam onto the specimen above; these discs enable film thickness to be measured directly after evaporation in an interferometer, although in practice the opacity of the film on the cover glass provides an adequate estimate of film thickness (Cosslett and Cosslett 1957). The rate of deposition during evaporation is judged from the opacity of a second cover glass slide placed between the source and an observation window.

Several source configurations were tried for aluminium evaporation (boats, baskets, helices), but the simple tungsten hairpin consistently provided the most reproducible results. Typical evaporation conditions are 4 sec evaporating time just above the melting point of aluminium in a vacuum of 10^{-5} torr; the same source can be used repeatedly until tungsten alloying with aluminium impairs evaporation performance.

3.6 Electron Microscopy of Alkali Halide Foils

Once suitable thin foils are available for examination in the microscope, it is desirable to ascertain what microscope conditions are optimum for foil observation and defect imaging. This is principally a matter of specific foil orientation, and requires

application of the dynamical theory of electron diffraction (Howie and Whelan 1961; Hirsch et al. 1965). In this section we shall develop a basic outline of this theory and illustrate specific application to the alkali halides, using many-beam computer calculations. Basic diffraction and absorption parameters relevant to this application are computed and tabulated. Many-beam computations were performed, in preference to simple two-beam calculations, because it was not inherently apparent whether satisfactory two-beam conditions could be obtained for specific diffraction conditions peculiar to two-species materials. A fundamental concern to the problem of radiation damage of the alkali halides in the electron microscopy is the limitation of incident electron flux; in large part reduction of the incident flux is dependent upon the electron statistics available at the recording position for adequate resolution. The latter are in turn directly related to the intensity transmitted through a crystal specimen under given imaging conditions for a given incident flux. An estimate for the relevant fraction is obtained as a function of specimen orientation and in relation to usual defect imaging conditions.

3.6.1 Dynamical theory of electron diffraction

In electron microscopy we are concerned with an electron of energy eE (typically 100 keV) and wave vector χ in vacuum entering by one surface a crystal with crystal potential $V(r)$ and finally leaving by another surface (so-called Laue case). We seek steady state wave functions describing the behaviour of the electron moving in such a

potential $V(\underline{r})$ which satisfy the Schrödinger wave equation

$$\nabla^2 \phi(\underline{r}) + (8\pi^2 me/h^2) \{E + V(\underline{r})\} \phi(\underline{r}) = 0. \quad (3.86)$$

When $V(\underline{r}) = 0$ in vacuum we have a solution given by

$$\phi(\underline{r}) = \exp(2\pi i \underline{\chi} \cdot \underline{r}), \quad (3.87)$$

provided $\underline{\chi}$ is chosen so that

$$h^2 \chi^2 / 2m = eE. \quad (3.88)$$

Inside a periodic crystal we have a crystal lattice potential

$$V(\underline{r}) = \sum_{\underline{g}} V_{\underline{g}} \exp(2\pi i \underline{g} \cdot \underline{r}), \quad (3.89)$$

where $V_{\underline{g}}$ are the Fourier coefficients of the crystal lattice potential and the summation extends over all reciprocal lattice vectors $\underline{g}$. Also, the incident wave vector $\underline{\chi}$ will change to $\underline{K}$ because of refraction from the mean inner crystal potential V_0 . The magnitude of $\underline{K}$ is then given by

$$K^2 = \frac{2me}{h^2} (E + V_0) \quad (3.90)$$

Since $V_0 \ll E$ for 100 keV electrons, we neglect the small addition of V_0 .

For the potential (3.89) solutions to (3.86) will be in the form of Bloch functions of wave vector $\underline{k}^{(i)}$

$$b^{(i)}(\underline{r}) = \sum_{\underline{g}} C_{\underline{g}}^{(i)}(\underline{k}) \exp\{2\pi i (\underline{k}^{(i)} + \underline{g}) \cdot \underline{r}\}. \quad (3.91)$$

Substituting (3.91) and (3.89) into (3.86) we obtain a system of linear equations

$$\{K^2 - (\underline{k} + \underline{g})^2\} C_{\underline{g}}^{(i)}(\underline{k}) + \frac{2me}{h^2} \sum_{h \neq 0} V_h C_{\underline{g}-h}(\underline{k}). \quad (3.92)$$

These sets of equations define in $\underline{k}$ space a set of surfaces, called dispersion surfaces, on which each Bloch wave vector is constrained to lie. If we define $\gamma^{(i)}$ as the perpendicular distance from the i 'th dispersion surface to a sphere a radius K centred on O (see fig. 3.13) and s_g as the deviation of the reciprocal lattice point $\underline{g}$ from the Ewald reflecting sphere of radius K centred at A , we have the approximate relation

$$\{K^2 - (\underline{k}^{(i)} + \underline{g})^2\} \approx 2K \{s_g - \gamma^{(i)}\} \quad (3.93)$$

and (3.92) reduces to an eigenvalue equation

$$2K \{s_g - \gamma^{(i)}\} C_g^{(i)}(\underline{k}) + \frac{2me}{h^2} \sum_{h \neq 0} V_h C_{g-h}^{(i)}(\underline{k}) = 0, \quad (3.94)$$

which can be solved by matrix methods to yield eigenvalues $\gamma^{(i)}$ and also $C_g^{(i)}$ as functions of the deviation parameter s_g .

The total crystal wave function $\phi(\underline{r})$ must be a linear combination of Bloch waves $b^{(i)}(\underline{r})$,

$$\phi(\underline{r}) = \sum_i \psi^{(i)} \sum_g C_g^{(i)}(\underline{k}) \exp \{2\pi i (\underline{k} + \underline{g}) \cdot \underline{r}\}, \quad (3.95)$$

where $\psi^{(i)} \approx C_o^{(i)}$ is the excitation of the i 'th Bloch wave. The wave amplitude of the g 'th diffracted plane wave at a point z in the crystal is given by

$$\phi_g(z) = \sum_i \psi^{(i)} C_g^{(i)} \exp (2\pi i \gamma^{(i)} z). \quad (3.96)$$

whence can be obtained the intensity of the g 'th beam at the bottom surface of the crystal.

We may include absorption in this treatment by making the crystal potential complex (Yoshioka 1957),

$$V(\underline{r}) + i V^i(\underline{r}) = \sum (V_g + i V_g^i) \exp 2\pi i \underline{g} \cdot \underline{r} . \quad (3.97)$$

Equations (3.92) become

$$\begin{aligned} \{K^2 - (\underline{k} + \underline{g})^2\} C_g^{(i)} + \frac{\hbar^2}{2me} \sum_{h \neq 0} V_h C_{g-h}^{(i)} \\ + i \frac{\hbar^2}{2me} \sum_{h \neq 0} V_h^i C_{g-h}^{(i)} = 0 , \end{aligned} \quad (3.98)$$

and the wave amplitudes become

$$\phi_g(\underline{z}) = \sum_i \psi^{(i)} C_g^{(i)} \exp \{ 2\pi i (\gamma^{(i)} + i q^{(i)} \underline{z}) \} . \quad (3.99)$$

In other words, the eigenvalues $\gamma^{(i)}$ are no longer purely real but have complex components $q^{(i)}$; each Bloch wave is therefore attenuated by the factor $\exp(-2\pi q^{(i)} \underline{z})$.

3.6.2 The lattice potential $V(\underline{r})$

The Fourier coefficients V_g of the crystal lattice potential may be obtained from kinematical scattering factors for electrons $f_{el}(\underline{g})$ derived from relativistic Hartree-Fock atomic potentials $\phi(\underline{r})$ by the Mott relation

$$f_{el}(\underline{g}) = \frac{8\pi me}{\hbar^2} \int_0^\infty r^2 \phi(\underline{r}) \frac{\sin 2\pi \underline{g} r}{2\pi \underline{g} r} dr \quad (3.100)$$

where $\underline{g} = 2 \sin \theta / \lambda$. For an ionic crystal we must include the Coulomb field; if Q is the ionic charge, we define

$$\phi'(\underline{r}) = \phi(\underline{r}) - eQ/4\pi \epsilon_0 r \quad (3.101)$$

where ϵ_0 is the crystal dielectric constant, and have

$$f_{el}(\underline{g}) = \frac{8\pi me}{\hbar^2} \int_0^\infty r^2 \phi'(\underline{r}) \frac{\sin 2\pi \underline{g} r}{2\pi \underline{g} r} dr + \frac{me^2 Q}{2\pi \hbar^2 \epsilon_0 \underline{g}^2} . \quad (3.102)$$

Doyle and Turner (1968) have computed $f_{el}(\underline{g})$ for all alkali and halogen

ionised atoms (except $|F^-|$) using (3.102), and have produced an analytical 8 parameter fit suitable for a non-linear least squares curve-fitting computer program.

$$V_g \text{ are related to } f_{el}(g) \text{ through the structure factor } F_g \text{ by}$$

$$V_g = \frac{1}{\Omega} \frac{h^2}{2me} F_g = \frac{47.87}{\Omega} F_g \quad (3.103)$$

where

$$F_g = \sum_j f_{el}^{(j)}(g) \exp(2\pi i \underline{g} \cdot \underline{r}_j), \quad (3.104)$$

and V_g and F_g are respectively in volts and Ångstrom units. $f_{el}^{(j)}(g)$ is the atom scattering factor for the ion in the j 'th position in the unit cell, and the summation in (3.104) is carried out over the volume of the unit cell Ω . For NaCl structure alkali halides,

$$F(hkl) = 4 \{ f_{el}^{(+)}(hkl) + f_{el}^{(-)}(hkl)(-1)^{(h+k+1)} \} \quad)$$

$$\text{unless } \{ 1 + (-1)^{(h+k)} + (-1)^{k+1} + (-1)^{1+h} \} = 0, \text{ in which case } \quad) \quad (3.105)$$

$$F(hkl) = 0, \quad)$$

A temperature dependence may be added to V_g via Debye-Waller factor corrections to $f_{el}^{(i)}(g)$. We note that V_g may be either positive or negative; this sign depends ultimately on our reference point in the unit cell. Another useful way of expressing V_g is via the two-beam extinction distance which has the dimensions of length,

$$\xi_g = \frac{h^2 K \cos \theta_B}{2 me |V_g|} = \frac{3398.5}{V_g} \text{ for 100 keV electrons,} \quad (3.106)$$

where ξ_g is given in Ångstrom units. Since the Bragg angle θ_B for 100 keV electrons is only $\sim 10^{-2}$ rad we can neglect $\cos \theta_B$ in (3.106).

Calculations (3.102), (3.105), (3.103) and (3.106) were combined into a single program to compute F_g , V_g and ξ_g for rock salt structure alkali halides. Suitable Debye-Waller factors, where known, were gleaned from the International Tables for X-Ray Crystallography (1962) for the low temperature and room temperature cases. Values of F_g , V_g and ξ_g for NaCl, KCl, KI and NaBr at ~ 20 K are listed in Table 3.4. Two features are of immediate interest. First, extinction distances for alkali halides are typically twice those for f.c.c. metals; since many electron microscopical contrast features scale with ξ_g , large values of this parameter are significant. Second, diffraction vectors of type 111, 131, 133, etc., (where $(h + k + l) = \text{odd}$) exhibit an anomalously large extinction distance. These are the reciprocal lattice vectors which have $V_g < 0$ in Table 3.4. The planes in real space corresponding to these g consist of alternate layers of all cation and all anion population; therefore, F_g and V_g reflect the difference of cation and anion ionic scattering factors, and ξ_g becomes very large for crystals such as KCl with very similar ions.

3.6.3 Absorbing potential V_g^i

Inclusion of the complex part of the potential corresponds to addition of inelastic scattering. The V_g^i contributions arise principally from two inelastic scattering components: i) phonon excitation and ii) electron excitations, primarily excitation of plasmons (valence electrons in alkali halides) and of tightly-bound (core) electrons. We shall denote these two components $V_g^i(\text{ph})$ and

$V_g^i(\text{el})$. These have been recently evaluated by Radi (1970) for most elements and the alkali halides at 20 K and 300 K; in the latter case, no plasmon losses were calculated, but such excitations contribute little to effective absorption since the corresponding scattering is very small angle, generally passes through the objective aperture, and has been shown to preserve contrast. Radi's core electron contribution is too large by at least a factor of two (A. Pogany, private communication) owing to neglect of significant exchange terms in the derivation of $V_g^i(\text{el})$. This component was therefore reduced accordingly in utilising Radi's data.

An absorption distance

$$\xi_g^i = \frac{h^2 K}{2me} \frac{\cos \theta_B}{V_g^i}, \quad (3.107)$$

analogous to the extinction distance ξ_g , can be derived from V_g^i , and ξ_g^i for KI have been included in Table 3.4. It has been found (from calculations detailed in §3.6.4 following) that the initially calculated value of V_o^i was too high to fit observed intensity damping in real foils, and had to be scaled down by a factor of two. With this adjusted value, about five thickness fringes appear in calculated thickness fringes profiles to agree with experiment. Since the principal contribution of V_o^i is $V_o^i(\text{el})$, it is concluded that Radi's values for $V_o^i(\text{el})$ are about a factor of four too high. Two commonly used ratios characteristic of absorption properties, $V_g/V_o^i = \xi_o^i/\xi_g$ and $V_g/V_g^i = \xi_g^i/\xi_g$, are also indicated. The former governs the mean absorption (equal absorption of all Bloch waves), while the latter reflects the so-called anomalous absorption (preferential absorption of Bloch waves

peaking near ion cores). The mean and anomalous absorptions calculated indicate that alkali halides behave similarly to silicon.

3.6.4 Bloch wave properties and bright field rocking curves

Fig. 3.14 illustrates the result of a 14-beam calculation for the 111 systematic row in KI at 20 K using a many-beam program derived by Humphreys (1967). In (a) the first four dispersion surfaces (from $\gamma^{(i)}$) are plotted as a function of crystal orientation. In (b) the excitations $C_o^{(i)}$ of the first four Bloch waves are indicated, and in (c) the absorptions $q^{(i)}$ for the same four Bloch waves. Near the 111 Bragg condition satisfied, we see that Bloch waves 1 and 2 are principally excited, with wave 1 dominant for $s_g < 0$ and wave 2 dominant for $s_g > 0$. From (c) we see that Bloch wave 1 is strongly absorbed; this corresponds to wave 1 having maxima in the vicinity of the ion cores where the absorbing potentials $V_g^i(\text{ph})$ and $V_g^i(\text{el})$ are most effective. Since the bright field amplitude

$$\phi_o(z) \propto \sum_i \psi^{(i)} C_o^{(i)} \exp(-2\pi q^{(i)} z) \exp(2\pi i \gamma^{(i)} z), \quad (3.108).$$

where $\psi^{(i)} \approx C_o^{(i)}$ if we neglect small imaginary parts of these quantities, we expect relatively poor overall transmission in bright field for $s_g < 0$ where wave 1 is most strongly excited ($C_o^{(i)}$) but also most strongly absorbed ($q^{(i)}$), and much better transmission for $s_g > 0$ where the strongly excited wave 2 is less strongly absorbed (channels). A similar condition obtains in the vicinity of 222 satisfied for waves 2 and 3. This expectation is confirmed in the bright-field rocking curve, fig. 3.15 for a KI foil 400 nm thick at 20 K. The dark-field

rocking curve, on the other hand, is symmetrical about the Bragg position as indicated for 222 dark field conditions.

The maximum transmitted intensity in bright field conditions is ~4% of incident intensity (for a 400 nm thick foil) and occurs positive of the 222 Bragg condition satisfied for a deviation parameter $w_g = s_g \xi_g \sim +1.0$. Fortunately, this deviated condition is also optimum for revealing defect strain field contrast.

Corresponding dark field intensities are considerably less, and are therefore generally less useful when illumination must be kept to marginal levels. It is possible in KI to obtain reasonable first order two-beam conditions for 111, although intensities are low; similar intensities would be unattainable for 111 excitation in KCl.

Figs. 3.16, 3.17, and 3.18 illustrate many-beam bright-field rocking curves for 200, 220 and 311 systematics for a KI foil 400 nm thick at 20 K. 311 conditions are utilised in an important analysis of radiation -induced defect clusters in KI, §5.5. Significant intensity can be obtained in 311 with acceptable two-beam conditions with little excitation of 622; the rocking curve is rather sharp, however, which renders it difficult to maintain large foil areas in proper diffracting conditions with foils that are customarily slightly buckled. Deviation parameters for maximum bright-field intensity in all major reflections are typically $1.0 < w_g < 2.0$, and transmitted intensities typically a few per cent of incident for foils of useful thickness. From these calculations we ascertain that satisfactory two-beam conditions may be obtained in all useful reflections (at least in KI) and that most defect contrast features studied in §5.3 - §5.5

may be interpreted satisfactorily on a two-beam theory.

3.7 Electron Microscopy at Low Illuminations

It should be evident from the discussion of §2.4 on energy loss rate obtaining in the transmission electron microscope (see Table 2.3) that catastrophic irradiation damage takes place in situ in the illuminating electron beam, and that it is therefore in one's interest to minimise the illuminating beam current density as much as possible. Unfortunately, the high current densities employed in the electron microscope are needed at the high magnifications utilised to provide acceptable electron statistics in the magnified image, and sacrificing illuminating intensity means sacrificing resolution as well. Additionally, one must be capable of focussing such a magnified image, which brings into play parameters of visual acuity and phosphor screen response. These factors are considered below, and an attempt is made to demonstrate those levels of illumination/magnification consistent with adequate resolution. Such conditions set an ultimate limit on permissible reduction of electron beam current density, and the implications for electron microscopy at these minimum conditions are discussed.

3.7.1 Phosphor response

Adequate focussing of the image prior to recording is one of the most critical operations in the use of the electron microscope.

For this operation one must rely on the response of the phosphor viewing screen to electrons forming the image, and also on the visual acuity of the eye at low levels of illumination.

3.7.1.1 Visual acuity

Haine (1961) has measured the variation of visual acuity with scene brightness for various levels of image contrast (fig. 3.19). Visual acuity clearly falls off rapidly with intensity and contrast; thus an improvement results from increasing the size of observed detail by increasing the electron optical magnification. However, for a maximum permissible irradiating current, the illuminating intensity diminishes as $1/M^2$ where M is the magnification. Hence, for focussing desired detail of a specific size, there will be some optimum magnification consistent with a level of visual acuity.

A sizeable improvement can be made if the angular distribution of light emitted by the phosphor can be modified so that more of it is directed into the narrow solid angle accepted by the eye (Haine 1961). The semi-aperture angle of the eye is $\sim 8 \times 10^{-3}$ radians, and, in fact, the eye collects only about 2×10^{-4} of all emitted light. It is possible to collect emission from a larger solid angle using a wide angle magnifying lens of such an aperture as to just fill the aperture of the eye. A factor of m^2 times as much light is then collected by the eye, if m is the magnification of the lens; since the image is m times larger, it appears at the same intensity as the original. This increase in magnification without sacrifice of intensity enables increased visual resolution by a factor of m .

Magnifications up to 20 x are possible without appreciable decrease in intensity, but there is no point in increasing the magnification beyond either the resolving power of the fluorescent screen or the electron statistics obtaining at the screen for a given screen illumination.

3.7.1.2 Phosphor properties

The ultimate resolving power of powdered phosphor screens has been determined by Hindever (1942), Kopp and Müllenstedt (1946) and Von Borries (1948) as 70 μm at 50 kV, 120 μm at 100 kV and 250 μm at 250 kV. Efficiencies up to 100 lumens/watt can be obtained with available phosphors (Bril and Klasons 1952) which represents a maximum efficiency of 25%. Higher resolution phosphors are available but with longer persistence or decreased efficiency; the eye integrates over ~ 0.1 sec, so there is little point, from considerations of dynamic focussing, in extending phosphor persistence much beyond this. The efficiency of a phosphor screen increases with accelerating voltages up to 30-40 kV, remains constant up to 100 kV, then falls off because the electrons at higher voltages penetrate so deeply that the emitted light is largely absorbed before reaching a free surface. At 100 kV the conversion factor is 10^7 Lambert $\text{A}^{-1} \text{cm}^2$.

3.7.1.3 Optimum magnification/minimum illumination

Assuming an incident beam current density $j_o \sim 5 \text{mA cm}^{-2}$ we have from §3.6.4 a transmitted intensity $j_t \sim 0.1 \text{mA cm}^{-2}$ available at the bottom of the specimen foil under optimum bright-field conditions.

At the screen this intensity will be diminished by the factor $1/M^2$ where M is the total electron optical magnification, and the image brightness will be $10^7 j_t/M^2$. If we consider some defect of image width ~ 20 nm, we must provide a magnification $\sim 10^4$ ($20 \text{ nm} \rightarrow 200 \text{ }\mu\text{m}$) in order to distinguish the image from the screen grain. The brightness at this magnification is 10^{-5} Lambert; and an image $400 \text{ }\mu\text{m}$ wide with 80% image contrast (typical for diffraction contrast) will be barely discernible. Introducing an additional optical magnification of two with no decrease in intensity, an object image 20 nm wide will then be adequately visible for focussing. In practice a line object can be far more readily recognised than a point object, so somewhat higher magnifications are possible for some image configurations at this illumination level. Magnifications above 2×10^4 at this illumination level, however, are clearly impractical. Also, for visual acuity at the $400 \text{ }\mu\text{m}$ level, there is no advantage to added optical magnification greater than four, since then the separation of individual incoming electrons (about $100 \text{ }\mu\text{m}$ at $j_t = 0.1 \text{ mA cm}^{-2}$ and $M = 10^4$ over the 0.1 sec integration time of the eye) begins to become evident in the image observed. The factor of ten afforded by standard microscope binoculars provides just too grainy an image. An added magnification of about two strikes the right balance; this is easily provided by a small magnifying lens attached to the microscope viewing port.

Fig. 3.19 shows the advantage of even small increases in illumination level, since we are operating in the very steep portion

of the acuity curve. A factor of two increase, made acceptable, for example, by a corresponding decrease in defect production rate (see §5.4) can lead to a marked improvement in image focussing.

3.7.2 Photographic emulsion

All information from the electron microscope is normally obtained from photographic emulsion recording. In this section we investigate the limits on illumination set by the image recording process. We follow the treatments of Valentine and Wrigley (Valentine and Wrigley 1964; Valentine 1965, 1966; Wrigley 1970) in investigating the response of photographic emulsions to fast electrons. Photographic emulsions have three principal characteristics which are of interest to electron microscopy recording: speed, contrast, and resolution. These are discussed in the following three subsections.

3.7.2.1 Density-exposure relation (speed)

Any grain of silver halide that is hit by an electron during exposure will be converted when it is developed into an opaque grain of silver. There is thus a fundamental distinction between exposure to light, which requires the simultaneous deposition of many photons, and exposure to fast electrons, for which recording is a single hit process. In fact, a single electron may well hit and expose n halide grains in its passage through the emulsion. Let n grains of area A be hit by such an electron. If E electrons fall on a unit area of

emulsion, there will be EnA hits per halide grain; from Poisson's law, the probability that a grain is not hit is $\exp(-EnA)$, so the probability that a grain will be hit is given by $1 - \exp(-EnA)$. If v is the number of grains of silver developed per unit area emulsion, and G the total number of halide grains per unit area of unexposed emulsion, then

$$v = G \{1 - \exp(-EnA)\} \quad (3.104)$$

Unexposed grains are removed by fixation, while exposed grains are converted to silver, rendering the emulsion partially opaque. We wish to relate the optical density D of the plate to the number of silver grains per unit area. We define the density D by

$$D = \log_{10} L_0/L. \quad (3.105)$$

where L_0 is the light intensity incident on the plate and L is the intensity transmitted through the plate. We now consider a thin layer of emulsion containing dv silver grains. These grains have a somewhat larger cross section for light scattering than the halide grains which gave rise to them, so we express the mean area of each silver grain as kA . Light of intensity L falling on this layer will be diminished by $-dL$ such that

$$\frac{dL}{L} = kA \, dv. \quad (3.106)$$

Integrating over the full thickness of the emulsion, we obtain

$$\ln L/L_0 = -kA \, v. \quad (3.107)$$

Combining (3.105) and (3.107) we obtain $d = kAv/2.3$, and with (3.104)

$$D = (kAG/2.3) \{1 - \exp(-EnA)\}. \quad (3.108)$$

The factor $(kAG/2.3)$ represents the maximum density when every grain has been developed, i.e. the saturation density D_s . Generally $D_s \sim 6$,

except for some sensitive emulsions when D_s is as much as 10 - 12.

Most enlargers cannot cope with $D > 2$, so that most useful range for an emulsion is $D \leq D_s/4$. To a good approximation, within this range,

$$D = D_s \text{ nAE} , \quad (3.109)$$

which implies that density is linearly related to exposure for useful emulsion densities.

3.7.2.2 Contrast

Contrast γ is defined as the differential $dD/d(\log_{10} E)$. We can then write

$$\gamma = dD/d \log_{10} E = 2.3 E \quad dD/dE. \quad (3.110)$$

Differentiating (3.108) in order to obtain dD/dE , we find that

$$\gamma = 2.3 (D_s - D) \ln \{D_s/(D_s - D)\} \quad (3.111)$$

For $D < D_s/4$, (3.111) simplifies to

$$\gamma = 2.3 D. \quad (3.112)$$

This states simply that contrast is a function only of density and is not a characteristic of the emulsion, i.e. it is the same for all emulsions. From (3.111), the maximum value of contrast ($\gamma_{\max} = 0.85 D_s$) occurs at $0.63 D_s$, and is clearly never realised in practice.

3.7.2.3 Resolution

The maximum obtainable resolution on a photographic emulsion is, of course, given by the size of the silver grains that form the image. However, as these grains are typically $\sim 1 \mu\text{m}$, they will never set the limit to resolution, except at ridiculously high enlargements

(> 100 x). The "graininess" which limits resolution is due instead to the statistically random arrival of electrons (or quanta) at the emulsion.

If we consider that each of the variables in (3.109) is independently subject to random fluctuations, the r.m.s. fluctuation (standard deviation) is given by

$$\left\{\frac{\sigma_D}{D}\right\}^2 = \left\{\frac{\sigma_E}{E}\right\}^2 + \left\{\frac{\sigma_n}{n}\right\}^2 + \left\{\frac{\sigma_A}{A}\right\}^2 . \quad (3.113)$$

If this fluctuation is measured over an area S on the emulsion where the mean electron density $E = N/S$, the fluctuation in N from area to area will be $\sqrt{N}$ and

$$\frac{\sigma_E}{E} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} . \quad (3.114)$$

This fluctuation is term "electron noise". Similarly,

$$\frac{\sigma_n}{n} = \frac{\sqrt{n}}{n\sqrt{N}} = \frac{1}{\sqrt{(nN)}} . \quad (3.115)$$

If σ is the standard deviation of the cross sectional areas of the silver halide grains, we can write

$$\frac{\sigma_A}{A} = \frac{\sigma}{A} \left\{ \frac{1}{\sqrt{(nN)}} \right\} . \quad (3.116)$$

Combining, we find

$$\frac{\sigma_D}{D} = \frac{1}{\sqrt{N}} \left\{ 1 + (1/n) (1 + \sigma^2/A^2) \right\}^{\frac{1}{2}} . \quad (3.117)$$

The scatter σ in the halide grainsize is always small with the efficient manufacturing processes of modern emulsions. 100 kV electrons fully penetrate the typical 30 μm emulsion thickness

(Valentine has given typical electron range (in μm) in emulsions as $V^2/100$, where V is the accelerating voltage in kV), and the number of grains hit per electron, n , is typically between 5 and 20, depending on the concentration of silver halide grains in the gelatin medium. Therefore the noise introduced by the plate is unlikely to exceed the electron noise in the incident beam by more than a factor of $(1 + 1/n) = 1.2$. Valentine (1965) has measured this factor for twelve common emulsions; the result for several useful emulsions is seen to deviate little from unity. Therefore we conclude that photographic emulsions are essentially perfectly noiseless electron recorders; the graininess in any emulsion is due nearly entirely to the electron statistics of the exposure, $1/\sqrt{N}$, and the limit to resolution is set only by the total number of electrons received.

A simple calculation illustrates the limitation which statistical electron noise places on image resolution. Suppose we have a transmitted electron density E_t available at the specimen level for eventual recording. The r.m.s. fluctuation in dose is $1/\sqrt{E_t}$, and the maximum fluctuation will be about $3/\sqrt{E_t}$. For the eye to distinguish a feature from background noise requires about a factor of five image-to-noise ratio, so the smallest linear dimension distinguishable in the object is

$$x = 15/\sqrt{E_t} . \quad (3.118)$$

Suppose we have a beam current density $j_i \sim 1 \text{ mA cm}^{-2}$ incident on the specimen and under optimum bright-field conditions we have a $\sim 2\%$

transmitted intensity $j_t \sim 20 \mu A \text{ cm}^{-2}$. This corresponds to an electron density immediately below the specimen of $\sim 10^{14}$ electrons cm^{-2} and for a ten-second photographic exposure to $\sim 10^{15}$ electrons cm^{-2} . The smallest linear dimension thus resolvable will be $\sim 5 \text{ nm}$. A dislocation in alkali halides exhibits an image typically $\sim 20 \text{ nm}$, and these conditions will be suitable for resolving dislocation images; they will probably be insufficient for resolving small defects with images in the 10 nm range. It should also be appreciated that in the vicinity of the defect itself, electron statistics are considerably poorer than in contrast-free regions.

3.7.2.4 Choice of emulsion

In general a maximum acceptable electron dose and chosen magnification govern the choice of photographic emulsion. If j_t is the transmitted intensity at the bottom of the specimen, the intensity available for photographic recording will be j_t/M^2 where M is the total electron-optical magnification. Focussing criteria, §3.7.1.3, generally govern the choice of magnification, and all that remains is to choose that emulsion which is exposed fully for the given tolerable electron dose. The speed of various emulsions for 100 keV electrons have been measured by Valentine (1965, 1966), and independently in this study. Table 3.5 lists the required 100 keV electron dose for an optical density of 1 for emulsion processed in medium grain developers. Fine grain developers (microdol, microphen) will slow down an emulsion by a factor of 2-5.

In §5.4, we shall find that for low temperature microscopy of the most sensitive alkali halides, a ten-second exposure to an incident beam current density $j_i \sim 2 \text{ mA cm}^{-2}$ is a sufficiently small dose to preclude observable damage formation. A useful magnification both for defect observation and for adequate focussing is 15,000. For a useful foil thickness ($\sim 500 \text{ nm}$), and 10 sec exposure we have an electron dose $\sim 10^7$ electrons cm^{-2} available at the emulsion for recording. From Table 3.5 we note that LN emulsion given this dose produces an optical density of ~ 1 , XK a density ~ 1.5 and XM a density ~ 2 .

3.7.2.5 Use of fast emulsion

Several points should be made about the use and processing of fast emulsion.

First, one has a choice between acetate or polyester film or glass plate backing. While film is considerably easier to store, the dimensional stability of acetate bases is very poor while polyester bases are still somewhat inferior to glass; furthermore these materials readily acquire a static charge when desiccated, often leading to static discharge trails showing up on the emulsion. Glass plates, on the other hand, can suffer from adhesion problems between emulsion and glass backing under desiccation. This has been particularly true of Ilford LN glass plates, although attempts are now being made by Ilford to incorporate a plasticiser into the emulsion base; XK and XM emulsions are manufactured by a different process and do not suffer from peeling.

Because these emulsions are fast, considerably more care must be taken in respect of exposure to ambient light in dark room conditions. Brown x-ray safelights (6BR) must be used in place of the normal red filters. It is also desirable to mask off any red or green pilot lights on the microscope.

These emulsions are developed in medium developers (PQ Universal 1:4; ID-2). Although the nominally quoted development time is 6 minutes, it was found that considerably more information could be obtained by development for long periods (up to 20 minutes), developing up to the fog level on unexposed areas of the plates. A stop bath was found necessary to prevent plates from yellowing, and fixation was in an acid fixer (Amfix 1:3). Thorough washing (1 hour) was also necessary to prevent discoloration. It is imperative that these plates are air dried for about one day at room temperature and not at elevated temperatures, else the emulsion melts and runs with as little as 20°C temperature rise above ambient.

3.7.3. Instrument considerations

3.7.3.1 Illumination system

The conventional electron source in electron microscopes is the emitting tungsten hairpin filament operating at temperatures $> 2500^{\circ}\text{K}$ and producing a source size of about 90 μm diameter at crossover. In a two condensor system, the first condensor C1 demagnifies by a factor up to about 100, while the second C2 projects the demagnified image onto the specimen with a magnification ~ 2 .

The excitation of the first condensor governs the minimum attainable spot size, which is about 2 μm with the Siemens Elmiskop I. It is necessary from considerations of radiation damage to illuminate only the area under current observation. The observation screen is 90 mm in diameter; so the area to be illuminated is 6 μm in diameter at a magnification of 15,000 or 3 μm in diameter at 30,000. In practice this mode of operation requires C2 nearly focussed. The angular divergence ϕ and current density j_i of the beam at the specimen are determined by the source divergence ϕ_s and current density j_s at the source. By observation we have

$$\frac{j_i}{\phi_i^2} = \frac{j_s}{\phi_s^2} . \quad (3.119)$$

For the Siemens Elmiskop I, $j_s (\text{min}) = 20 \text{ mA cm}^{-2}$ and $\phi_s = 2.5 \text{ m rad}$, so we have

$$j_i (\text{min}) = 2.4 \times 10^5 \phi_i^2 . \quad (3.120)$$

ϕ_i and thus j_i are determined by the diameter D of the condensor 2 aperture from the relation (neglecting the objective prefield)

$$\phi_i = D/l , \quad (3.121)$$

where l is the distance between the condensor 2 aperture and the specimen (l = 124 mm for the Siemens Elmiskop I for the slightly elevated specimen position used in the helium stage; see §4.8).

Table 3.6 lists the minimum attainable beam divergence and beam current density as a function of condensor aperture size (to achieve these minima the beam current controller balance must be accurately set). From these data we see that sufficiently low beam currents

for alkali halide microscopy ($\sim 1 \text{ mA cm}^{-2}$) are attained only with very small condensor apertures, 100 μm and 50 μm . Fortunately in compensation for the smaller aperture sizes (and the correspondingly low beam current densities), the beam divergence for focussed illumination approaches a more acceptable value. The effect of large incident beam divergence is that the resolution is severely limited by lens aberrations (see §4.8) and by artificial broadening of the reciprocal lattice points (introducing a Δs ; see §3.6.1 and Fig. 3.13). For the reason it is better to use a 50 μm aperture and higher gun currents if necessary than to use a 100 μm aperture and lower currents for the same desired current density at the specimen.

3.7.3.2 Intensity monitoring

It was found necessary to incorporate an in-line intensity monitoring system for study of alkali halides, both to set safe initial beam current densities and to evaluate radiation rates, absorption parameters, etc. A Siemens picoammeter was coupled to the phosphor viewing screen to provide a continuous indication of intensity, in such a way that either the entire screen or an area 1/100 as large could be used as electron collecting surfaces. Flat screens cannot be 100% efficient collectors because of reflection and secondary emission; therefore the indicated flat plate intensities were calibrated against a Faraday cup positioned in the viewing chamber (Grubb 1971). The screen collection efficiency varied from 55% for 40 eV electrons to 65% at 100 keV electrons,

and the appropriate factor was used to scale observed flat plate collected intensities.

3.7.3.3 Ambient light

The requirement for operating near the limits of visual acuity necessitate a substantial period of dark adaptation, usually about ten minutes, while, for example, the helium stage is cooling. Shorter periods are not adequate for lowest intensity observations. All sources of ambient light in the microscope room must be masked or sealed, including microscope pilot lights, both to protect the sensitive photographic emulsion while loading, unloading or exposing, and to maintain dark adaptation. It is desirable, moreover, to record all comments during an experiment on a portable tape recorder, rather than to introduce sufficient light for writing; the tape is left running continuously during the course of the experiment, and the added ease of commentary elicits more information than normally recorded by hand. Transcription to written records is, unfortunately, slow, but a very complete record is thus obtained.

Table 3.1
 Typical Surface Energies

 (ergs cm⁻²)

	{100}				{110}	
	(Theoretical)		(Experimental)		(Theoretical)	
LiF	414 ¹	169 ²	340 ³	480 ⁴	1120 ¹	832 ²
NaCl	151 ¹	188 ²	276 ³	300 ⁵ 340 ⁶	403 ¹	445 ²
NaBr	127 ¹	177 ²	119 ³		343 ¹	396 ²
KCl	108 ¹	163 ²	252 ³	110 ⁷	292 ¹	352 ²

¹ Born-Stern Formula

² van Zeggeren and Benson (1957)

³ Gilman (1960)

⁴ Burns and Webb (1970)

⁵ Balk and Benson (1959)

⁶ Gutshell and Gross (1965)

⁷ Westwood and Hitch (1963)

Table 3.2

Typical Preparation Sequences

	<u>Section</u>	<u>Pre-thin</u>	<u>Polish</u>
LiF	H ₂ O	H ₃ PO ₄ , PrOH, ether	H ₂ O, acetone
NaCl	MeOH	H ₂ O/HCl, PrOH, ether	MeOH, ether
KCl	MeOH	H ₂ O/HCl, PrOH, ether	MeOH, ether
KBr	MeOH	H ₂ O/EtOH, PrOH, ether	EtOH, ether
KI	EtOH	MeOH, PrOH, ether	EtOH, ether
NaBr	EtOH	MeOH, PrOH, ether	EtOH, ether

Table 3.3

Polishing Solvents

Solubilities indicated are in $\text{cm}^3/100 \text{ cm}^3$ solvent; preferred range for dish polishing is between 0.2 and $1.5 \text{ cm}^3/100 \text{ cm}^3$

<u>H₂O</u>	<u>EtOH</u>	<u>i-Am OH</u>
LiF 0.10	NaBr 1.52	LiCl 5.64
NaF 1.51	KBr 0.07	NaI 5.37
	RbBr 0.40	
<u>MeOH</u>	KI 0.94	<u>Acetone</u>
NaF 0.20	RbI 0.38	LiCl 5.03
KF 0.10	CsI 0.70	LiBr 8.40
NaCl 0.81		LiI 12.1
KCl 0.40	<u>n-PrOH</u>	NaI 10.0
RbCl 0.68	KI 0.19	RbI 0.24
KBr 1.05	NaBr 0.21	CsI 0.48
CsBr 0.66	RbI 0.08	
RbI 4.10		
CsI 3.24		

Table 3.4

Electron Diffraction Parameters

g	NaCl (20K)			g	NaBr (20K)		
	$F_g^\dagger$	$V_g^\P$	$\xi_g^\dagger$		$F_g^\dagger$	$V_g^\P$	$\xi_g^\dagger$
000	31.56	8.42	404	000	41.88	9.41	361
111	-5.47	-1.46	2330	111	-11.53	-2.59	1312
200	19.74	5.27	645	200	26.12	5.87	579
220	14.58	3.89	874	220	19.29	4.34	784
222	11.59	3.09	1099	222	15.38	3.46	983
311	-3.66	-0.98	3481	311	-7.41	-1.67	2040
331	-2.09	-0.56	6093	331	-4.83	-1.08	3132
333	-1.35	-0.36	9425	333	-3.48	-0.78	4349
400	9.58	2.56	1329	400	12.75	2.87	1186
420	8.15	2.17	1563	420	10.85	2.44	1394
422	7.08	1.89	1798	422	9.42	2.12	1606

† in Angstrom units

‡ in volts

Table 3.4 (contd)

KCl (20K)				KBr (20K)			
g	F _g [†]	V _g [¶]	ξ _g [†]	g	F _g [†]	V _g [¶]	ξ _g [†]
000	40.78	7.83	434	000	51.10	8.52	399
111	3.05	0.59	5806	111	-3.61	-0.60	5641
200	27.34	5.25	647	200	35.54	5.93	573
220	20.28	0.89	873	220	27.56	4.60	739
222	15.85	3.04	1116	222	22.62	3.77	901
311	0.67	0.13	26480	311	-3.84	-0.64	5308
331	0.73	0.14	24153	331	-2.76	-0.46	7372
333	0.70	0.14	25149	333	-2.19	-0.36	9319
400	12.78	2.46	1384	400	19.17	3.20	1063
420	10.54	2.02	1679	420	16.59	2.77	1228
422	8.84	1.70	2002	422	10.68	2.43	1396

† in Angstrom units

¶ in volts

Table 3.4 (contd)

g	KI (20K)					ξ_g^i / ξ_g
	$F_g^\dagger$	$V_g^\ddagger$	$\xi_g^\dagger$	$V_g^i \ddagger$	$\xi_g^{i\dagger}$	
000	68.98	9.36	363	0.573*	5940*	16.4
111	-14.36	-1.95	1744	-0.207	16411	9.4
200	46.81	6.35	535	0.276	12303	23.0
220	35.72	4.85	701	0.260	13039	18.6
222	28.97	5.93	865	0.240	14178	16.4
311	-10.15	-1.38	2467	-0.183	18552	7.5
331	-7.13	-0.97	3513	-0.178	19144	5.5
333	-5.43	-0.74	4612	-0.171	19878	4.3
400	24.28	3.30	1031	0.234	14543	14.1
420	20.78	2.82	1205	0.228	14904	12.4
422	18.07	2.45	1386	0.223	15232	11.0

† in Angstrom units

* adjusted to fit experimental data

‡ in volts

Table 3.5

Response of Photographic Emulsions to Fast Electrons

Values represent electron exposure for a specular optical density $D = 1.0$. Emulsions were all developed in Ilford PQ developer 1:4, except HP4 (microphen) and XM (D 19 B).

Emulsion	Exposure (electrons μm^{-2})
N60 Photomechanical	3.0
N50 Thin Film Half Tone	2.2
EM4	1.0
N40 Process	0.8
Special Lantern, Contrasty	0.7
HP4	0.5
LN	0.14
XK	0.09
XM	0.07

Table 3.6

Electron Beam Parameters

Values are for approximately focussed illumination, Condensor 1 adjusted for 5 μm diameter spot size.

Condensor 2 aperture (μm)	ϕ_i (rad)	j_i , min (A cm^{-2})	j_i , max (A cm^{-2})
400	3.2×10^{-3}	1.6×10^{-2}	1
200	1.6×10^{-3}	4×10^{-3}	2.4×10^{-1}
100	0.8×10^{-3}	1×10^{-3}	6×10^{-2}
50	0.4×10^{-3}	2.5×10^{-4}	1.5×10^{-2}

Fig. 3.1. Cleavage geometry used in the cleavage analysis of §3.2.1. A moving reference frame is utilised with $x = 0$ at the crack tip and $x = L$ at the opened end in a crystal of width w . The entering wedge is assumed to produce equal forces F acting on cleavage arms of thickness p_1 and p_2 displacing them respectively distances y_1 and y_2 relative to the cleavage plane.

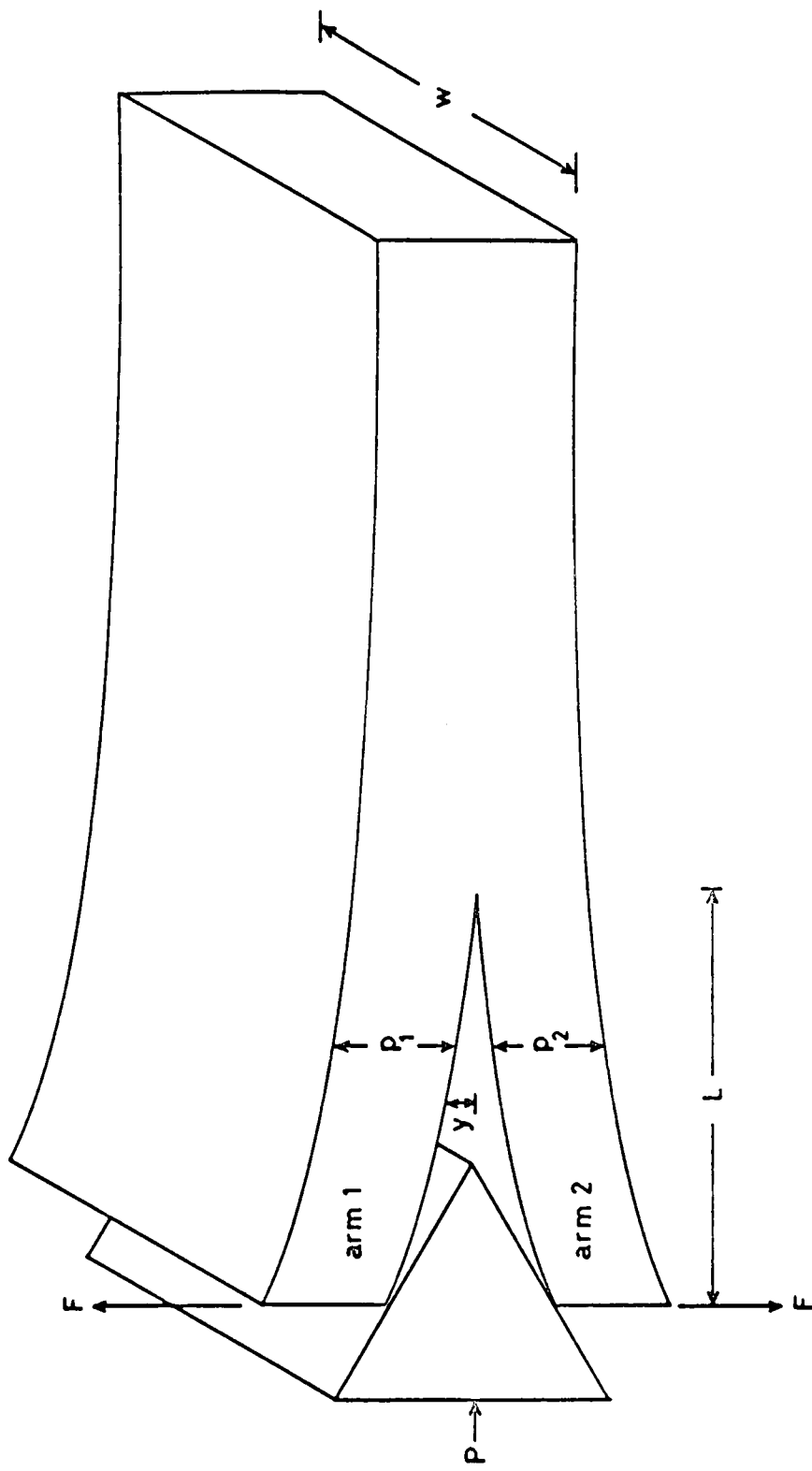
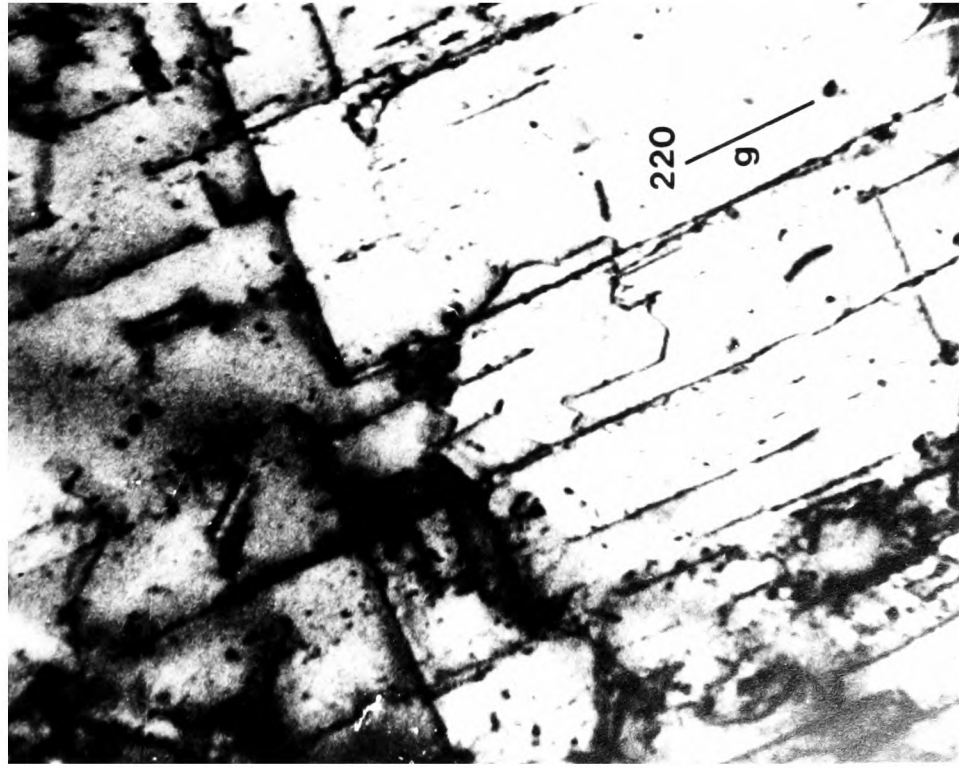


Fig. 3.2. Bending deformation characteristic of cleavage in foils of (a) KCl and (b) NaCl thinned from 0.5 mm sections cleaved from bulk crystal. The predominant feature is long arrays of screw dislocations and screw dipoles. In regions, the dislocation density approaches 10^9 cm cm^{-3} . These foils were examined at 10 K using techniques described in §5.4.



A



B

Fig. 3.3. The chemical string saw described in §3.2.2. A reciprocating cutting string S is drip fed from capillary tubes F with solvent from bottle B. A rotating arm A provides simple harmonic reciprocation of the string which rides over precision ball-race pulleys P and advances every rotation from spool G. A weight W provides constant string tension, while the counterbalance system C maintains the specimen in contact with the string.

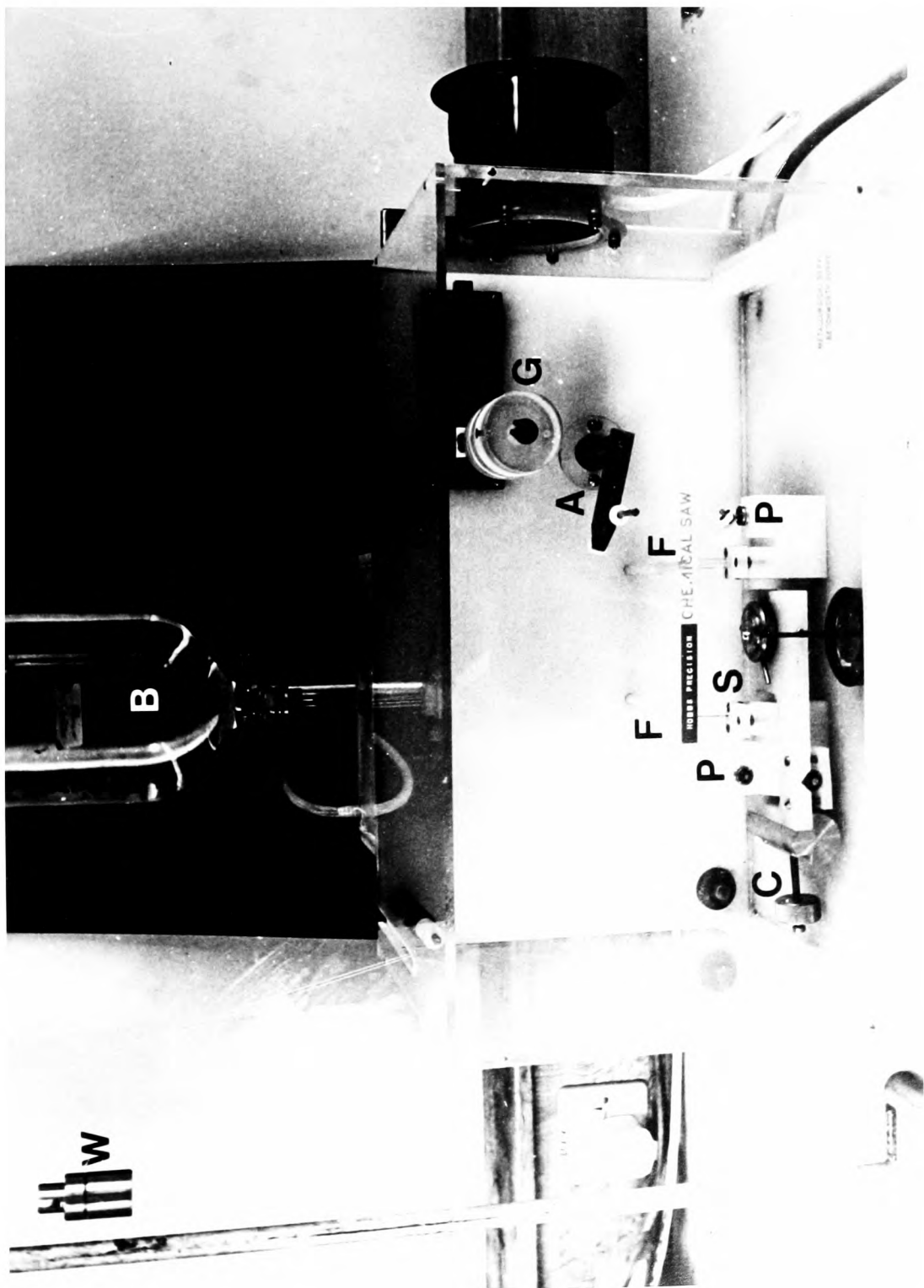
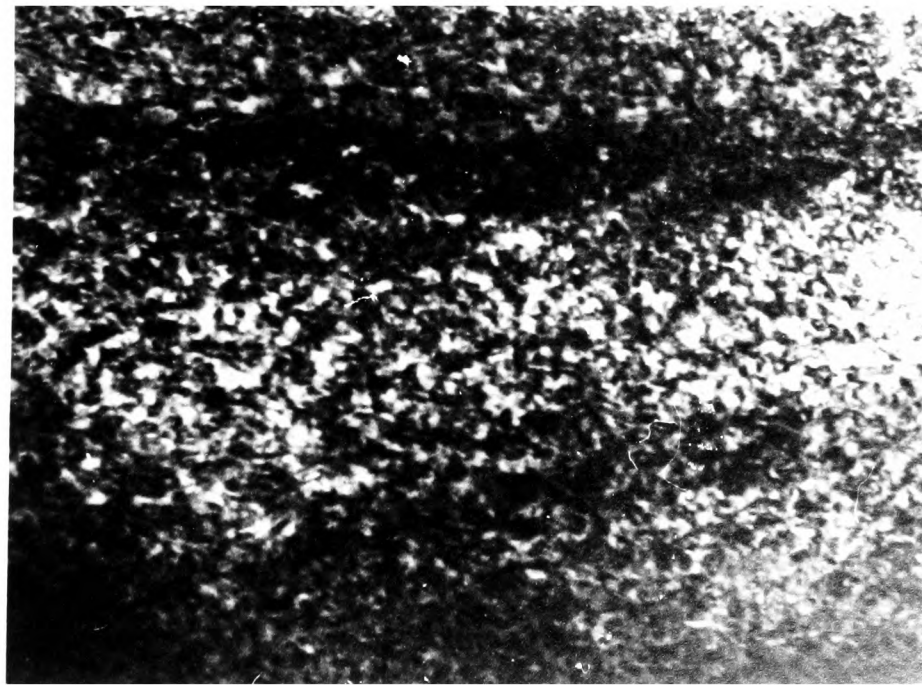


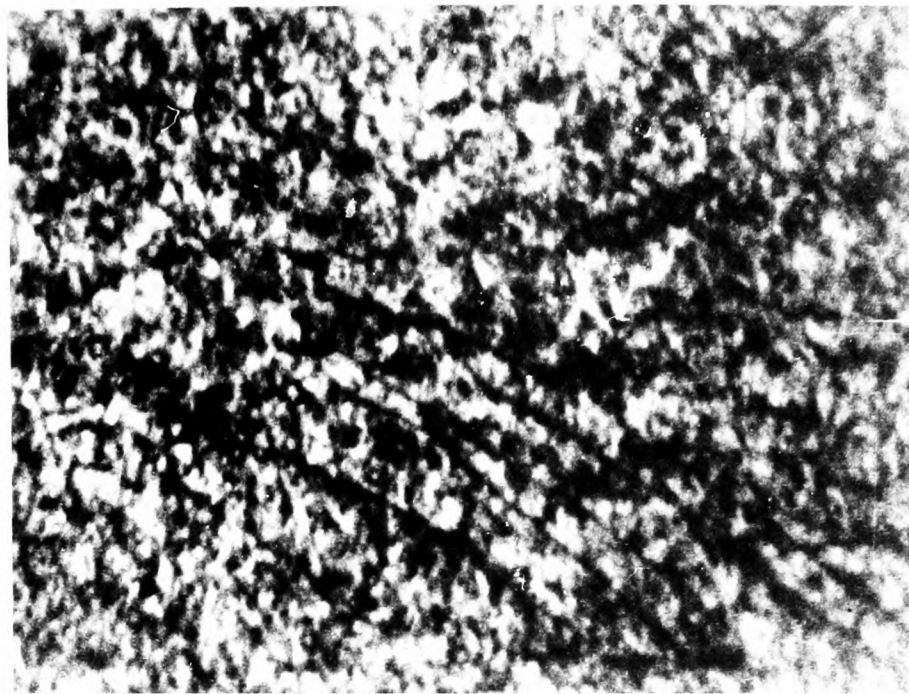
Fig. 3.4. Ion beam thinning damage in a {101} foil of KCl bombarded with 6 KeV argon ions.

(a) Wedge shaped foil region indicating that, at least in thin regions, the projected damage density increases as the foil thickness increases.

(b) Dislocations appearing beneath the ion damage, presumably in a central unaffected foil layer.



A



B

100nm

Fig. 3.5. The principal of dish polishing. Polishing solution is forced through a small jet and produces a dished dissolution profile in the specimen. Note that the profile produced is considerably larger than the initial jet diameter. Thin regions around the circumference of the hole eventually produced in the specimen are utilised for microscopy.

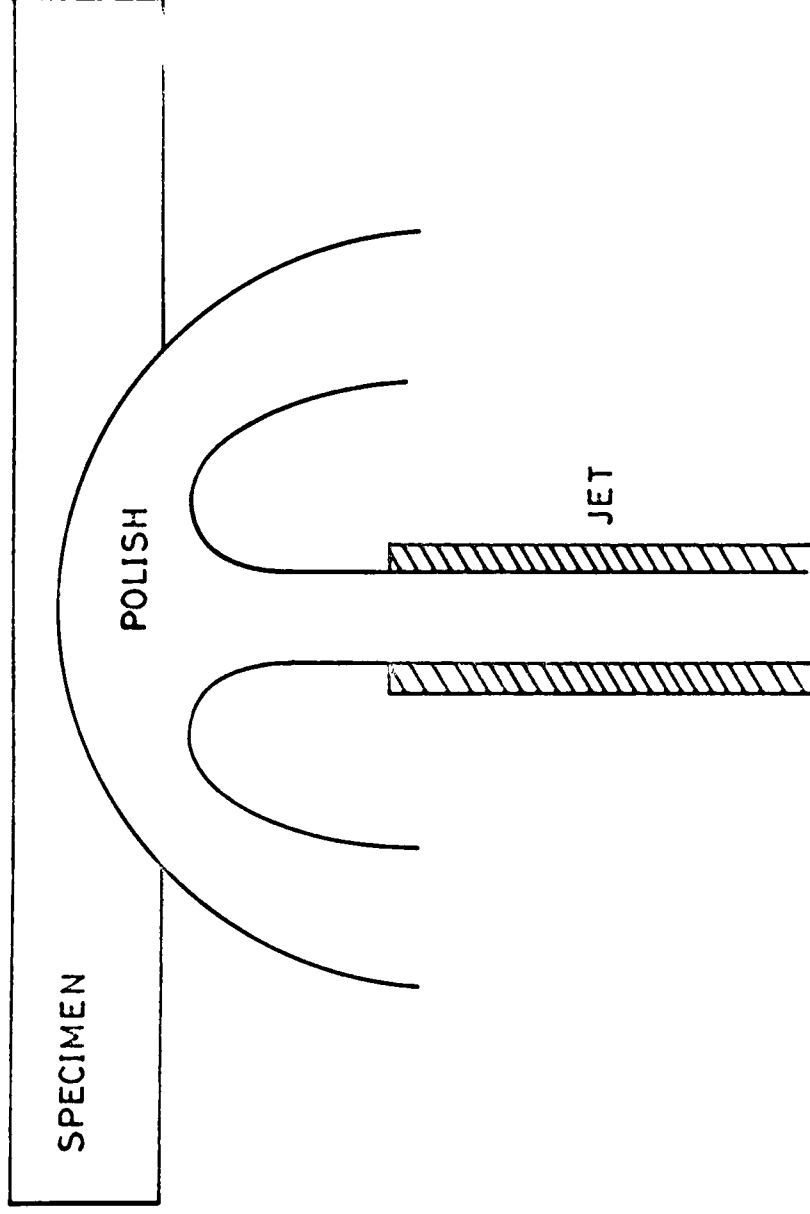


Fig. 3.6. Essential features of the dish polishing apparatus. Concentric hypodermic needles are used for polishing and washing jets, and are mounted in glass discs so that light can be transmitted through the assembly to the specimen. All seals are PTFE.

PTFE
RETAINING RING

WASH JET
COVER GLASS WINDOW

SCREW-ON CAP

PTFE SEAL

POLISH JET
GLASS WINDOW
SCREW-IN
CARTRIDGE

WASH INLET
POLISH INLET
> MOUNTING GROOVES
(for micrometre stage)
COVER GLASS WINDOW

EXPLODED

STEREO
BINOCULAR MICROSCOPE

ROTATING
BELT-DRIVE PULLEY

PIVOTED ARM
(with ball bearing race)

ADJUSTABLE SEATING
SPECIMEN CARTRIDGE

CO-AXIAL JETS

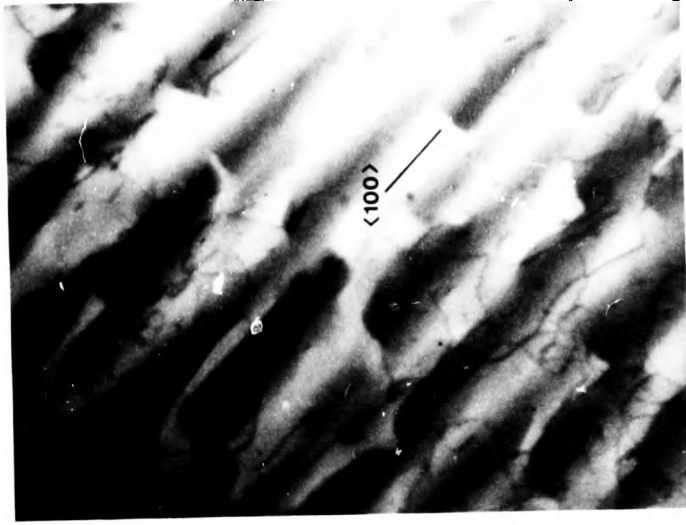
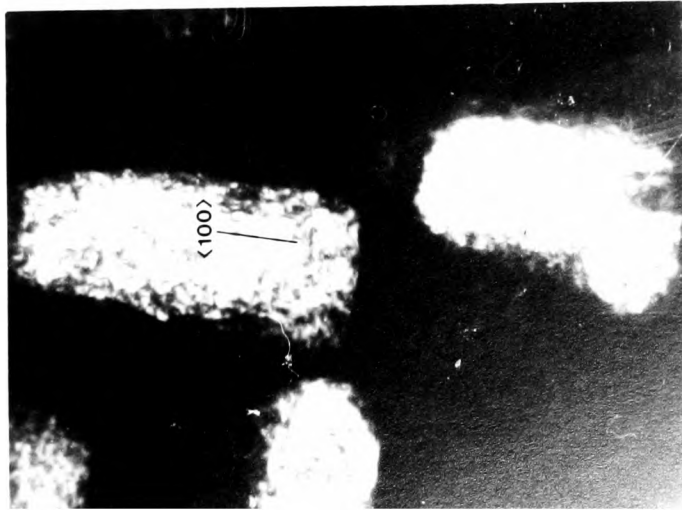
LIGHT
ASSEMBLED

Fig. 3.7. Specific problems in polishing alkali halide foils for electron microscopy.

(a) Cubic etching in an (001) KCl foil dish polished in atmosphere, due to condensation of atmospheric moisture following washing solvent evaporation. Polishing in dry inert atmosphere with dry solvents prevents moisture condensation.

(b) Etching and recrystallisation in a (101) NaBr foil dish polished and dried in inert atmosphere but exposed to normal atmosphere for 15 sec prior to examination in the electron microscope. Transfer in vacuum to the microscope eliminates such atmospheric attack in hygroscopic alkali halides.

(c) Selective etching along $\langle 010 \rangle$ in a (101) foil of KCl where polishing was allowed to proceed statically on one foil surface. Dynamic polishing leads to more uniform dissolution.



C

B

A

Fig. 3.8. Inert atmosphere chamber housing the dish polishing head illustrated in Fig. 3.6. The stainless steel block houses the 100 w quartz-iodine illumination source, providing a large thermal sink for the heat produced, and also serves as a catch basin for polishing and washing fluids which subsequently drain into a liquid nitrogen-cooled trap below. The specimen cartridge mounts in the belt-driven ball-race which can be positioned and rotated above the polishing jets by a drive external to the chamber. The opening of the vacuum transfer lock appears at left. A glass shield can be swung over the polishing jets during initial adjustments to prevent obscuring the observation port.

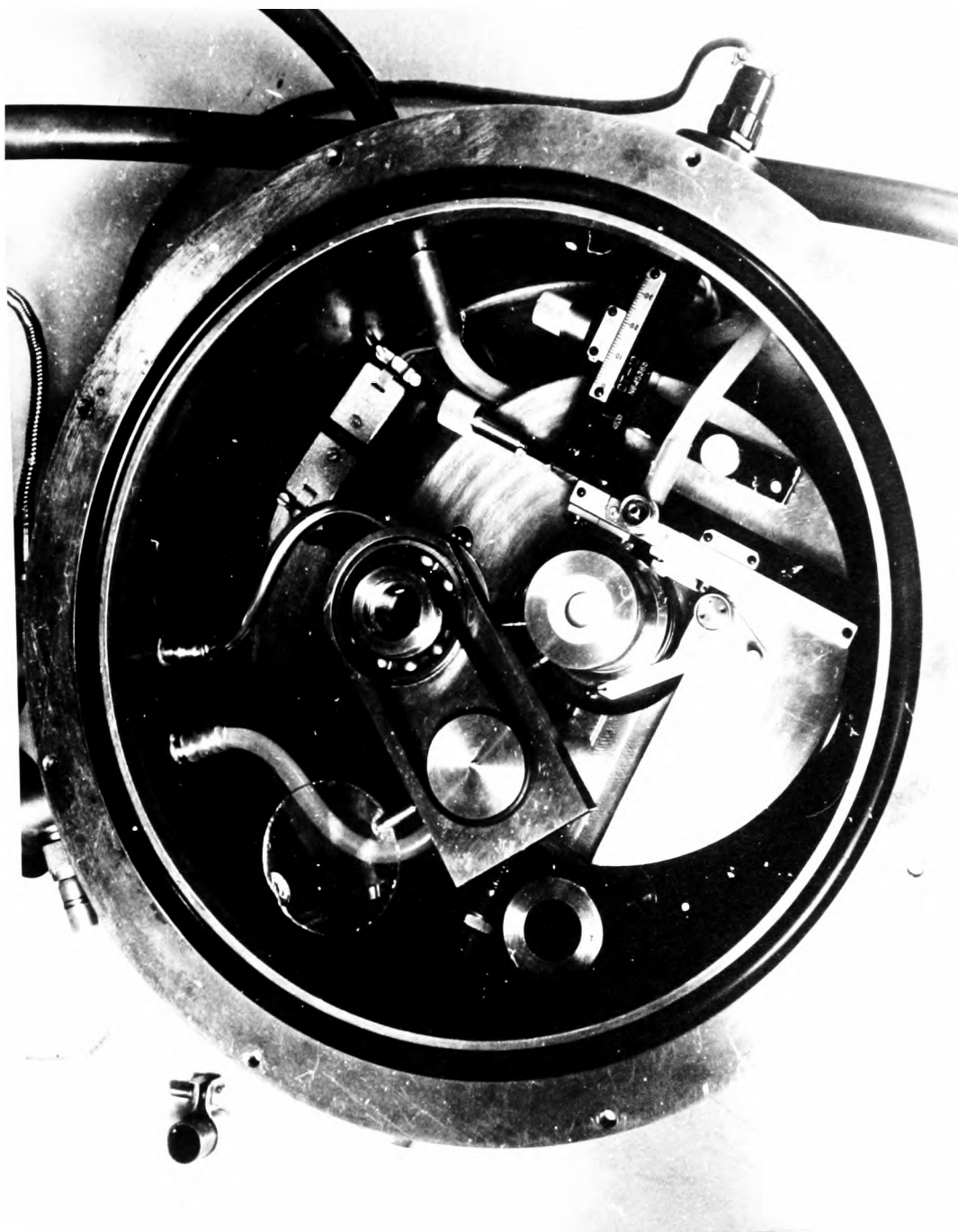


Fig. 3.9. Assembled polishing equipment. A binocular viewing microscope can be seen mounted above the polishing chamber, as well as the rod for loading the specimen cartridge into the vacuum transfer lock below. Several dried polish and wash solvents are available in the bottles above. A dewar below cools the liquid nitrogen trap. The rotary pump evacuates the chamber, and dry helium gas for purging is available from the gas cylinder and drying tube. The control unit supplies power to the quartz-iodine lamp and the solenoid valves in polish and wash lines. Needle valves behind the chamber control polish and wash flow and polish dilution.

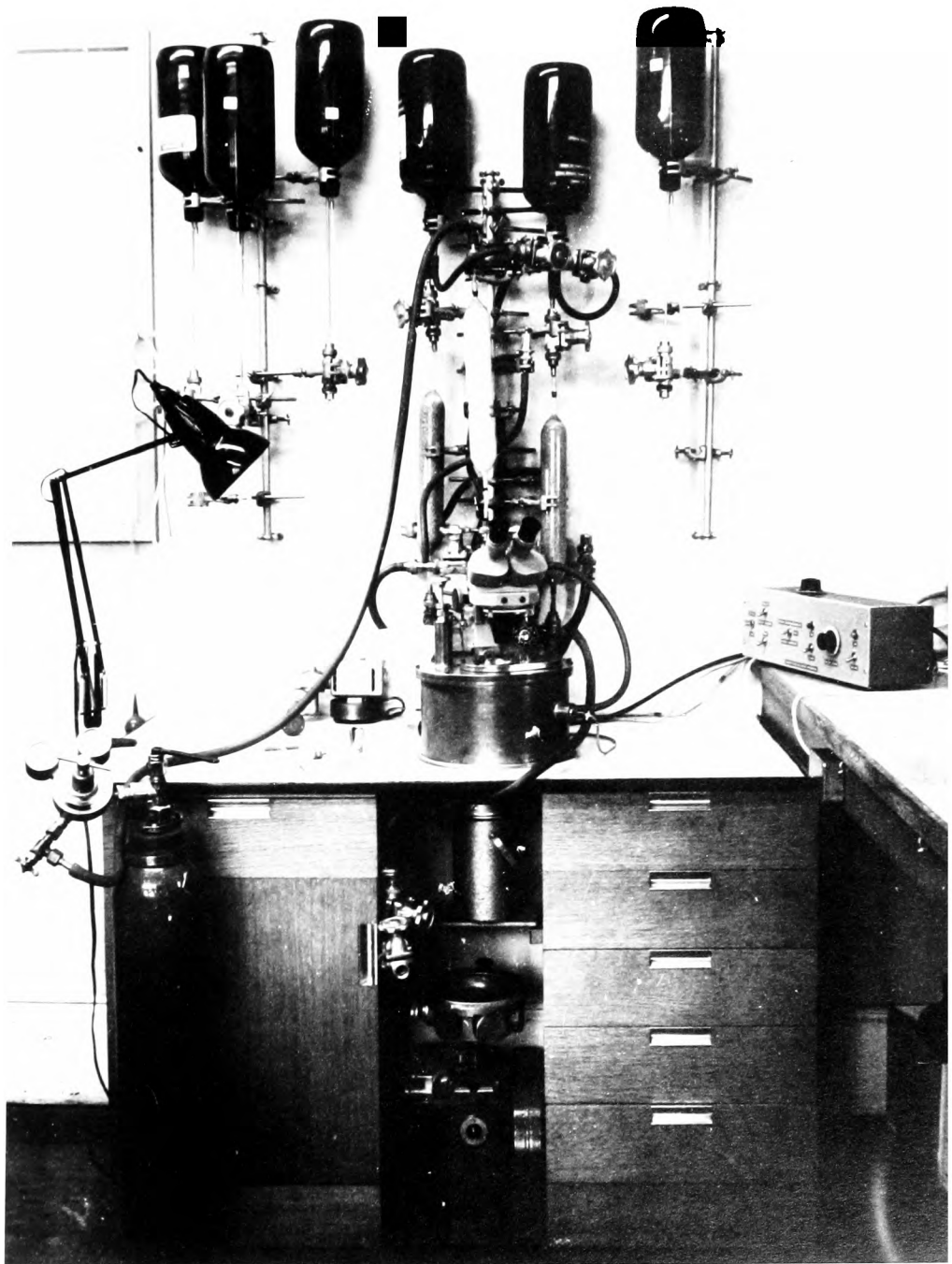


Fig. 3.10. Disassembled and assembled vacuum transfer lock. The specimen cartridge, attached by a pivoted yoke to a sliding plug is loaded through the open end of the long sliding tube. A cut out in the latter allows the cartridge to pivot into the microscope chamber when the sliding tube is pushed through the lock. The spring-loaded shell enclosing the sliding plug attached to the specimen cartridge steadies the yoke when this is being initially screwed into the specimen cartridge. During loading the sliding plug and cartridge slide out of the shell into the sliding tube. Knurled knobs provide independent rotation of both tube and specimen cartridge, while a collet at the end of the lock body enables sliding tube to be locked in any position.

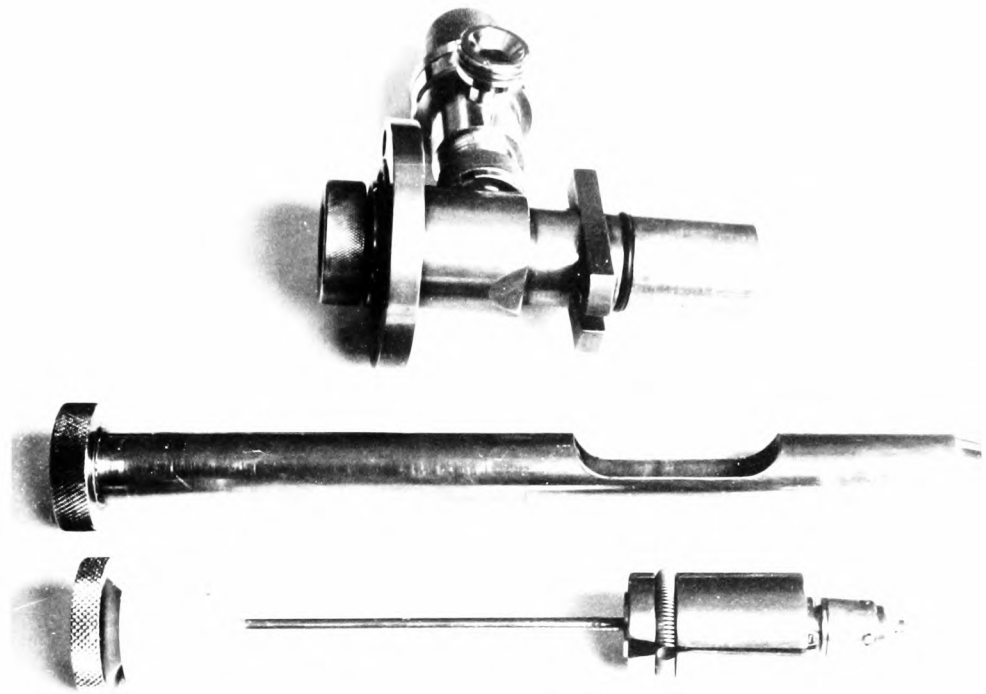


Fig. 3.11. Electric field distribution external to an irradiated specimen area situated $50\text{ }\mu\text{m}$ off the symmetry axis expressed in volt cm^{-1} as a multiple of the specimen charging potential V_0 . Note that a substantial field $\sim 100 V_0\text{ v cm}^{-1}$ still exists $10\text{ }\mu\text{m}$ above (or below) the specimen.

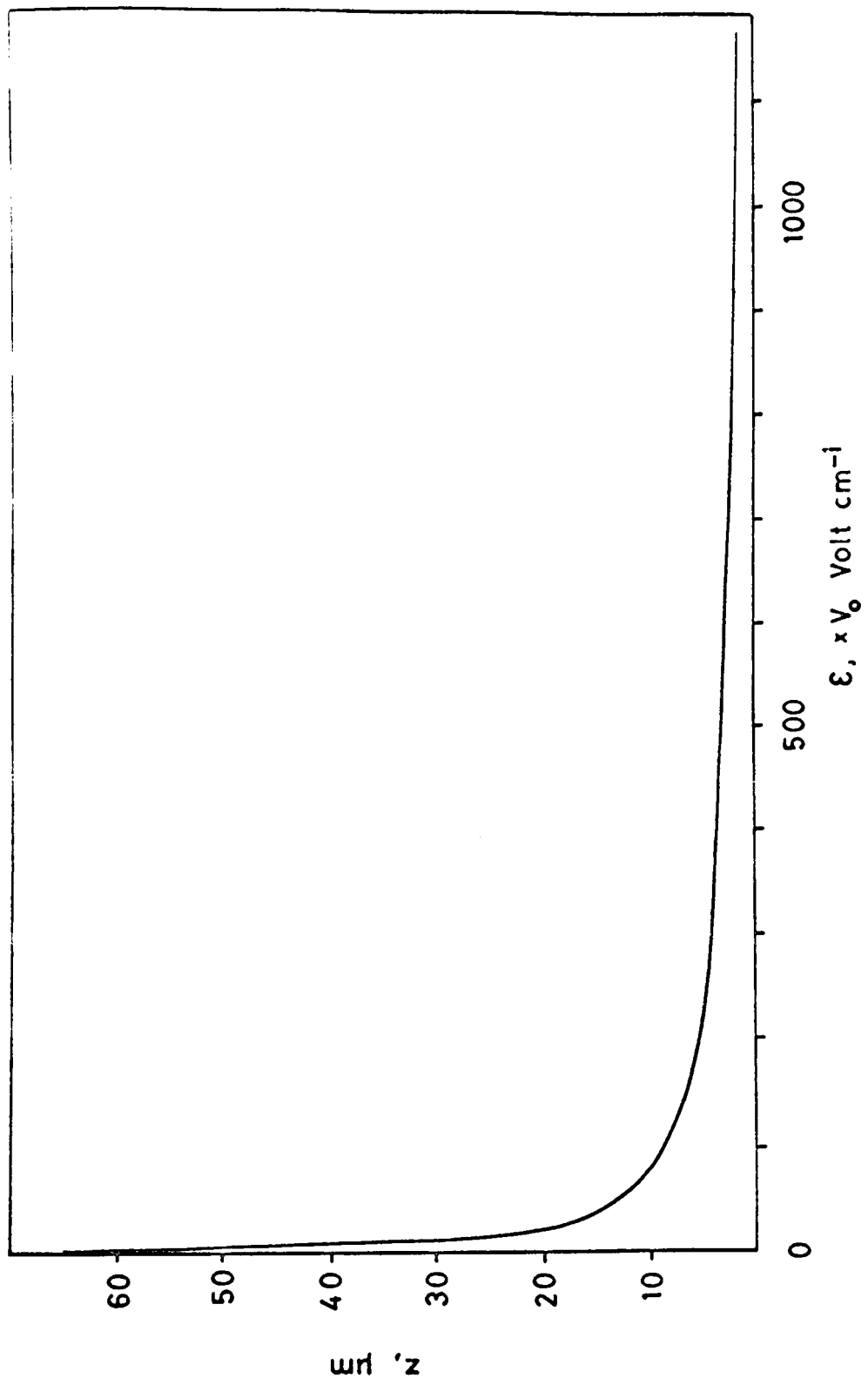


Fig. 3.12. Evaporation chamber used for depositing a thin layer of aluminium onto a polished specimen foil to prevent charging effects. The specimen cartridge containing the foil loads via the vacuum transfer lock of fig. 3.10 into the central cone positioned above a tungsten hairpin evaporation filament. A shutter is controlled externally. Viewing ports are incorporated at the top and sides of the chamber. A square glass cover slip can be seen interposed between the filament and the side viewing port to monitor deposition rate. The evaporation assembly easily removes from the chamber for filament renewal.

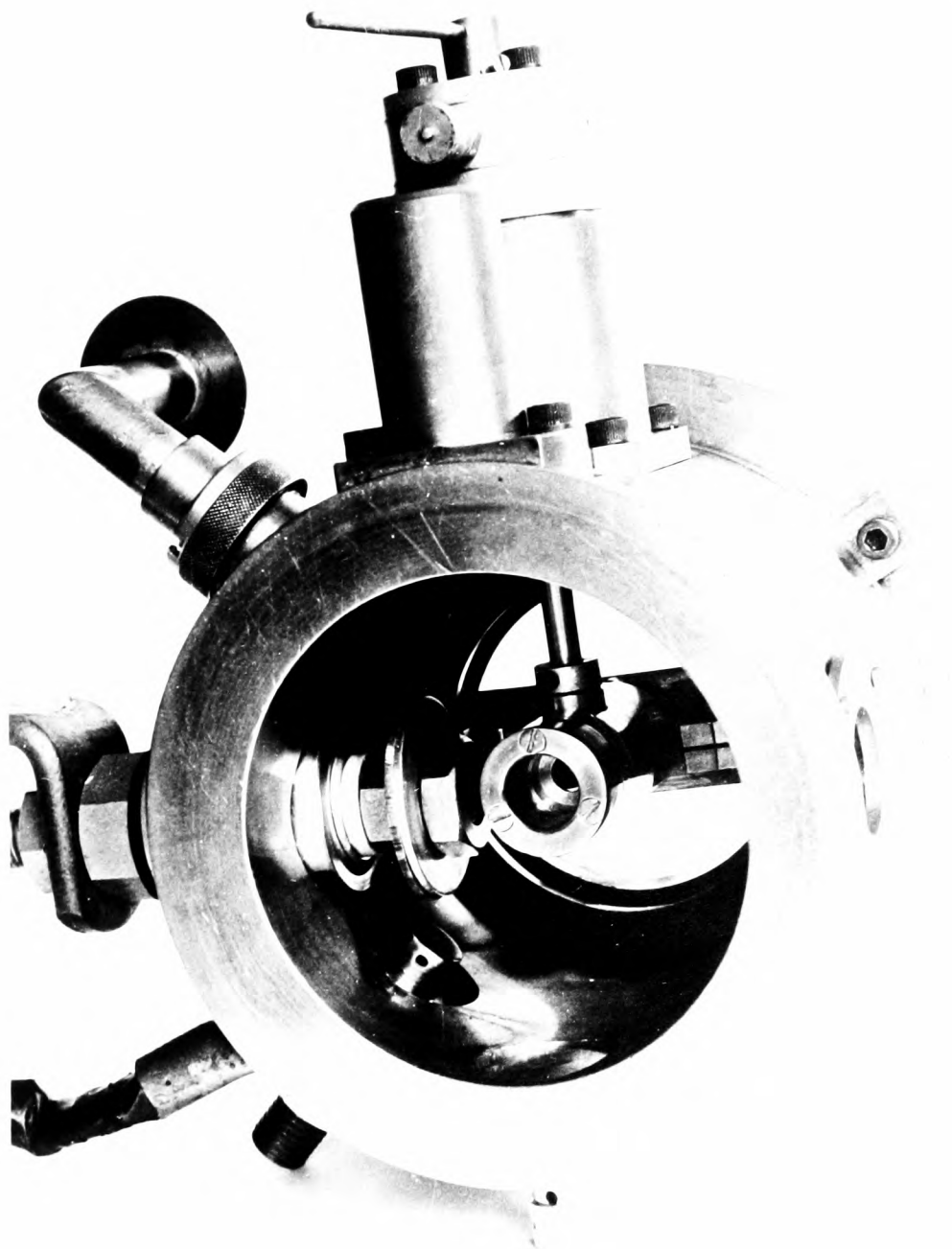


Fig. 3.13. Dispersion surface and Ewald sphere constructions used in the electron diffraction treatment, §3.6. The first two dispersion surfaces are illustrated, as well as the definitions of $\gamma^{(i)}$ and s_g .

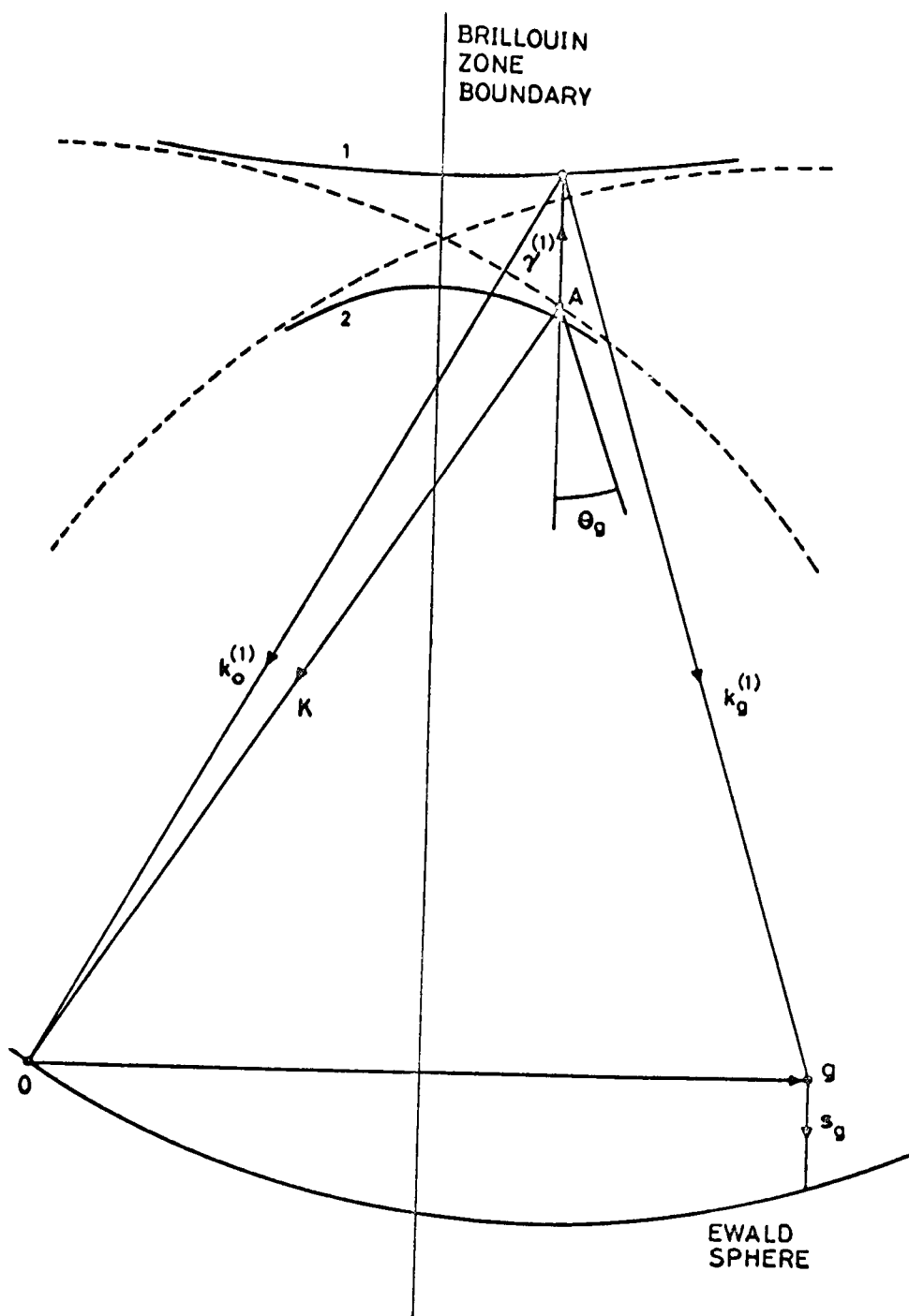


Fig. 3.14. Computed Bloch wave behaviour for the 111 systematic row in KI at 20 K, illustrating dispersion surfaces $\gamma^{(i)}$, excitations $C_0^{(i)}$ and absorptions $q^{(i)}$. For 111 excitation, Bloch waves 1 and 2 are principally involved; for 222 excitation, waves 2 and 3 are principally involved. The chief difference between 111 and 222 orientations is the large absorption of Bloch wave 1 for the 111 case. This absorption also minimises its subsequent effect in the 222 orientation.

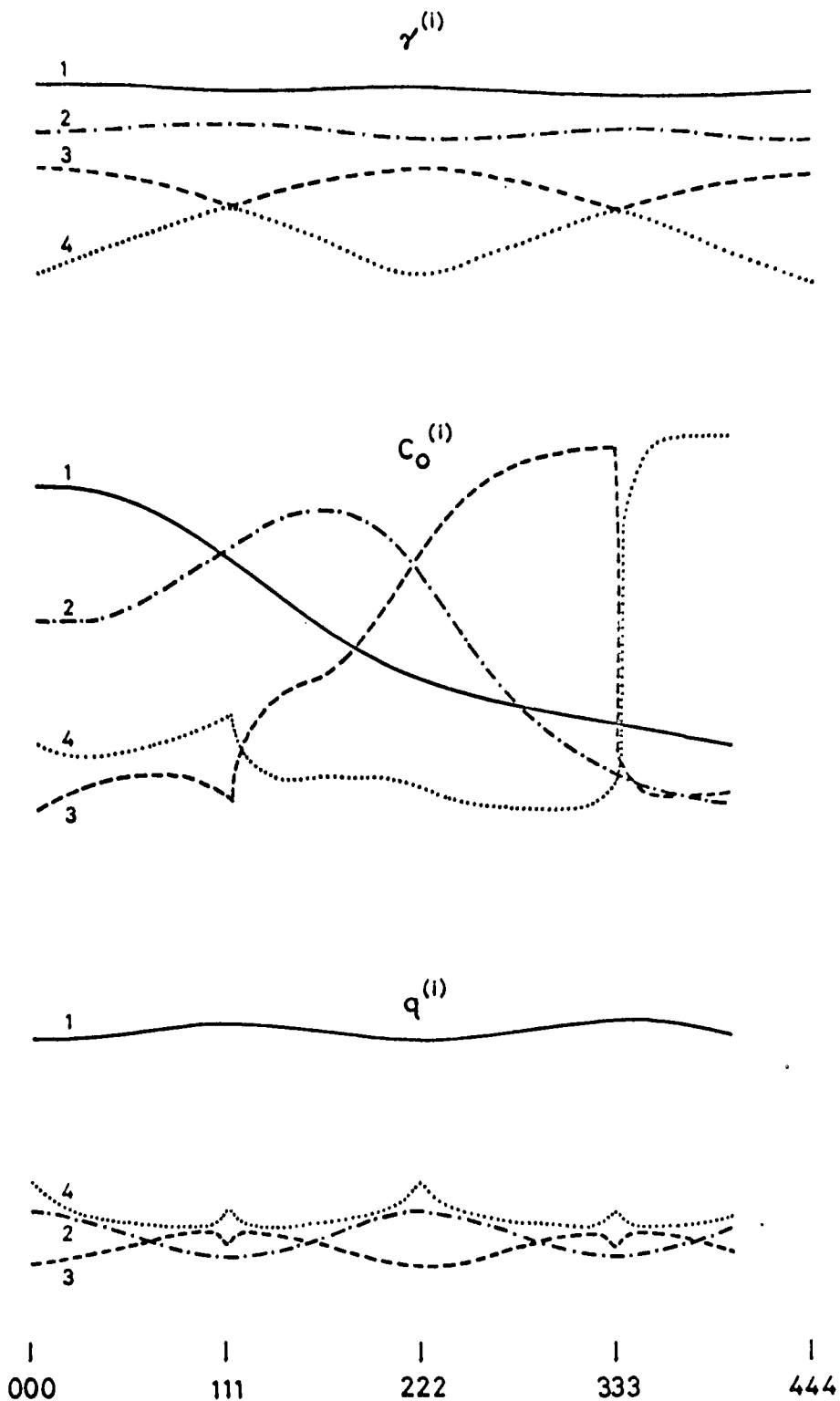


Fig. 3.15. Computed 13-beam rocking curves for the 111 systematic row in a 400 nm thick KI foil at 20 K. Bright field, broken line; dark field, dotted line. Note that 111 bright field conditions yield less intensity than 222 bright field conditions. Maximum transmitted intensity occurs for the 222 orientation with $w_g \sim 0.7$.

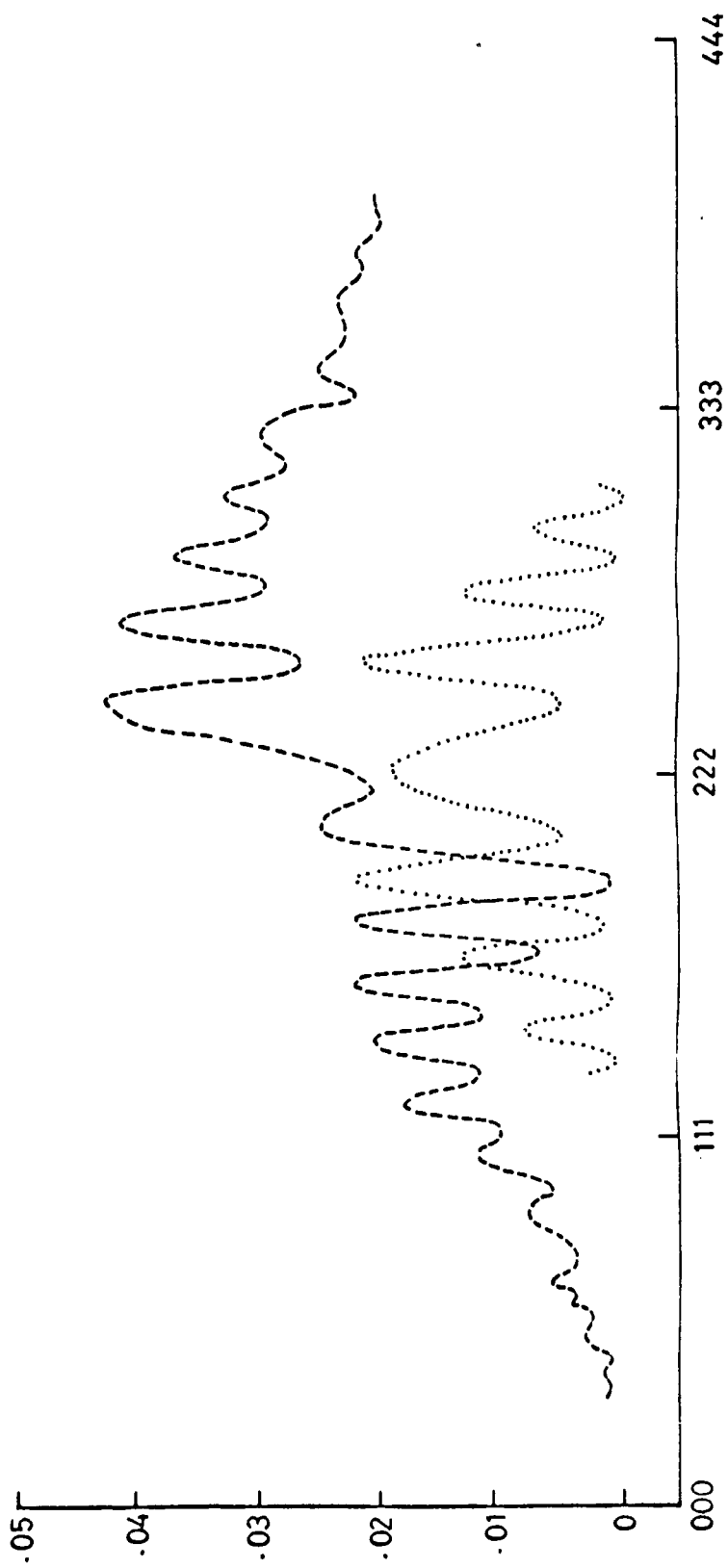


Fig. 3.16. Computed 13-beam bright field rocking curve for the 200 systematic row in a 400 nm-thick KI foil at 20 K. Maximum transmitted intensity occurs for 200 with $w_g \sim 1.4$. Relative insensitivity to orientation beyond 200 arises because Bloch waves 2 and 3 have nearly equal absorptions.

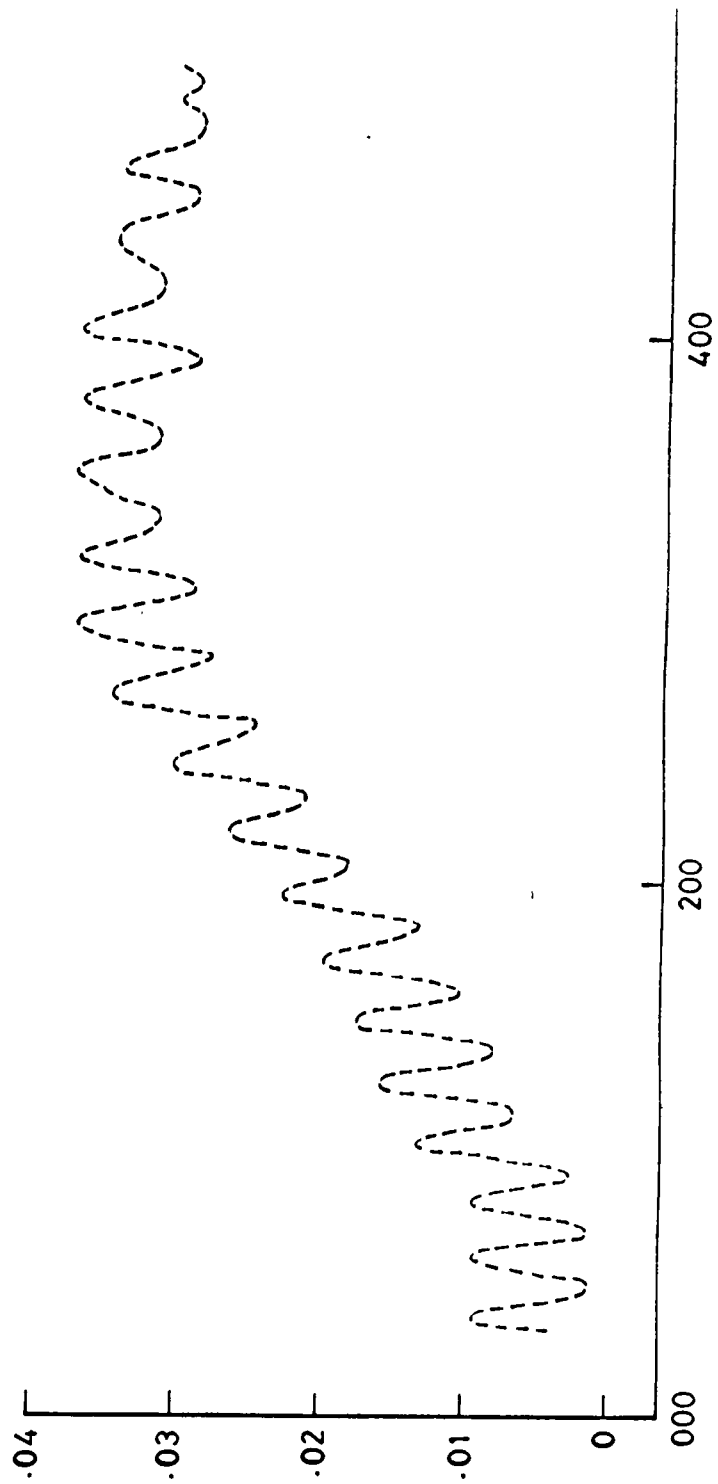


Fig. 3.17. Computed 9-beam bright field rocking curve for the 220 systematic row in a 400 nm-thick KI foil at 20 K. Maximum transmitted intensity occurs for 220 with $w_g \sim 1.4$.

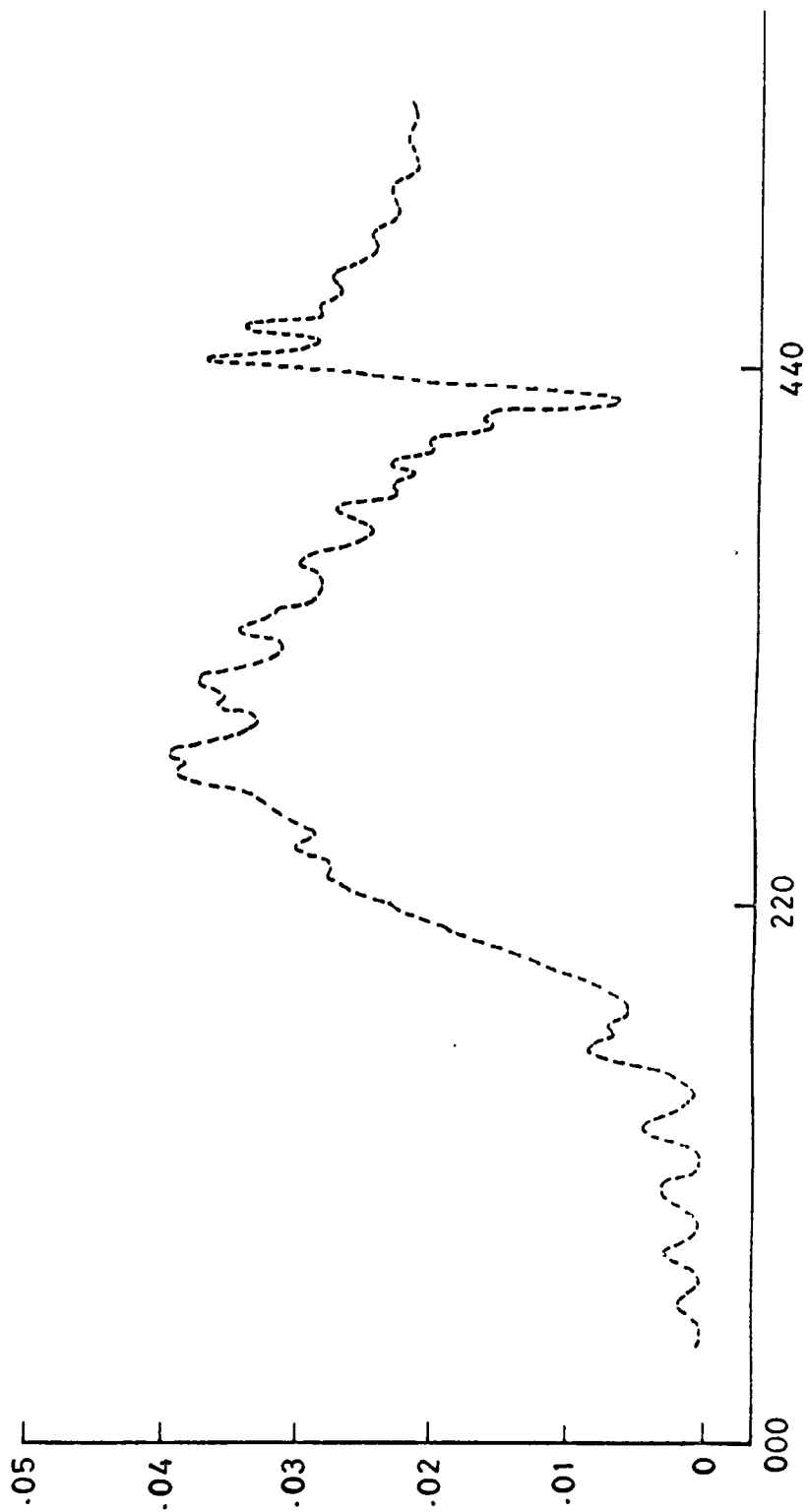


Fig. 3.18. Computed 9-beam bright field rocking curve for the 311 systematic row in a 400 nm-thick KI foil at 20 K. Well defined two-beam conditions are obtainable for 311, with an acceptable maximum transmitted intensity occurring with $w_g \sim 1.8$. The sharpness of the rocking curve renders considerably more difficult maintenance of a desired orientation over large foil areas, for even relatively unbent foils, than for 200, 220 or 222 orientations.

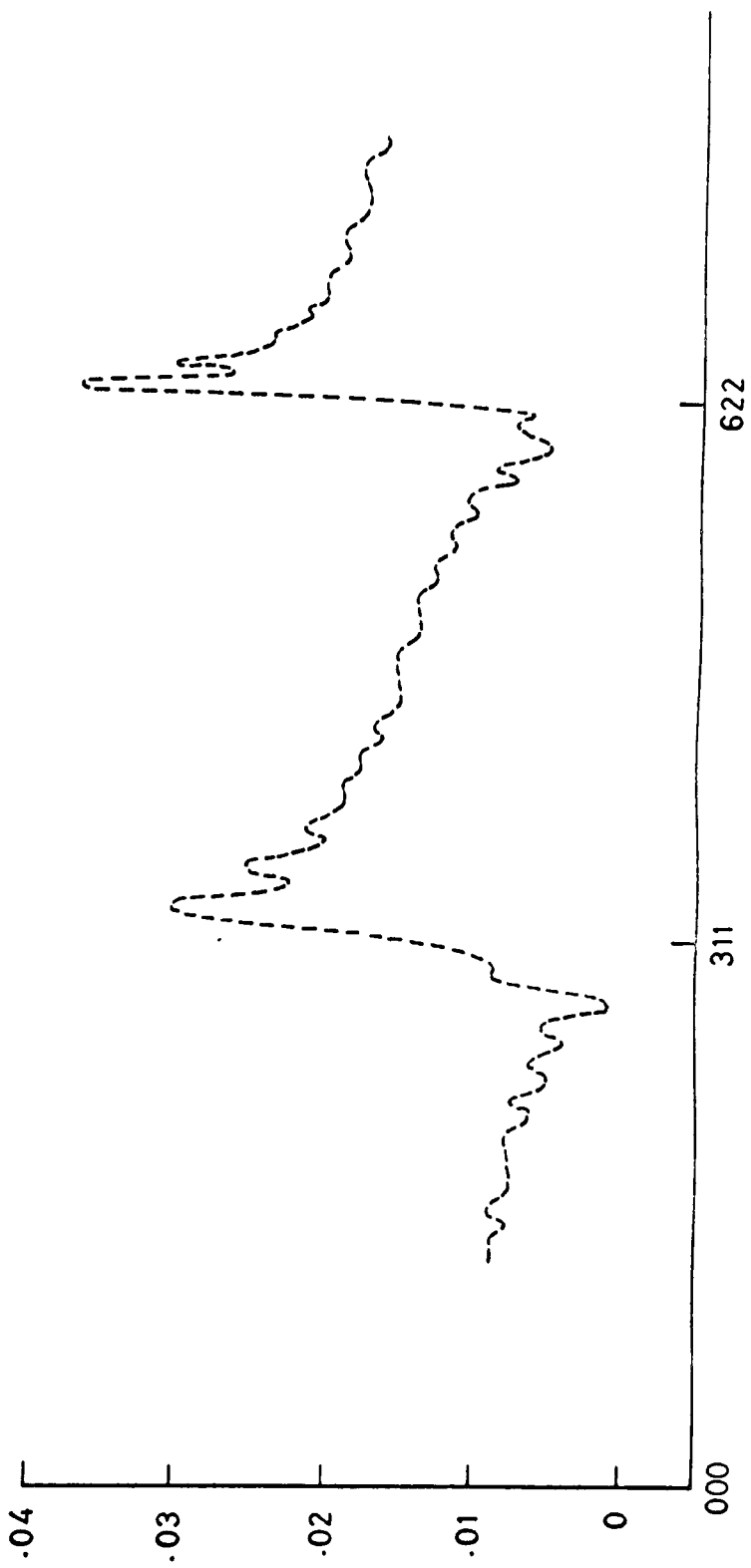
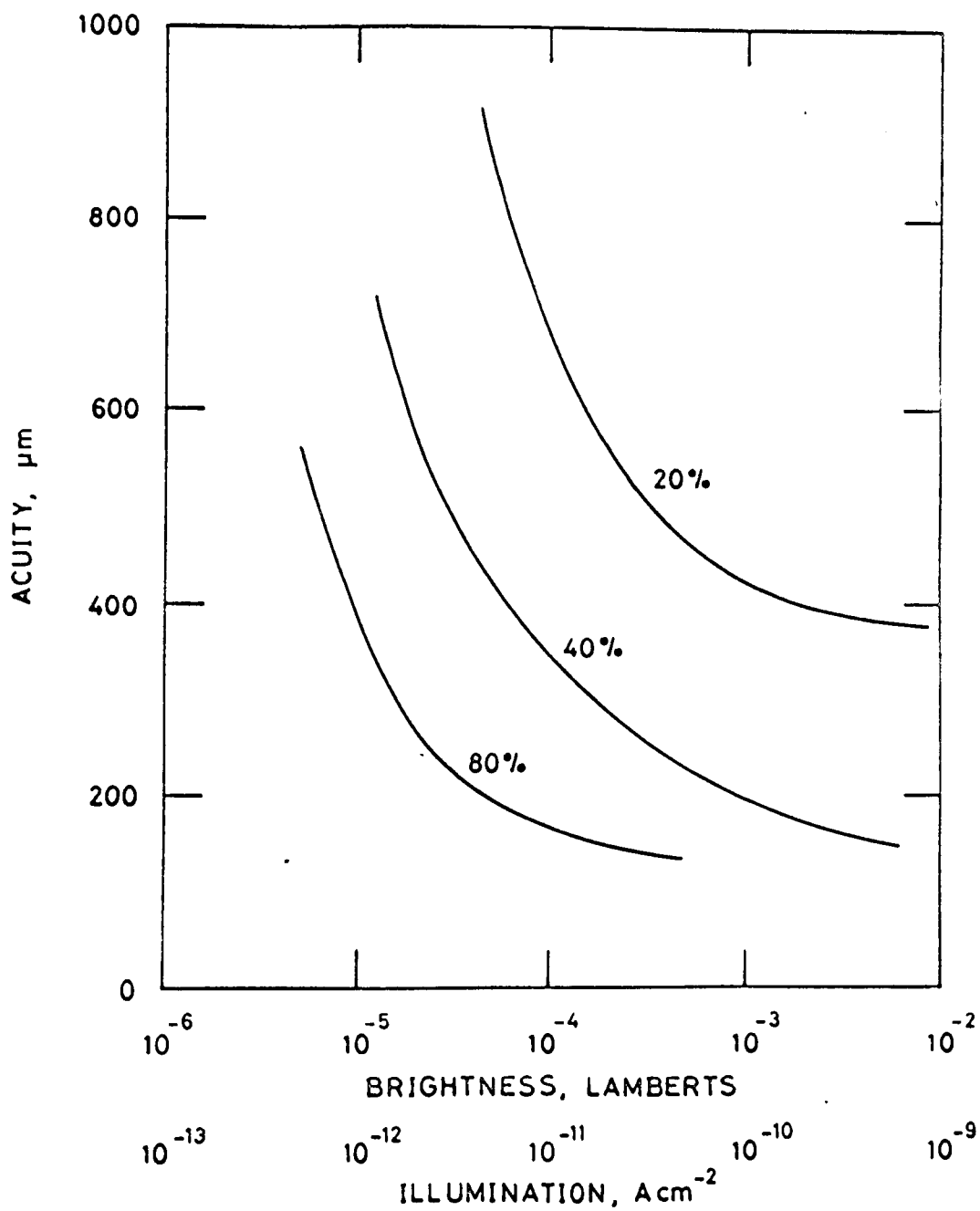


Fig. 3.19. Visual acuity as a function of scene brightness upon a phosphor screen. The limit to screen resolution at infinite brightness is $\sim 120 \mu\text{m}$ for 100 KeV electrons. 20% and 40% data are from Haine (1961). 80% data is for diffraction contrast.



§4. Electron Microscopy at Liquid Helium Temperature

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Alkali Halides

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4.1 Introduction

It was indicated in §2.5, §2.6 and §2.7 that electron microscopy at very low temperatures (~ 10 K) would have the two-fold advantage of retarding defect aggregation (thus altering saturation kinetics) in all alkali halides and reducing defect production in certain alkali halides. In this chapter we shall consider those cryogenic techniques consistent with successful low temperature microscopy and the design of stable low temperature electron microscope stages. To this end, a considerably detailed analysis will be presented of heat sources, heat transfer from cryogenic coolants, and the problems of thermal stability, contamination, resolution and adequate tilt which are encountered in low temperature microscopy. A system incorporating these design considerations will be illustrated. This system has produced eminently satisfactory results and renders low temperature microscopy little less than routine. Finally, particular problems in the specific cryomicroscopy of alkali halide crystals will be discussed.

4.2 Specimen Heating

The temperature eventually attained by a body being cooled by a heat sink at constant temperature is a function of its own thermal conductivity and the various heat inputs to the body. For a body maintained at low temperature but locally heated, we can neglect the heat reradiated from the heated region to its slightly cooler surroundings because the heat conducted from the body to the sink is invariably much greater than that reradiated. For simplicity, we

assume radial symmetry and define $\dot{h}(r)$ as the time rate of heat input per unit volume at radius r in a body of thermal conductivity κ . We then must satisfy the radial heat conduction equation

$$\frac{\partial T}{\partial t} = \frac{\kappa}{C_p \rho} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{\kappa} \dot{h}(r) \right\} \quad (4.1)$$

In the steady state we have

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{\kappa} \dot{h}(r) = 0 \quad (4.2)$$

We consider two geometries representative of those most likely to be encountered in electron microscope specimens: (1) a foil of uniform thickness p bounded by a circular sink at radius s of infinite conductivity held at a fixed temperature T_0 ; (2) the dished specimen considered in §3.2 with radius of dish curvature R , a central hole of radius s' , and bounded by a circular sink at s as in (1). We consider two specific heat inputs $\dot{h}(r)$ in (4.2).

4.2.1 Thermal radiation

The total rate of heat input $\dot{Q}$ by radiation over all wavelengths from a body of surface area A_T at temperature T to a body of surface area A_0 at T_0 is given by

$$\dot{Q} = A_T F_{T0} \sigma (T^4 - T_0^4), \quad (4.3)$$

where σ is Stefan's constant ($5.67 \times 10^{-12} \text{ J sec}^{-1} \text{ cm}^{-2} \text{ K}^{-4}$) and F_{T0} is the radiative exchange factor

$$F_{T0} = \frac{1}{f_{T0}} + \frac{A_T}{A_0} \left\{ \frac{1}{\epsilon_0} - 1 \right\} + \left\{ \frac{1}{\epsilon_T} - 1 \right\} \quad (4.4)$$

encompassing the geometry, configuration and emissivity of each body. f_{T0} is the configuration (angle) factor, and ϵ_0, ϵ_T the emissivities.

We shall suppose that $T \gg T_o$, and therefore that the rate of heat input per unit volume $\dot{h}(r)$ for our two selected specimen geometries is

$$(1) \quad \dot{h}(r) = \frac{A_T}{A_o p} F \sigma T^4 \quad s \geq r \geq 0 \quad (4.5a)$$

$$(2) \quad \dot{h}(r) = \frac{A_T}{A_o} \frac{R}{r^2} F \sigma T^4 \quad s \geq r \geq s' \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \quad (4.5b)$$

$$\dot{h}(r) = 0 \quad s' > r \geq 0 \quad \left. \begin{array}{l} \\ \\ \end{array} \right\}$$

Integrating (4.2), we find a maximum temperature rise for each geometry

$$(1) \quad T(o) - T(s) = \frac{A_T}{4\kappa p A_o} F \sigma T^4 s^2 \quad (4.6a)$$

$$(2) \quad T(s') - T(s) = \frac{A_T R}{2\kappa A_o} F \sigma T^4 \left\{ \ln \frac{s}{s'} - \frac{1}{2} \right\} \quad s \gg s' \quad (4.6b)$$

We evaluate F in each expression for two sorts of specimen enclosure.

4.2.1.1 Specimen totally enclosed by walls at temperature T

We assume a specimen area on each side $A_o = \pi s^2$ of emissivity ϵ_o . For this geometry we find that (Christensen 1883)

$$\frac{1}{F_{To}} = \frac{A_T}{2A_o \epsilon_o} + \left\{ \frac{1}{\epsilon_T} - 1 \right\}. \quad (4.7)$$

We assume the worst case, i.e. black body radiation ($\epsilon_T = 1$), and find

$$F_{To} = 2 \epsilon_o A_o / A_T \quad (4.8)$$

For a uniform disc specimen, we then have a maximum temperature rise

$$T(o) - T(s) = \frac{\epsilon_o \sigma T^4}{2\kappa} \frac{s^2}{p}; \quad (4.9a)$$

and for the dished specimen

$$T(s') - T(s) = \frac{\epsilon_0 \sigma T^4}{\kappa} R \left\{ \ln \frac{s}{s'} - \frac{1}{2} \right\} \quad s \gg s'. \quad (4.9b)$$

In the absence of any low temperature shielding, $T \sim 300K$, and if the specimen surfaces are smooth and reflect well, $\epsilon_0 \sim 0.1$.

Let us assume the disc specimen is a grid-mounted, 10 nm thick evaporated carbon film used as a substrate for gas solidification (for example, for temperature measurement, see §4.5.3). For a 100 mesh copper grid, $s \sim 100\mu m$; the thermal conductivity of a carbon film is $\kappa < 10 \text{ mw cm}^{-1} \text{ K}^{-1}$ at low temperatures, leading to a temperature rise $> 20 \text{ K}$ from (4.9a).

If we assume the dished specimen is an alkali halide which has good thermal conductivity $\kappa \sim 1 \text{ w cm}^{-1} \text{ K}^{-1}$ at low temperatures (Rosenbaum, Chau and Klein 1969), with $R \sim 1 \text{ cm}$, $s \sim 1 \text{ mm}$, $s' \sim 10 \mu m$ (foil thickness $\sim 10 \text{ nm}$ at s'), we have a maximum temperature rise 20 mK . If the specimen totally absorbed all incident radiation the rise would be only 0.2 K .

Clearly, then, a carbon film or materials of poor thermal conductivity are not suitable as low temperature substrates unless some sort of thermal shielding is provided. However, even thermal shielding appears unnecessary for dished specimens of relatively good thermal conductivity at low temperatures such as metals and alkali halides.

4.2.1.2 Partially shielded specimen

We next reduce radiative heat input with a shield at sink

temperature $T(s)$. In general, if we are to maintain an adequately large specimen area for examination, a much smaller solid angle for shielding can be realised above the specimen than below it, due to the short focal length of the objective lens below the specimen and the relatively much longer distance available for collimation above. We therefore define the solid angle for radiation from below by the three parameters u , v , and w representing respectively the radius of the exposed specimen area, the radius of the radiating area and the distance between them. Under these conditions F is given by

$$F = \frac{f(u, v, w)}{\frac{1}{\epsilon_o \epsilon_T} - \left(\frac{1}{\epsilon_o} - 1\right) \left(\frac{1}{\epsilon_T} - 1\right) \frac{\Lambda_T}{\Lambda_o}} f^2(u, v, w) \quad (4.10)$$

where $f(u, v, w)$, the solid angle factor (Keene 1913), describes the fraction of radiation emitted from surface $\Lambda_T = \pi v^2$ eventually reaching surface $\Lambda_o = \pi u^2$. Under black body conditions $\epsilon_T = 1$ (4.10) simplifies to

$$F = \epsilon_o f(u, v, w)$$

For a thin shield $\Lambda_o = \pi s^2$, and since the radiating area $\Lambda_T = \pi b^2$ and typically $u \sim v \sim s$ for a shield midway between Λ_o and Λ_T , we have for our two specimen geometries

$$(1) \quad T(o) - T(s) = \frac{\epsilon_o \sigma T^4}{2\kappa} \left\{ \frac{f}{2} \right\} \frac{s^2}{p} \quad (4.11a)$$

$$(2) \quad T(s') - T(s) = \frac{\epsilon_o \sigma T^4}{\kappa} \left\{ \frac{f}{2} \right\} R \left\{ \ln \frac{s}{s'}, -\frac{1}{2} \right\} \quad s \gg s'. \quad (4.11b)$$

(4.11) then differ from (4.9) by the factor $f/2$. For our improved geometry, $f \sim 10^{-3}$, so that a suitable shield at $T(s)$ reduces temperature rises from radiative sources to negligible proportions. A shield held at some intermediate temperature T' , $T(s) < T' < T$, will however, contribute additional heat from the shield itself at the rate given by (4.9) with T^4 replaced by $\{T' - T(s)\}^4$. A shield maintained at liquid nitrogen temperatures (77 K) will only reduce radiative heat input to a specimen at 0 K by a factor of 10 over the unshielded condition; this can still lead to temperature rises ~ 2 K for a carbon substrate.

4.2.2 Electron beam heating

Electrons of high energy penetrating a thin specimen foil lose energy by inelastic processes during their propagation through the material (see §2.4). It can, in fact, be shown that nearly every electron passing through a foil of useful thickness ($\sim$ the plasmon mean free path) has suffered at least one inelastic collision. A large proportion of the resulting energy loss is converted into heat which elevates the temperature of a specimen foil under observation. Gale and Hale (1961) and Ling (1965) have treated foil heating for both metallic and non-metallic specimens respectively, using the Thomson-Whiddington law to estimate energy losses and a Gaussian beam current distribution; while Fisher (1970) has extended the analysis to higher accelerating voltages using the relativistic Bethe-Bloch stopping power relation (Bethe 1933). We have previously chosen

the Bethe-Bloch relation to estimate energy losses in alkali halide foils (§2.4), and will apply these results together with a useful beam current density $\sim 10 \text{ mA cm}^{-2}$ to determine temperature elevation in a foil maintained either at room temperature or at low temperature.

We consider an electron beam of radius b and energy E incident near the centre of a specimen whose perimeter at radius s is firmly fixed to a sink at temperature $T(s)$. Given the relatively good thermal conductivity of alkali halides at low temperatures a single point contact at the perimeter (§3.4.3.3) is adequate provided the perimeter is considerably thicker than the central thin region.

For simplicity we approximate the Gaussian beam current distribution with a square distribution

$$\begin{aligned} j(r) &= j & r \leq b &) \\ j(r) &= 0 & r > b &) \end{aligned} \quad (4.12)$$

We define $\zeta = dE/dz$ as the energy lost per electron per unit thickness of the foil; in general ζ will be a function of foil thickness z . However, for sufficiently thin foils, we can assume E and thus ζ is constant over the foil thickness. For alkali halides $\zeta \sim 10^7 \text{ eV cm}^{-1}$; with a foil thickness $1 \mu\text{m}$, we find the error in assuming ζ constant for 100 k eV electrons amounts to only 1%. Since j is per unit area and ζ per unit thickness, we have that the rate of energy deposition per unit volume is

$$\begin{aligned} \dot{h}(r) &= j\zeta & r \leq b &) \\ \dot{h}(r) &= 0 & r > b &) \end{aligned} \quad (4.13)$$

We shall consider two specimen geometries as before. Substituting

(4.13) into (4.2) we obtain solutions for a foil of uniform thickness p ,

$$T(r) - T(s) = \frac{j\zeta b^2}{2\kappa} \ln \frac{s}{r} \quad s > r > b \quad (4.14a)$$

$$T(r) - T(b) = \frac{j\zeta b^2}{2\kappa} \left\{ \frac{b^2 - r^2}{2b^2} \right\} \quad r \leq b. \quad (4.14b)$$

The maximum temperature rise will occur in the centre of the irradiated area.

$$T(o) - T(s) = \frac{j\zeta b^2}{2\kappa} \left(\frac{1}{2} + \ln \frac{s}{b} \right) \text{ for } s \gg b \quad (4.15)$$

Gale and Hale obtain for a Gaussian distribution

$$T(o) - T(s) \approx \frac{j\zeta b^2}{2\kappa} (0.577 + 2 \ln \frac{s}{b}). \quad (4.16)$$

For a dished specimen with radius of curvature R being irradiated in an area of thickness p near the centre, we calculate

$$T(r) - T(s) \approx \frac{j\zeta b^2}{2\kappa} \left\{ \frac{b^2 + pR}{2Rp} \ln (r^2 + Rp) \right\} \quad s > r > b \quad (4.17a)$$

$$T(r) - T(b) = \frac{j\zeta b^2}{2\kappa} \left\{ \frac{b^2 - r^2}{2b^2} \right\} \quad r \leq b. \quad (4.17b)$$

The maximum temperature rise in the centre of the irradiated area is

$$\begin{aligned} T(o) - T(s) &\approx \frac{j\zeta b^2}{2\kappa} \left\{ \frac{1}{2} + \frac{b^2 + Rp}{2Rp} \ln \left(\frac{b^2 + Rp}{b^2} \right) \right\} \\ &\approx \frac{j\zeta b^2}{2\kappa} \left\{ \frac{1}{2} + \ln \frac{\sqrt{Rp}}{b} \right\} \text{ for } b^2 \ll Rp, \end{aligned} \quad (4.18)$$

which is to be compared with (4.15) or (4.16). Typically, $Rp \sim 10^{-5}$ and $b^2 \sim 10^{-6}$, so that $b^2 \ll Rp$ approximation is valid and (4.18) is smaller than (4.15). This treatment neglects the presence of a central hole of radius $s' \gg b$, whose effect will be to increase

(4.18) by a factor ~ 2 .

For either geometry we see that

(a) There is little thickness dependence of the temperature rise, as a consequence of assuming ζ constant over thickness.

(b) As b increases for the same maintained current density the foil temperature increases as b^2 for $s \gg b$. Therefore, to avoid undue heating, the illuminated area should be as small as possible during normal observation.

(c) For a constant beam current $i = \pi b^2 j$, we substitute $j = i/\pi b^2$ and find no b dependence in foil heating for large b . Therefore, one may safely defocus the beam initially (increasing b) to search for thin regions, at no increase in beam heating over normal viewing conditions, provided the total beam current is kept the same.

Typical low temperature observation of dished alkali halide specimens involves the conditions $\zeta \sim 10^7 \text{ eV cm}^{-1} = 2 \times 10^{-12} \text{ J cm}^{-1} \text{ electron}^{-1}$, $j \sim 10^{17} \text{ electrons cm}^{-2} \text{ sec}^{-1}$, $\kappa \sim 1 \text{ W cm}^{-1} \text{ K}^{-1}$, $b \sim 10 \text{ }\mu\text{m}$, $p \sim 100 \text{ nm}$ and $R \sim 1 \text{ cm}$. Evaluating (4.18),

$$T(o) - T(s) = 0.15\text{K}$$

The same conditions at room temperature, where $\kappa \sim 50 \text{ mW cm}^{-1} \text{ K}^{-1}$, lead to temperature rises only $\sim 3 \text{ K}$. However, an order of magnitude increase in beam current (more normal viewing conditions for electron microscopists, $j \sim 100 \text{ mA cm}^{-2} \approx 10^{18} \text{ electrons cm}^{-2}$) can lead to appreciable temperature rises.

The very minimum conditions for observation at low temperatures of a uniformly thin carbon film $\sim 10 \text{ nm}$ thick supported on a 200 mesh

copper grid, $s \sim 100 \text{ } \mu\text{m}$, $b \sim 5 \text{ } \mu\text{m}$, $\zeta \sim 6 \times 10^6 \text{ eV cm}^{-1} \approx 10^{-12} \text{ J cm}^{-1} \text{ electron}^{-1}$, $\kappa \sim 2 \text{ mw cm}^{-1} \text{ K}^{-1}$ and $j \sim 10^{16} \text{ electrons cm}^{-2} \text{ sec}^{-1}$, lead to a temperature rise

$$T(o) - T(s) > 2 \text{ K}$$

indicating that carbon films are not the best substrates for, for example, cold stage temperature determinations by gas condensation.

4.2.3 Rate of beam heating

We have assumed steady state conditions in the derivation of temperature rise in §4.2.2. It remains to find how quickly this equilibrium condition is established.

The specimen configuration can be approximated for short times by an infinite cylinder at zero temperature along the axis of which is a continuous line source emitting heat at the rate $\dot{q} = \pi b^2 j \zeta \text{ J sec}^{-1} \text{ cm}^{-1}$; in other words, we initially neglect the sink at s and consider only the role of specimen thermal conductivity κ and specific heat C_p in establishing a condition near equilibrium. The continuous line source heat conduction problem has been solved (Carslaw and Jaeger 1959) and yields solutions

$$T(t, r) = \frac{\dot{q} \rho C_p}{4\pi\kappa} E_1 \left\{ \frac{r^2 \rho C_p}{4 \kappa t} \right\}. \quad (4.19),$$

where ρ is the specimen density and E_1 is the exponential integral of form

$$E_1(x) = \int_x^\infty \frac{e^{-u}}{u} du. \quad (4.20)$$

If we consider the temperature rise T very close to the source ($r = b$), where we know the steady state rise is $\sim 0.15 \text{ K}$, we can discover from (4.19) how quickly this temperature rise is attained.

For $(r^2 \rho C_p / 4 \kappa t) \ll 1$, (4.19) reduces to

$$T(t,r) = \frac{\dot{q} \rho C_p}{4\pi\kappa} \left\{ \ln \frac{4\kappa t}{\rho C_p r^2} - 0.577 \right\}.$$

Setting $\dot{q} = \pi b^2 j \zeta \approx 0.6 \text{ J sec}^{-1} \text{ cm}^{-1}$, $\rho \approx 2 \text{ g cm}^{-3}$, $C_p \approx 0.8$, $\kappa \approx 1 \text{ W cm}^{-2} \text{ K}^{-1}$, $r = b \approx 10 \text{ } \mu\text{m}$, and $t = 4 \text{ } \mu\text{ sec}$, we find

$$\begin{aligned} r^2 \rho C_p / 4 \kappa t &\sim 10^{-1} \quad \text{and} \\ T &= 0.15 \text{ K} \end{aligned} \quad \begin{array}{l}) \\) \\) \end{array} \quad (4.21)$$

Therefore we conclude thermal equilibrium is achieved very quickly ($\sim 4 \text{ } \mu\text{ sec}$) in or near the irradiated area, and the steady state solution is justified.

4.2.4 Specimen thermal contact

Thus far in this analysis we have assumed the specimen to be in intimate thermal contact with the heat sink. Insofar as the bulk rim region of the specimen may be considered an effective heat sink, this condition is fulfilled. We must, however, investigate the contact of the specimen rim itself with the cold stage to ensure that a sufficiently adequate thermal path exists to maintain the specimen rim at the temperature of the cold stage.

The most effective way to ensure an adequate thermal path is to cement the specimen entirely about its circumference with a thermally conducting cement. This method, however, exposes the specimen to severe differential thermal contraction stresses as the specimen and stage are both cooled (§5.11), and is to be avoided. An alternative method is to clamp the specimen mechanically. The effective thermal

conductivity through such a junction is a function of the contact pressure, and obviously not very much compressive stress can be applied to brittle specimens such as alkali halides. Furthermore, Berman (1956) and Berman and Mate (1958) have demonstrated that very poor thermal conductivity results from low temperature mechanical contacts, even metallic contacts under relatively high pressures. The remaining method is to cement the specimen in one place only on the periphery, and we shall now investigate the adequacy of this procedure.

We shall first assume that the thermal conductivity of the bulk specimen is sufficient that a constant temperature is maintained over the entire rim. This is certainly true if the rim is thicker than $\sim 1 \mu\text{m}$, in the case of metallic conductors and $\sim 10 \mu\text{m}$ in the case of poorer conductors. The maximum rate of heat input to a shielded specimen from thermal radiation $\dot{Q}_r$ will be

$$\dot{Q}_r = 2 f \epsilon_o A_o \sigma T^4; \quad (4.22)$$

assuming the worst possible conditions, $f \sim 10^{-2}$, $\epsilon_o = 1$, $s = 1 \text{ mm}$

$A_o = \pi s^2 = 3 \text{ mm}^2$, $T = 300 \text{ K}$, we have

$$\dot{Q}_r = 30 \mu\text{w}.$$

Similarly, the maximum rate of heat input from beam heating is given by

$$\dot{Q}_b = j \zeta \pi b^2 p;$$

we will again assume somewhat extreme conditions, $j = 10^{17} \text{ cm}^{-2}$,

$\zeta = 10^7 \text{ eV cm}^{-1}$, $b = 10 \mu\text{m}$, $p = 1 \mu\text{m}$, and find

$$\dot{Q}_b = 60 \mu\text{w}.$$

We then have a total $\dot{Q}_{\max} \sim 100 \mu\text{w}$ which we must dispose of through the specimen-holder contact. If we ensure that the cement layer is 1 mm wide, 100 μm thick and the distance between specimen and holder bridged by the cement is $< 100 \mu\text{m}$, we have the requirement for the cement that

$$\dot{Q} = 10^{-1} \kappa_c \{T(s) - T\} ; \quad (4.23)$$

$$T(s) - T \approx 10^{-3} / \kappa_c$$

where κ_c is the thermal conductivity of the cement, $T(s)$ the perimeter temperature and T the cold stage temperature. A good conducting cement, such as a colloidal suspension of silver, might be expected to have a thermal conductivity κ_c between 10 and 100 $\text{mw cm}^{-1} \text{K}^{-1}$ at 10 K, implying an acceptable maximum temperature rise of 10 to 100 mK. Polymeric cements, such as perspex, araldite, polyisobutylene, polyesters, typically have a thermal conductivity $\kappa_c \sim 0.1$ to 1 $\text{mw cm}^{-1} \text{K}^{-1}$ at 10 K; their use could result in unacceptable temperature rises 1 - 10 K. Berman and Mate (1958) have reported that for copper-copper mechanical contacts under 50 kg load, the maximum conductance at 10 K is $\sim 10 \text{ mw K}^{-1}$ the thermal conductance varies nearly linearly with pressure, and hence is relatively insensitive to change in area for a given load. A load of 5 kg applied to specimen clamping would result in an acceptable temperature rise ~ 0.2 K; but since this load could not sensibly be applied to more than the whole specimen area (3 mm^2), the minimum resultant compressive stress in the specimen would amount to 1.5 kg mm^{-2} which would result in severe mechanical deformation. It is unlikely that thin alkali halide specimens could survive this

stress without catastrophic fracture. The standard practice of mounting with lightly pressed clip rings is most unsuitable and might be expected to result in substantial temperature rise.

We therefore see that, in fact, the most important contribution to specimen heating comes from inadequate anchoring, and that a good thermally conducting cement is the only sensible anchoring system consistent with adequate thermal conductance and preservation of brittle specimens.

4.3 Heat Losses

The energy expended in maintaining a body at some specified temperature is a function of the heat losses from that body to its surroundings. For the case of cooling a body to a temperature below that of its surroundings, the quantity of energy to be removed must be equal to the heat transferred to the body from its surroundings at that temperature. We shall here discuss radiative and conductive heat inputs in all parts of the cooling chain and how they influence cold stage and supply system design.

4.3.1 Cold stage

4.3.1.1 Radiation

We take as our model for a low temperature cold stage a convex surface, of area A_0 and emissivity ϵ_0 maintained at zero temperature,

completely surrounded by an enclosure of surface area A_T and emissivity ϵ_T maintained at temperature T . From (4.3) the total rate of heat radiation from surface A_T and absorbed by surface A_O is

$$\dot{Q} = A_T F_{To} \sigma T^4, \quad (4.24)$$

where $F_{To} = 2A_O \epsilon_O / A_T$ from (4.7) for $\epsilon_T = 1$.

If the area cooled $A_O \sim 20 \text{ cm}^2$ and no intermediate shielding is employed so that $T = 300 \text{ K}$,

$$\dot{Q} = 2 \epsilon_O A_O \sigma T^4 = 1.8 \epsilon_O \text{ w.} \quad (4.25)$$

This is a large loss for values of ϵ_O near unity, but for most metals $\epsilon \sim 0.1$. If ϵ_T then is also < 1 we have from (4.7)

$$F_{To} = \frac{2A_O \epsilon_O \epsilon_T}{A_T \epsilon_T + 2A_O \epsilon_O - 2A_O \epsilon_O \epsilon_T}; \quad (4.26)$$

in the limiting case $A_O \sim A_T$, a condition which may be approached in a crowded microscope chamber,

$$F_{To} = \frac{2 \epsilon_O \epsilon_T}{\epsilon_T + 2 \epsilon_O (1 - \epsilon_T)}. \quad (4.27)$$

For ϵ_O and $\epsilon_T \sim 0.1$, $F = 0.07$ and $\dot{Q} = 70 \text{ mw}$. This value may be still further reduced by polishing both cold stage and room temperature surfaces. For highly polished copper used in the stage, ϵ_O can be as low as 0.03 and for polished steel used in the pole piece bore and cold stage surrounds $\epsilon_T \sim 0.05$ (White 1967). Therefore we conclude that without additional shielding or decreasing the stage dimensions we are faced with a radiative heat input $\sim 30 \text{ mw}$. This will be shown

to be small compared with conductivity inputs; and it implies that in the case of a stage operating at liquid helium temperature additional liquid nitrogen shielding is unnecessary unless comparable steps are taken to isolate conductive stage mountings from room temperature as well. The importance of shielding the specimen itself, however, was discussed in §4.2.1. Radiative heat input to such shielding is discussed in §4.6.6.

4.3.1.2 Conductivity

A stable cold stage must have a minimum of three point supports. We shall assume that these supports are at one end at room temperature and at the other at 0 K. For reasons of thermal contraction stability discussed in §4.7, these supports must be short and contact the cooled stage under considerable pressure. We will take as our support dimensions a rod of diameter d and length $\ell = 2$ mm. We assign to this rod a mean thermal conductivity $\bar{\kappa}$ which should be as small as possible. Reference to the table of thermal conductivity (Table 4.9) shows that silica, glasses and polymeric materials have mean thermal conductivities $\bar{\kappa} \lesssim 10 \text{ mw cm}^{-1} \text{ K}^{-1}$, a factor of ten less than stainless steel and 200 - 500 less than copper.

The rate of heat input through these contacts, assuming perfectly conducting interfaces, is given by

$$\dot{Q} = 3 \bar{\kappa} T \pi d^2 / 4 \ell \approx 1 \text{ w.} \quad (4.28)$$

Pressed contacts, however, are known to exhibit rather poorer conductance across them than continuous material. Berman (1956) and Berman

and Mate (1958) have investigated thermal conductivity in gold-gold, copper-copper, copper-diamond, and sapphire-sapphire contacts under 50 Kg loads between 4 K and 300 K. The contact conductance values for conductance across the junction at temperature T_J are respectively 1 w K^{-1} , 20 mw K^{-1} , 5 mw K^{-1} and 1 mw K^{-1} at 10 K, increasing roughly as T_J^3 . They found that the total conductance varies linearly with pressure, hence is insensitive to area for a given total load. We may therefore expect that the total heat input due to conductivity in the stage may be made somewhat less than the 1 w value calculated in (4.28).

We note in passing that mean conductivity values for most materials differ by a factor of only 2 or 3 in averaging over 300 and 4 K with compared averaging over 77 K and 4 K, indicating that intermediate support from a body at liquid nitrogen temperature will not reduce the conductivity input drastically. This input can be reduced as the supports are made longer, within the limits of fragility of fused quartz and the absolute thermal contraction of long rods.

4.3.1.3 Measured stage heat loss (from warming curves)

The heat loss to the stage can be determined directly from the slope of the warming curve $\dot{T}$ after cryofluid flow has ceased. If we know the specific heat $C_p^s(T)$ and mass M of the stage, then the rate of heat input at T , $\dot{Q}_{in}(T)$, is given by

$$\dot{Q}_{in}(T) = M C_p^s(T) d\dot{T}. \quad (4.29)$$

A typical warming curve for the stage described in §4.10.2 is shown in

fig 4.1. The inset shows behaviour at very low temperature. The corresponding specific heat of copper is also plotted on fig.4.1. The slope is very large at first because the specific heat is very small at low temperatures and varies as T^3 , while the heat input is approximately constant for $T \ll 300$ K. Later the warming rate becomes more nearly constant. In this region, $d\dot{T}$ is easily and accurately determined. At 77 K the slope $d\dot{T}$ is 70 mK sec^{-1} , while $C_p^s(77)$ is $\sim 0.19 \text{ Jsec}^{-1} \text{ K}^{-1}$. For a stage mass $M = 42 \text{ g}$, we have

$$\dot{Q}_{in}(77) = 0.56 \text{ w.}$$

Assuming that the major portion of the heat input is from conductivity and proportional to $(300 - T)$, we can deduce that

$$\dot{Q}_{in}(25 \text{ K}) = 0.69 \text{ w,}$$

$$\dot{Q}_{in}(10 \text{ K}) = 0.72 \text{ w,}$$

$$\dot{Q}_{in}(4 \text{ K}) = 0.74 \text{ w.}$$

To verify this extrapolation we may investigate the earlier portions of the warming curve. $T = 25 \text{ K}$ represents about the limit for accuracy, since C_p varies so quickly with T below this temperature. At 25 K the slope $d\dot{T}$ is 1.02 K sec^{-1} and $C_p^s(25) = 16 \text{ mJsec}^{-1} \text{ K}^{-1}$. We therefore calculate a heat input $\dot{Q}_{in}(25) = 0.69 \text{ w}$ which agrees with the rate extrapolated from 77 K, and differs only marginally from the rate calculated in (4.28).

In passing, we note from the inset that the maximum rate occurs at 25 K and barely exceeds 1 K sec^{-1} ; this rate has relevance to the stresses induced in the specimen due to temperature changes, but in fact initial cooling down rates are shown later (§4.4.7) to be somewhat greater than the warming rate.

4.3.2 Transfer tube

The transport of coolant fluids to a cold stage is most conveniently effected in continuous flow from an external reservoir via a transfer tube. Such a device consists of an inner tube of thin cryogenic alloy (stainless steel or copper-nickel) separated from a larger concentric tube by intermittent polymer spacers (usually ~ four), the space between the tubes being evacuated. This configuration will suffer from various radiative and conductive heat inputs.

4.3.2.1 Radiation

For coaxial cylinders of finite length ℓ , radius r_o and r_T , the angle factor f for $\ell/r_T > 10$ is given by

$$f \approx \frac{r_o}{r_T} = \frac{A_o}{A_T} . \quad (4.30)$$

The radiative exchange factor f_{To} is then

$$f_{To} = \frac{A_o \epsilon_o \epsilon_T}{A_T \epsilon_T + A_o \epsilon_o (1 - \epsilon_T)} = \frac{r_o \epsilon_T \epsilon_o}{r_T \epsilon_T + r_o \epsilon_o (1 - \epsilon_o)} , \quad (4.31)$$

and the radiative heat input rate

$$\dot{Q} = \frac{2\pi r_T \ell r_o \epsilon_T \epsilon_o}{r_T \epsilon_T + r_o \epsilon_o (1 - \epsilon_o)} \sigma r^4 . \quad (4.32)$$

A convenient length transfer tube is about 2 m with $r_o \sim 3$ mm

$r_T \sim 10$ mm, and $\epsilon_o = \epsilon_T \sim 0.06$. Two right angle bends in the tube will only have marginal effect on the angle factor. The rate of radiative heat input for this configuration is $\dot{Q} \sim 0.4$ w.

4.3.2.2 Conduction

Polystyrene, PTFE or nylon spacers have about the same mean thermal conductivity as fused silica, $\bar{\kappa} \sim 10 \text{ mw cm}^{-1} \text{ K}^{-1}$. For four triangular spacers of conductance path length $\sim 3 \text{ mm}$ we have a heat input $\dot{Q} \sim 0.1 \text{ w}$. The terminations of the inner tube are soldered to the outer tube, providing a thermal path over that length ℓ' of the outer tube wall that remains below room temperature. (Experimentally, ℓ' is found to be $\sim 10 \text{ cm}$ for thin wall stainless steel tube.) Any arrangement coupling the transfer tube to the stage will have a configuration similar to fig.4.2. One of these junctions is in cold dewar gas and will affect only consumption in the dewar; the other one will affect consumption of coolant flowing in the inner tube. For 10 mm diameter stainless steel tubing with 0.2 mm wall thickness, $A = 6 \text{ mm}^2$ and $\bar{\kappa} = 0.1 \text{ w cm}^{-1} \text{ K}^{-1}$, leading to a heat input

$$\dot{Q} = 2 \bar{\kappa} TA/\ell = 0.54 \text{ w}. \quad (4.33)$$

4.3.2.3 Minimizing transfer tube losses

For the whole transfer tube we have radiative and conductive inputs about 0.5 w each or a total heat input of $\sim 1 \text{ w}$, which is comparable with that of the helium stage. About all that can be done to minimize these losses if the convenience of a transfer tube is to be preserved is to shorten the tube length as much as possible to reduce the radiative component. The shortest length physically possible with a 17 l dewar is still about 1.5 m. The transfer tube can be made very short and the junction lock eliminated, however, by

installing a small dewar just outside the stage chamber filled from a larger dewar before each run. This has been done by Venables, Ball and Thomas (1968), but it introduces the inconvenience of refilling and maintaining another dewar, and can be effective only if the heat inputs to the stage are equivalently reduced, such that a considerably reduced total cryofluid consumption results, making a smaller dewar practical. Since the heat leak at the termination of the transfer tube is a large proportion of the transfer tube loss, a second way to minimize transfer tube losses is to cool the region of the transfer tube entry lock with exit gas from the cold stage. Of course, for liquid helium flow, heat inputs to the transfer tube add only to the proportion of gas in the stream reaching the stage, with marginal reduction in total heat transfer capacity as will be seen in §4.4. However, for gas flow cooling the heat inputs in the tube can establish a higher unit temperature from the tube, and thus a higher minimum stage temperature. This temperature rise in the transfer tube will be shown to be small in §4.4.2.

4.4 Heat Transfer

In this section we shall consider the utilization of cryogenic fluids, both in liquefied and gaseous form, for the cooling of objects subjected to the heat inputs discussed in the preceeding section.

4.4.1 Continuous flow cooling with cryogenic fluids

4.4.1.1 Cryofluid properties

In Table 4.1 we list the principal properties of the five most

useful cryogenic fluids: helium, hydrogen, nitrogen, oxygen, and argon in their liquid and gaseous states. We shall be concerned principally with cryogenic helium, as the lowest temperatures are attained with this fluid, and with continuous flow systems rather than cryostats.

Continuous flow cooling is preferable for microscopical applications for the following reasons: (1) Cryostats, in which only the latent heat of vapourization of a static liquid reservoir is utilized, are not particularly suited to electron microscopical applications because the continuous nucleate boiling can introduce unacceptable vibration. Continuous high velocity liquid flow is usually accompanied instead by film boiling, in which regime the fluid transforms more smoothly to a gas from the outer tube walls and introduces considerably less vibrational instability. (2) The specimen temperature can be readily and continuously varied from 4.2 K to room temperature using only a single cryogenic fluid (cryofluid) as the refrigerant. (3) The consumption of cryogenic fluid decreases as the permissible operating temperature increases. This must be compared with a conventional static cryostat which raises the specimen temperature by the input of an additional heat source to the specimen and so always results in an increase in cryofluid consumption. (4) An experiment may be terminated with virtually no wastage of cryofluids, whereas a partially emptied cryostat reservoir always leads to wastage. Rapid warm-ups can also be achieved in continuous flow systems by substitution of warm gas for the cryofluid.

Helium liquid is in many ways the poorest of the cryogenic fluids in cooling capability, with a small latent heat of vapourisation and poor thermal conductivity. However, its low viscosity makes it useful for continuous flow applications, and the gas form has a relatively high specific heat. Hydrogen is by far the best cryogenic fluid in either state for applications down to 20 K, but it is considerably more dangerous to use, particularly in continuous flow applications where there is appreciable continuous gaseous output to cope with.

4.4.1.2 Forced convection in cylindrical flow

We now consider the mechanism of heat transfer from walls at some temperature T and the cryogenic fluid under steady state temperature conditions for five flow conditions. For the stage we consider the flow tube geometry indicated in fig 4.3, because this configuration is employed in the cold stage described in §4.10.2 and because this geometry provides a larger surface area for an equivalent flow diameter than does a circular cross section tube. We define an effective flow diameter

$$D_h = 4 A/P \quad (4.34)$$

where A is the total cross sections area and P is the perimeter of the cross section. For a normal 3 mm o.d cryogenic tube, wall thickness 0.25 mm, this value of D_h is of course equivalent to the internal diameter 2.5 mm. For the configuration illustrated in fig 4.3, $D_h = 2.4$ mm which is near enough equivalent. The surface area S (per unit length) and cross sectional area A are approximately twice

that of the simple cryogenic tube. We shall base all our calculations on a flow rate equivalent of 1 l hr^{-1} cryogenic liquid, since the cryogenic liquid will always be the initial source and consumption economy is most easily measured in terms of the liquid. We set $D_h = 2.5 \text{ mm}$, $\ell = 6.9 \text{ cm}$, $A = 9 \times 10^{-2} \text{ cm}^2$ and $S = 10 \text{ cm}^2$.

In addition to the fluid properties listed in Table 4.1 (specific heat C_p , dynamic viscosity μ , thermal conductivity κ , density ρ) and the flow geometry (D_h , A , S , and ℓ), we define the following parameters relevant to heat transfer by fluid flow:

$$G = \dot{m} / A, \text{ areal mass flow rate in } \text{g sec}^{-1} \text{ cm}^{-2}.$$

$$h, \text{ heat transfer coefficient in } \text{w cm}^{-2} \text{ K}^{-1}.$$

$$(\text{Re}) = G D_h / \mu, \text{ Reynolds number.}$$

$$(\text{Pr}) = \mu C_p / \kappa, \text{ Prandtl number.}$$

$$(\text{Nu}) = h D_h / \kappa, \text{ Nusselt number.}$$

$$\dot{q} = hS, \text{ rate of heat transfer per deg K above the bulk fluid temperature } T_b \text{ in } \text{w K}^{-1}.$$

$$\dot{Q} = \dot{q} (T_w - T_b), \text{ total time rate of heat transfer from walls at temperature } T_w, \text{ in watts.}$$

Heat is transferred to a moving fluid from the enclosing walls via a thermal boundary layer which is analagous to but not necessarily coincident with the velocity boundary layer, and defines beyond it the region of constant fluid temperature. Beyond the boundary layer the flow is assumed to be inviscid. Inside the boundary layer the viscous flow may be either laminar or turbulent, and the heat conduction, which takes place through this layer to the fluid sink beyond, depends critically on the flow properties in this region. This model assumes a single phase fluid and does not accurately represent flow conditions

or heat transfer in the presence of a phase change, discussed in §4.4.4.

For the case of laminar boundary flow in forced convection through short tubes, Sieder and Tate (1936) have provided the approximate relation:

$$(\text{Nu}) = h D_h / \kappa = 1.86 (\text{Re})(\text{Pr}) (D_h / \ell)^{1/3} (\mu / \mu_w)^{0.14} \quad (4.35)$$

where all properties are evaluated at the bulk fluid temperature except μ_w which is evaluated at the temperature of the wall surface. The viscosity term may be neglected in most instances where the wall temperature is very little different from the fluid temperature, except where a phase change occurs. We shall neglect this term, except in our later consideration of film boiling.

For the case of turbulent boundary flow in forced convection, which begins to occur for Reynolds numbers > 2300 , McAdams (1940) has suggested the following empirical relation based on the bulk fluid temperature

$$(\text{Nu}) = 0.023 (\text{Re})^{0.8} (\text{Pr})^{0.3} ; \quad (4.36a)$$

whereas, for cryogenic fluids, Clark (1968) recommends

$$(\text{Nu}) = 0.021 (\text{Re})^{0.8} (\text{Pr})^{0.4} ; \quad (4.36b)$$

in practice, there is little difference in the two expressions, since $(\text{Pr}) \sim 0.7$.

We now evaluate these expressions for the five flow conditions following, for a flow rate equivalent to 1 l h^{-1} liquid helium. The results are tabulated in Table 4.2.

4.4.2 Forced convection cooling, helium gas

We evaluate helium gas flow properties at two temperatures, 4 K and 10 K, the former the temperature of the gas immediately after transformation from the liquid, the latter the probable mean temperature of the conducting boundary layer for a stage temperature of 15 K. Boundary layer properties are, of course, particularly important when there is an appreciable temperature differential between the cooled walls and the bulk fluid; we note, however, little degradation in heat transfer capability for gas between 4 and 10 K. Because of the high Reynolds number at the prescribed mass flow rate (equivalent to 1 lh^{-1} liquid), it is probable that turbulent boundary flow is the dominant transfer mechanism and accounts for twice the heat transfer as would laminar flow. Since for the stage $\dot{q} \sim 0.12 \text{ w K}^{-1}$, and the heat loss to the stage has been measured at $\sim 0.7 \text{ w}$, we expect that the prescribed flow rate can produce a stage temperature no lower than about 10 K. Increased mass flow will result in increased cooling and lower temperatures at the rate $G^{0.8}$. For the transfer tube, $\dot{q}$ is high ($q \sim 20 \text{ w K}^{-1}$), and the total radiative heat loss is in the region of 0.4 w . We expect then a negligible temperature rise $\sim 0.02 \text{ K}$, and gas should reach the stage with little change in temperature. The heat input at the transfer tube termination (fig 4.2) is nearly a point input, extending over only $\sim 1 \text{ cm}$ (i.e. $< 0.5 \text{ cm}^2$); subsequent turbulence in the gas flow will even out the effect of such heat inputs (but not that of the liquid; see next section), and a net gas temperature rise more than $\sim 0.1 \text{ K}$, is not expected. Transfer tube heat inputs will not contribute to the consumption in the same way as does the stage, since

we do not need to maintain the transfer tube termination walls at any specific low temperature.

4.4.3 Forced convection cooling, liquid helium

The Reynolds number for the specified mass flow in the case of liquid helium ($Re = 2430$) is sufficiently close to the laminar-turbulent changeover to evaluate heat transfer for both sorts of flow. There is, in fact, less difference between these mechanisms for liquid helium flow than for gas flow; and it should be appreciated that the changeover is not an abrupt one. At intermediate Reynolds numbers, $2300 < Re < 10000$, heat transfer is likely to occur via both mechanisms (see e.g. Clark 1968) with a laminar sublayer beneath the turbulent boundary layer. Certainly, for flow rates much in excess of 1 lh^{-1} , turbulent boundary flow is likely to be dominant feature.

The values in Table 4.2 assume no internal conversion to gas phase; that is, the calculations are strictly for stage temperatures close to 4.2 K with very small gas content in the boundary layer. Surprisingly, we note that at a flow rate of 1 lh^{-1} the heat transfer rates for gas and liquid are identical but these cannot be compared directly, since as we have seen the minimum stage temperature under these conditions is ~ 10 K and an appreciable gas boundary layer is likely to form at these temperatures, isolating the wall from the liquid. This problem will be dealt with in the next section. For no appreciable gas formation, flow rates approaching 10 lh^{-1} are required to maintain a temperature of ~ 5 K. This is considerably in excess of (experimentally) observed consumption at this temperature; the discrepancy can be explained by considering

the latent heat of vapourization, under conditions where even small quantities of gas are formed.

4.4.4 Film boiling in forced convection

The heat of vapourization λ of liquid helium is 21 J g^{-1} at 4.2 K, or 0.66 w for a flow rate of 1 lh^{-1} . Provided the heat exchanger at the cold stage is infinitely long (or even sufficiently long) we could hope to utilize the whole heat of vapourization. In addition, subsequent gas flow would provide additional cooling $\sim 12 \text{ mw K}^{-1}$ per unit exchanger surface area; so that temperature of 4.2 K should be attainable with $< 1 \text{ lh}^{-1}$ liquid flow. Since for reasons of space the surface exchanger area cannot be expanded indefinitely (see §4.4.8), we will not in fact convert the entire liquid flow to gas; we must therefore calculate the distribution of gas and liquid during flow. If the wall temperature $T_w > T_b$, the bulk fluid temperature at the boiling point, gas will always nucleate at the walls and will establish a gaseous boundary layer through which heat transfer must be accomplished to a central core mixture of liquid and gas. Furthermore, transfer tube heat inputs may convert a substantial fraction of the liquid to gas before it even reaches the stage. We may consider the problem one of heat transfer in the presence of saturated film boiling of a two phase fluid.

An excellent survey of forced convection boiling heat transfer correlations for cryogenic fluids has been made by Giarratano and Smith (1966). Correlation methods are based largely on their work and that of Hendricks et al. (1962) who evaluate heat transfers at average flow velocities and mean film properties using two phase Reynolds numbers for turbulent flow based on the vapour mass fraction χ . Two

densities are defined: an average bulk core density

$$\rho_b = \left\{ \frac{\chi}{\rho_v} + \frac{1-\chi}{\rho_l} \right\}^{-1} ; \quad (4.37)$$

and a mean film density

$$\rho_{\bar{f}} = \left\{ \frac{\chi}{\rho_{f,v}} + \frac{1-\chi}{\rho_l} \right\}^{-1} , \quad (4.38)$$

where the subscripts v and l refer to the vapour and liquid phase properties at the bulk temperature, $\bar{f}$ to mean film properties and f,v to film properties when the film is supposed a pure vapour at a mean temperature

$$T_{\bar{f}} = \frac{T_w + T_b}{2} . \quad (4.39)$$

The average flow velocity $\bar{V}$ is based on the average core density

$$\bar{V} = \dot{m} / \rho_b A = G / \rho_b \quad (4.40)$$

and the two phase Reynolds number on the mean film density and this average velocity,

$$(Re)_{\bar{f}} = \rho_{\bar{f}} \bar{V} D_h / \mu_{f,v} . \quad (4.41)$$

The Prandtl number is defined solely on vapour film properties,

$$(Pr)_{f,v} = C_{p f,v} \mu_{f,v} / \kappa_{f,v} ; \quad (4.42)$$

and the calculated Nusselt number is given by

$$(Nu)_{calc} = 0.023 (Re)_{\bar{f}}^{0.8} (Pr)_{f,v}^{0.4} . \quad (4.43)$$

The calculated Nusselt number is found to deviate from the experimentally obtained Nusselt number by the approximately consistent relation

(Giarratano and Smith 1966)

$$\frac{(Nu)_{exp}}{(Nu)_{calc}} = \exp \{ 1.11 + 0.771 \ln x + 0.0571 (\ln x)^2 \}. \quad (4.44)$$

A slightly better correlation can be made using the boiling number concept (Ellerbrock, Livingood and Straight 1962) which is beyond the scope and necessary accuracy of this analysis.

The heat transfer coefficient h is derived from the relation

$$(Nu)_{exp} = h Dh / k_{f,v}. \quad (4.45)$$

The parameters relevant to (4.37) through (4.45) are collated in Table 4.2 for 10% and 50% mass fractions of vapour, leading to heat transfer rate $\dot{q}_f$ for the stage. It is significant that, even for 10% prior conversion, the transfer rate is appreciably reduced (by a factor ~ 2) compared with an all-liquid flow; for 50% prior conversion the rate is one-tenth the all-liquid rate.

However, the loss in heat transfer capacity will be offset by the heat vapourisation $\dot{Q}_\lambda$ (which is listed in Table 4.2) for further conversion in the stage. The total heat transfer rate is, in fact, the same for both all-liquid flow and 10% gas/liquid flow with additional 10% conversion. It is just this utilisation of the latent heat of vapourisation, however, that introduces considerable problems of instability. Experimentally, one finds that for low flow rates (1 hr^{-1}) and stage temperatures $T > 10\text{K}$ the stability attained is $\sim 10^{-4} T$. For increased flow and temperatures $5 \text{ K} < T < 10 \text{ K}$, the stability is no better than $0.5 T$, while for large flows ($> 3 \text{ hr}^{-1}$) and corresponding low temperature $\sim 5 \text{ K}$, stability returns to $10^{-4} T$. This observation suggests that

stability is initially attained for flows $< 1 \text{ lhr}^{-1}$ where the vapour fraction is large before coolant enters the stage. Stability is also attained at low temperature ($< 5 \text{ K}$) where negligible boiling occurs, the wall temperature approaching that of the liquid. To explain the unstable intermediate region, we must consider the stability of flow pressure in the presence of vapourisation.

4.4.5 Flow pressure and instability

The pressure P required to accelerate a coolant initially at rest to an areal mass flow rate G at an elevation e through a flow system of length ℓ is given by

$$P = P_E + \ell p_F + P_M \quad (4.46)$$

where P_E is the pressure head, P_M is the momentum pressure drop and p_F is the frictional pressure drop per unit length.

The pressure head P_E is given by

$$P_E = \rho g e. \quad (4.47)$$

For a stage elevation $e = 1 \text{ m}$ above the liquid level in the storage dewar, $P_E = 1.2 \times 10^4 \text{ dyne cm}^{-2}$ (9 torr) for liquid helium at 4.2 K and 980 dyne cm^{-2} (0.75 torr) for gaseous helium at 4.2 K. At least this pressure difference must be maintained for fluid to reach the level of the helium stage. The fluid pressure at the cold stage will then be zero, and an additional pressure difference must be provided to maintain a desired fluid momentum through the stage and to overcome the flow friction stresses acting on the moving fluid.

Part of the friction stress contribution will arise from wall friction (this depends on the wall surface), the rest from internal

friction in the fluid (this depends on the state of flow). We define a friction factor f such that the friction pressure drop p_F per unit length of flow path is given by

$$p_F = f G^2 / 2 \rho D_h , \quad (4.48)$$

or roughly as ρ for a given mass flow rate. For pure laminar flow ($Re < 2300$), f is found to vary inversely as the Reynolds number,

$$f = 64 / (Re) , \quad (4.49)$$

from integration of the Navier-Stokes equations. For fully developed turbulent flow in smooth pipes, f is derived from the expression

$$1/\sqrt{f} = 2 \log_{10} ((Re) \sqrt{f}) - 0.9 \quad (4.50)$$

from analytical fit to universal velocity profiles (Sabersky and Acosta 1964). Martinelli and Nelson (1948) suggest a simplified version for turbulent cryogenic flow

$$f = 0.148 / (Re)^{0.25} \quad (4.51)$$

but values are slightly less consistent than those given by the full expression.

The momentum pressure drop P_M is obtained from the Bernoulli equation,

$$P_M = G / \rho . \quad (4.52)$$

Referring to Table 4.2, where each of these contributions is tabulated, we make the following observations:

(1) The pressure required to force liquid helium at 4.2 K at a rate 1 lhr^{-1} through a 300 cm flow system (equivalent to the transfer tube plus cold stage) is only 60 m torr, exclusive of pressure head. The latter amounts to some 9 torr for 1 m elevation, but of course disappears in that portion of the flow attaining this elevation.

(2) . The pressure to force liquid helium at 10 lhr^{-1} exclusive of pressure head is 1.3 torr, or twenty times that for 1 lhr^{-1} flow and one-seventh the pressure head (which is, of course, the same for both flow rates).

(3) The pressure required to force gaseous helium at 4.2 K, exclusive of pressure head, at the same 1 lhr^{-1} liquid equivalent is 0.6 torr or ten times that of the liquid equivalent; in this case, the pressure head (0.75 torr) is comparable with the flow pressure.

(4) Assuming an outside exit line sufficiently long for all entering fluid or gas at 4.2 K to transform to helium gas at 300 K over its length ($\sim 3 \text{ m}$ of 3 mm bore thick-walled rubber tubing is required) for purposes of gas recovery, cryopumping or flow rate monitoring, the pressure required to maintain the initial 1 lhr^{-1} flow rate is 10 torr, while for 10 lhr^{-1} the pressure necessary is 1000 torr (20 psi!).

A number of important conclusions may be drawn from these observations.

(1) The pressure head P_E is always the largest term, unless there is an exit line. It is so much larger than the flow pressure $P_M + \lambda p_F$ for 1 lhr^{-1} liquid helium flow that small variations of flow rate at the stage are unavoidable, e.g. pressure stability 1 part in 1000 is necessary to maintain flow rate stability of 10%; on the other hand, if the pressure head could be eliminated, it would be difficult to regulate the extremely small residual flow pressure. At larger flow rates, the flow pressure is a more sizable fraction of the total applied pressure ($\sim 1/10$ at 10 lhr^{-1}), leading to increased flow

stability. An even better situation obtains for helium gas flow, even at only 1 lhr^{-1} equivalent (flow pressure and pressure head are then comparable), or for flows a sizable portion of which is gaseous.

(2) Exit pipe friction dominates all other pressure contributions and renders the available flow pressure almost totally pressure dependent on prevailing conditions in the exit line. These conditions eventually change as the exit line cools progressively along its length. The exit line also leads to increased helium consumption because the pressures maintained ahead of the liquid helium flow depress vapourisation and its attendant heat capacity. A reduction of only 10% in conversion to vapour is equivalent to loss of 1 lhr^{-1} flow cooling. The larger pressures that must be maintained in the dewar for higher flow rates also raise the helium fluid temperature by 0.5 K. Pressures in excess of 5 psi are dangerous to maintain in the dewar, and 20 psi would be disastrous.

(3) Friction stresses dominate momentum pressures in the transfer tube for either gas or liquid. This condition contributes to flow stability in the transfer tube throughout most of its length. In this regard, it is better to use a transfer tube of narrow bore than one of large bore because of the stabilising effect of the greater friction stress.

(4) Momentum pressure dominates flow in the stage, or over any small region where there is a concentrated heat source; small momentum changes, for example due to vapourisation, can lead to considerable instability at these points (this is discussed below).

For two phase flow, for example in the presence of film boiling where a mass fraction χ is gaseous, a large reduction in stream density can occur, so that the flow accelerates and causes an additional momentum pressure drop P_M . This incremental momentum pressure drop can be computed from (Martinelli and Nelson 1948)

$$\Delta P_M = \frac{G^2}{\rho_l} \left\{ \frac{(1 - \chi)^2}{R_l} + \frac{\chi^2}{R_v} \frac{\rho_l}{\rho_v} - 1 \right\}, \quad (4.53)$$

and must be added to P_M (liquid) to obtain the total momentum pressure drop. R_l and R_v are the liquid and gas volume fractions for the given gas mass fraction χ , and are tabulated in Table 4.3, together with values of ΔP_M and P_M .

Also listed in Table 4.3 is the fractional momentum pressure change for an incremental mass fraction $\Delta\chi$ over the initial conversion region. This result is particularly revealing. The momentum pressure change introduced by 5% mass conversion from the pure liquid is an astounding 130%, which arises due to the very large vapour volume fraction resulting from this small mass conversion. The fractional pressure change introduced by this same mass conversion increment decreases with increased prior conversion to 7 - 8% at $\chi = 0.15$, a level which persists up to pure gas flow. Significantly, even a 1% change in conversion rate can lead to substantial pressure changes. Such behaviour implies that the smallest changes of vapourisation rate when the flow is primarily liquid can lead to appreciable instability. If pressure is applied which is sufficient to maintain, for example, flow at 1 lhr^{-1} with only a few per cent prior conversion, a momentary additional 1% conversion (from flow variations, etc.) introduces the

requirement for 50% more pressure. As this is unlikely to be forthcoming, the flow will slow, in fact eventually cease as larger and larger quantities of gas are vapourised. After this gas has exited the stage, flow begins again, and the cycle repeats. The observable temperature behaviour during this process is a sharp drop in temperature, corresponding to mounting vapourisation as the flow slows, and thereafter a sharp temperature rise as coolant in the stage is exhausted. This cycling behaviour is unavoidable at stage temperatures below 10 K or after sudden applied pressure changes.

Table 4.3 suggests that one way to maintain stable helium flow is to ensure that the entering fluid has a vapour content greater than 10 - 15% by mass (70 - 75% by volume), which means (from Table 4.2) operating at stage temperatures > 10 K; alternatively, the flow may be increased to such a rate that virtually no vapourisation occurs anywhere in the system (this really requires dispensing with the exit line and exhausting helium liquid directly into the atmosphere), or that that vapourisation which does occur introduces momentum pressure changes small in comparison with the large friction pressure drop occurring with high flow rates.

Clearly, such large flow rates are uneconomic for routine work except when the lowest temperatures must be maintained ($> 3 \text{ lh}^{-1}$ are, in fact, required to maintain stability at ~ 5 K), and an alternative is to sacrifice a bit of temperature and operate, slightly less efficiently but infinitely more stably, with pure gas flow cooling. A rough guide to the consumption expected is that a 1 lh^{-1} rate of gas flow results in a stage temperature ~ 15 K, so that n times this

rate, continuing to maintain only gas flow cooling, further reduces the temperature difference from 4.2 K by $\sqrt{n}$. Gas cooling is probably the best compromise between low temperature, cost and stability if all are equally important. Klipping, Schönherr and Schultz (1970) have shown that helium gas cooling can be effective with not unreasonable increase in helium consumption (a factor of 2 at 7 K, unity at 15 K) and temperature stability maintained at 10^{-4} T. A simple system for ensuring only gas flow is illustrated in fig 4.4. Cold helium gas is taken from just above the liquid level and spiralled through a heat exchanger in the liquid layer to the transfer tube inlet; a spring loaded valve at the base can be opened to admit liquid helium for economy in the very lowest temperature application. Fig 4.5 illustrates schematically the efficiency and stability of the various heat transfer modes outlined above.

So far, nothing has been said as to the means of applying the necessary pressure differential between inlet and outlet. There are two ways to achieve the differential: overpressure of the liquid reservoir (usually a 17 l dewar), or underpressure at the exit using a rotary vacuum pump. For pumping to be sufficiently smooth, the pump must be ballasted with a large tank, and even pump vibrations transmitted along the exit tube or exit gas can degrade image resolution at the stage. If pumping is employed, the exit line must be made as large a diameter as possible; from the pressure drop data in Table 4.2 we see that the exit line must be at least 2 cm diameter to reduce the pressure drop to levels comparable with that of the stage or unrestricted exit conditions. This requirement presents difficulties in practice. If the dewar is closed to external atmosphere during pumping, a considerable

underpressure can accumulate above the liquid; while this in fact reduces the fluid temperature (by $\sim 2\text{K}$), the continually changing pressure differential leads to difficulty in maintaining constant temperature. The alternative procedure is to supply the dewar with warm helium gas suitably filtered from the recovery system to maintain precisely 1 atm above the dewar. Because the helium flow responds so sensitively to small pressure changes, however, it is difficult to regulate gas flow to the dewar with sufficient precision.

Overpressure in the dewar provides a much simpler method for promoting fluid flow, although of course no boiling point depression occurs. The pressures involved are very small, ~ 9 torr for 1 lh^{-1} liquid flow, ~ 1 torr for equivalent gas flow, and do not increase the boiling point measurably. The gas flow technique has been used successfully with both helium and nitrogen gas.

4.4.6 Cooling rate and consumption

In the preceding analysis it was assumed that all parts of the flow system maintained at equilibrium temperature, and no mention was made of the consumption of cryofluid during initial cooling. We shall now introduce this realistic consideration and investigate both the rate of cooling and the total cryofluid consumption in cooling. The rate of cooling is particularly important to the consideration of quenching stresses given in § 4.11.1

(a) Cold stage

Consider the case that helium arrives at the cold stage as a liquid at 4 K, the stage being initially at temperature $T = 300\text{ K}$. We first

assume that only the latent heat of liquid vapourisation contributes to the cooling. If the cold stage made of copper weighs ~ 42 g, and the enthalpy of copper at 300 K is 79.6 Jg^{-1} , we need 3184 J to cool the stage (the enthalpy at 4 K is negligible) and therefore 147 g helium liquid. Assuming a flow rate of 1 lh^{-1} , this cooling mechanism results in a consumption of 1.1 l and requires 1 hr 10 min cooling time. The initial cooling rate $\dot{T}_s(\lambda)$ is 50 mK sec^{-1} and the final rate $\sim 1 \text{ K sec}^{-1}$. These values are listed in Table 4.4. As it is clearly unrealistic to neglect the cooling afforded by the resultant gas flow after vapourisation, we must consider this contribution to cooling rate.

We therefore neglect the latent heat contribution and assume that helium gas flows into the stage at 4 K, at a mass rate equivalent to liquid flow of 1 lh^{-1} , and flows out of the stage at some exit temperature T_e . The maximum possible value of T_e will be T_s , the stage temperature. Because the stage is compact and the thermal conductivity good, we can assume the stage temperature is constant across its whole extent. We define some average fluid (gas) flow temperature $\bar{T}_f$ and consider that the average rate of heat transfer $\dot{q}$ takes place at this fluid temperature. We probably have $\bar{T}_f \sim T_e/2$; in general $T_e < T_s$, and we note that T_s , $\bar{T}_f$ and T_e are all functions of time.

From heat balance considerations, we have that the rate of heat loss of the stage = rate of heat absorbed by the gas = the rate of heat transferred by fluid flow, i.e.

$$\dot{m} C_p^f T_e = M C_p^s (T_s) \dot{T}_s = \dot{q} (T_s - T_f) \quad (4.54)$$

where $\dot{m}$ is the helium mass flow rate, C_p^f the specific heat of helium gas, M the stage mass, $C_p^s(T_s)$ the stage specific heat at T_s . From the first equality we have

$$\dot{T}_s = \dot{m} C_p^f T_e / M C_p^s ; \quad (4.55)$$

and from the second equality, since $\bar{T}_f \sim T_e/2$,

$$T_e = \bar{q} T_s / (\dot{m} C_p^f + \dot{q}/2) . \quad (4.56)$$

We make the following comments about the variables appearing in these two expressions, for which we make reference to the tabulations of Table 4.4:

C_p^f is constant ($= 5.8 \text{ Jg}^{-1}$) over the range $10 < \bar{T}_f \leq 300 \text{ K}$;
 C_p^s for copper can be approximately expressed as $T_s (1.33 \times 10^{-3})$
in the range $50 \leq T_s < 300 \text{ K}$.

For $\bar{T}_f > 20 \text{ K}$ we can evaluate the heat transfer $\bar{q}$ on the basis of laminar flow.

Using equation (4.56), and substituting the maximum and minimum possible values of $\bar{q}$ for $T_{f \text{ max}} = 150 \text{ K}$ and $T_{f \text{ min}} = 20 \text{ K}$, we find that

$$1/3 \leq T_e/T_s \leq 3/5 \quad (4.57)$$

for the exit temperature range $50 \leq T < 300$.

We use an average value $T_e = 0.46 T_s$ from (4.57) and substituting into equation (4.55) we have

$$\dot{T}_s = 1.8 \text{ K sec}^{-1}.$$

We note, then, that the cooling rate is approximately constant in the range $50 \leq T < 300$, and the time to cool to 50 K is $2\frac{1}{2}$ minutes. The attendant helium consumption is 42 cm^3 , which is considerably less than the estimate from vapourization above, and justifies our neglect of latent heat. In Table 4.4 we have calculated the actual cooling rate

$\dot{T}_s(f)$ using (4.55) and actual values of C_p^s ; this rate is to be compared with $\dot{T}_s(\lambda)$.

In the range $10 \leq T_s \leq 50$ K we see we must begin to consider both the latent heat contribution and the heat input into the stage $\dot{Q}_{in}$. At $T_s = 50$ K we see that $\dot{T}_s(\lambda)$ has become an accountable fraction of the total cooling rate, and at $T_s = 20$ as large as the flow contribution at $T_s = 50$, assuming that all the liquid is still being vapourized. At progressively lower temperatures both $T_s(\lambda)$ and $T_s(f)$ will diminish as less vapourization takes place and the temperature differential $(T_s - \bar{T}_f)$ becomes diminishingly small. In these regions, account must be taken of the heat input to the stage, which becomes increasingly important compared with the enthalpic contribution $C_p^s M$. At $T_s = 50$ K, it represents about 13% of the total cooling load, while by $T_s = 20$ K it is $2\frac{1}{2}$ times the enthalpic contribution. This will have the effect of slowing the rate of approach to temperatures below ~ 50 K.

In fig 4.6 we have plotted the calculated cooling rate $\dot{T}_s$ as a function of temperature, extrapolated below 50 K. This is to be compared with the actual cooling rate measured for the cold stage described in §4.10.2 and plotted in fig. 4.6.

(b) Transfer tube

A similar calculation for the transfer tube is complicated by the fact that we can no longer assume a constant tube temperature, because the tube is long and the thermal conductivity of the stainless steel tube is poor. If we consider a single tube element, we can no longer assume the input fluid temperature constant, but instead a function both of the element position and time. Moreover, since the fluid flowing

in the long tube is initially at 300 K and eventually at 4 K, we have a widely varying flow friction, which could be neglected in the short stage; we must determine both the pressure required to initiate flow at the desired rate and the flow rate change for a constant maintained pressure.

The pressure drop in the tube per unit length is given by (4.48). We consider a 300 cm stainless steel transfer tube, 2.5 mm diameter with 250 μm thick walls. From Table 4.4 we see that, certainly down to ~ 50 K, we can consider the flow laminar, and we have from (4.48) and (4.49),

$$p = 64 \mu G / 2\rho D_h^2 \quad (4.58)$$

For the gas we can neglect hydrostatic pressure, so for initial flow $T_f = 300$ K and $p = 0.34 \text{ torr cm}^{-1}$. Thus the total pressure $P = 102$ torr, or over ten times what is needed to maintain liquid flow once the tube is cold. Obviously, if this pressure were maintained, the flow rate would accelerate, as it is difficult to quickly reduce overpressure in a cold dewar. This would lead to undesirably rapid stage cooling rates (see §4.11). In practice it is found convenient to use an overpressure about twice that required for the final flow rate, and to reduce this once helium liquid has appeared at the end of the transfer tube. We therefore take $P = 18$ torr (i.e. $p = 60 \text{ m torr cm}^{-1}$) and calculate initial and final flow rates from (4.48). Assuming the flow is initially gaseous and laminar with no hydrostatic head, and finally liquid and turbulent with hydrostatic pressure 9 torr,

$$\begin{aligned} G_i &= 0.11 \text{ g sec}^{-1} \text{ cm}^{-2} ; \\ G_f &= 9 \text{ g sec}^{-1} \text{ cm}^{-2} . \end{aligned}$$

The final flow rate amounts to $\sim 14 \text{ l h}^{-1}$, and clearly the overpressure must be reduced as soon as this sort of rate is reached.

Now, the weight of the inner transfer tube is $\sim 46 \text{ g}$ and for an enthalpy at 300 K of 81 J g^{-1} , we find that 3730 J are required for cooling. If we first consider that the cooling takes place entirely by vapourisation, which might appear to be a better assumption for the long transfer tube than for the compact state, we find we need 17.8 g or 1.4 l helium.

To ascertain the cooling time we must determine the flow rate G , since the cooling rate from vapourisation will vary directly as the flow rate. These are tabulated in Table 4.4 for a pressure of 18 torr. We see that over the larger portion of cooling, $50 < T < 300$, the flow rate (and thus cooling rate) can be represented fairly well by an average flow rate $\bar{G} \sim 0.4 \text{ g sec}^{-1} \text{ cm}^{-2}$. Below 50 K the flow rate (and the cooling rate) accelerate, and these last 46 K will not contribute appreciably to the total cooling time. Thus, the 18 g required is consumed in an average time of ~ 15 minutes.

Evaluation of the gas flow cooling contribution is more difficult. To avoid an intractable formulation, we make the following sweeping assumption: since T_s is initially at 300 K and ends up at 4 K when the tube is completely cooled, we suppose that the average exit behaviour can be described by a single average temperature $\bar{T}_e$ and that the total enthalpic contribution for the helium gas will be $C_p^f (300 - \bar{T}_e)$. Setting $\bar{T}_e \sim 150 \text{ K}$, we find $\sim 850 \text{ J g}^{-1}$ contributed from cold gas flow. The required mass is then $\sim 4.4 \text{ g}$, and for an average mass flow $\bar{G} \sim 0.4 \text{ g sec}^{-1} \text{ cm}^{-2}$, we have cooling time of ~ 4 minutes. The consumption is a

mere 35 cm^3 . We have neglected the heat inputs at the end of the transfer tube, which will retard the cooling rate at the exit and marginally increase time and consumption. An experimental cooling time of <5 minutes at $p = 18$ torr is actually obtained, with cooling consumption $<50 \text{ cm}^3$. A long transfer tube, therefore, does not introduce an inconveniently large addition either to total stage cooling time or to initial helium consumption.

4.4.7 Nitrogen in forced convection

While helium is useful in the range $4 - 80 \text{ K}$ where hydrogen is considered too dangerous, the comparative economy (Table 4.1) of liquid nitrogen renders it an attractive coolant for applications above 77 K . We shall therefore investigate the properties of nitrogen liquid and gas in forced convection cooling.

In comparison with helium, nitrogen has a very high density, viscosity and latent heat. There is also a very large volume change in vapourisation (200 times). These properties pose entirely different problems for forced convection nitrogen cooling. In particular, the latent heat far outweighs all other heat transfer mechanisms. These are listed in Table 4.5 together with friction factors and pressure drops. We note that for a liquid flow rate of 1 lh^{-1} , only $1/100$ of the flow need transform to gas to provide sufficient heat sink to maintain 77 K ; furthermore, the flow is strictly laminar. This result implies that the largest part of the flow will exit the cold stage in liquid form; when this liquid eventually transforms to gas there will be rather violent nucleate boiling because of the large volume change

associated with vapourisation; by comparison, helium transforms rather smoothly . The vibrations there engendered are readily transferred via the liquid medium and exit pipe to the cold stage, and induce marked image vibration. Surprisingly, if a quantity of liquid nitrogen is placed in the stage, utilised as a reservoir, very little vibration occurs once the stage has cooled completely, and stage temperature is maintained at 77 K. This behaviour results from the efficiency of the cold stage as a vacuum dewar and the high latent heat of nitrogen, resulting in a slow boil off rate. Under the same conditions helium would boil off very much more quickly and induce serious stage vibration (this has been observed in dewar-type helium stages which are necessarily limited to low magnifications: for example, Tischer 1970).

An obvious way to circumvent the problem is to do away with the liquid and circulate cold nitrogen gas using the procedure outlined in §4.4.5. Table 4.5 indicates the comparative efficiency of this technique. At nitrogen temperatures the principal heat input (conductive) is apt to be about 2/3 that at liquid helium, or ~ 0.4 w, so a temperature of ~ 81 K can be maintained with the gas equivalent of 1 lh^{-1} liquid consumption, which should be adequate. The flow rate cannot, however, be increased indefinitely; at the gas equivalent of 10 lh^{-1} over four atmospheres pressure is required to force the gas through the 300 cm flow system, a condition which is, of course, wildly prohibitive.

4.4.8 Improving heat transfer efficiency

If gas cooling, particularly, is used, and the latent vapourisation heat not utilised, it is important to optimise heat transfer from the

cold stage for best economy.

We shall now show how design for heat transfer can be optimised within the limits imposed by space and resolution constraints. We seek the functional dependence of $\dot{q}$, the total heat transfer rate (in W K^{-1}), upon the geometrical parameters of stage design. Since $\dot{q}$ depends on the heat transfer coefficient h and the total surface area for transfer S , we may expect that, to a fair approximation, simply introducing additional surface area will effect an increase in the heat transferred. One way to show this is to divide the flow with a partition. Fig.4.7 (1) illustrates a cross section of the cold stage cylindrical flow channel taken as the initial model in §4.4.1.2 with height b , width a , $b > a$, area ab , perimeter $2a + 2b$. In fig.4.7 (2) and (3), we illustrate two possible partitions for producing parallel divided streams. The heat transfer for these two configurations will be different for $b \neq a$. To demonstrate this, we derive the functional dependence of the heat transfer rate for parallel streams, q_p , on the flow area A , perimeter u , and surface area S , from the analysis of §4.4.1.2. For the case of the divided stream, we have for each channel

$$\begin{array}{ll}
 G \text{ remains constant} & \\
 D_h \propto A u^{-1} &) \\
 (Re) \propto A u^{-1} &) \\
 (Nu) \propto A^{0.8} u^{-0.8} \text{ assuming turbulent flow} &) \quad (4.59) \\
 h \propto A^{-0.2} u^{0.2} &)
 \end{array}$$

For the whole configuration,

$$S \propto u A^{-1} \text{ for a given occupiable volume.} \quad (4.60)$$

Therefore, $\dot{q}_p \propto u^{1.2} A^{-1.2}$, (4.61)

which is the relationship sought. We immediately see that configurations (2) and (3) produce different heat transfer, and for $b > a$ $\dot{q}_p$ (3) will be greater than $\dot{q}_p$ (2). They will differ from $\dot{q}$ (1) by the factors $\{2(a + 2b)/(a + b)\}^{1.2}$ and $\{2(2a + b)/(a + b)\}^{1.2}$ respectively.

For the volume available, $a = 1.5$ mm, $b = 6$ mm and defining $\dot{q}$ (1) $\equiv 1.0$ we have

$$\dot{q}_p(2) = 1.2$$

$$\dot{q}_p(3) = 2.0$$

in units of $\dot{q}$ (1).

An alternative arrangement is to feed the two channels sequentially rather than in parallel. This has the effect of increasing the average mass flow rate G and thus the Reynolds number (which has the added advantage of ensuring that, at the reduced flow rate made possible by more efficient transfer, turbulent flow is still maintained), as well as increasing the surface area. For this series flow geometry we have

$$\begin{aligned} G &\propto A^{-1} &&) \\ D_h &\propto A u^{-1} &&) \\ (Re) &\propto u^{-1} &&) \\ (Nu) &\propto u^{-0.8} &&) \quad (4.62) \\ h &\propto u^{0.2} A^{-1} &&) \\ S &\propto u A^{-1} ; &&) \end{aligned}$$

and therefore

$$\dot{q}_s \propto u^{1.2} A^{-2}, \quad (4.63)$$

which differs from (4.61) by the additional areal factor of $A^{-0.8}$.

Again we see that for $b > a$, $\dot{q}_s$ (3) $>$ $\dot{q}_s$ (2) $>$ $\dot{q}$ (1). Evaluating

$\dot{q}_s$ (2) and $\dot{q}_s$ (3) as above, we find

$$\dot{q}_s (2) = 2.2$$

$$\dot{q}_s (3) = 3.5$$

Since we have very nearly quadrupled the flow by the simple expedient of subdividing the flow compartment, it is instructive to consider how far this subdivision can be reasonably carried. It is mechanically unfeasible to further subdivide vertically, as in (3), so we divide by three horizontally in fig 4.7 (4). The criterion for $\dot{q}_s (4) > \dot{q}_s (3)$ is that $9\{(6a + 2b)/3\} > 4(2a + 2b)$ or $a > 0.236 b$. For the available volume we have $a = 0.25 b$ and

$$\dot{q}_s (4) = 3.6,$$

which is only marginally better than $\dot{q}_s (3)$.

We may reasonably enquire whether the thin partitions added are adequate to conduct heat ^{at} the rate assumed in the heat transfer calculations. We shall assume a partition wall thickness of 0.1 mm and a channel radius of 8.5 mm. In the configuration (3) the partition comprises about 0.45 the total surface area, and therefore from Table 4.2 must conduct $\dot{q} = 0.125 \times 3.5 \times 0.45 = 0.2 \text{ w K}^{-1}$. Assuming a thermal conductivity of $0.1 \text{ w cm}^{-1} \text{ K}^{-1}$ for phosphorous-deoxidized copper (Powell, Rogers and Roder 1957), a maximum conductance length 3 mm and an average conductance length of 1.5 mm, we find that the partition in (3) only conducts at an average of $\dot{q} = 35 \text{ mw K}^{-1}$ and is clearly inadequate.

The partitions in (4) are each expected to account for ~ 0.15 the total conduction, or $\dot{q} = 0.126 \times 3.6 \times 0.15 = 70 \text{ mw K}^{-1}$. Assuming a maximum conduction length of .75 mm, we find $\dot{q} \sim 70 \text{ mw K}^{-1}$, which is adequate.

A convenient way to achieve the configuration in (4) is to screw cut double helical channels of $1\frac{1}{2}$ turns about a bored cylinder as illustrated in fig.4.7 (5). The helical channels are joined at the bottom; and there is the added convenience that both inlet and outlet are situated at the top. This configuration can be expected to produce nearly four times the heat transfer flow of the original configuration (1) with the same flow rate. The Reynolds numbers for (5) are about twice and the areal mass flow G three times those for (1). Since the flow friction coefficient f varies only slowly with (Re) for turbulent flow, we have from (4.48) that

$$p \propto u A^{-3} ; \quad (4.64)$$

we note that the added heat transfer is achieved at the expense of greater flow pressure. In fact, $p(5) \sim 13 p(1)$; but $p(5)$ still amounts only to 0.1 torr for gas flow or 10 m torr for liquid flow at 4.2 K.

4.5 Temperature Measurement

There are three principal methods for measuring low temperatures in a cold stage in an electron microscope. These are resistance thermometry, thermoelectric thermometry and gas solidification. Each method exhibits particular advantages in either sensitivity, range, linearity or ease of application.

4.5.1 Resistance thermometry

The variation of resistivity with temperature in electrically conducting or semiconducting materials can be used to measure temperature

over wide ranges. We shall investigate three specific cases.

4.5.1.1 Resistivity in metals

The free electrons in metals responsible for conductivity are scattered by imperfections and by lattice phonons, giving rise to two components ρ_i and ρ_p of the total resistivity ρ . The thermometric property $\partial\rho_p/\partial T$ determines the sensitivity of the metallic sensing element, and for most metallic elements $\partial\rho_p/\partial T$ is approximately constant to temperatures $\sim\theta_D/3$, where θ_D is the Debye temperature, thereafter rapidly decreasing with decreasing temperature to the limit of sensitivity $\theta_D/50$. In exceptionally pure metals a lower limit of $\theta_D/100$ may be achieved. However, metals of low Debye temperature cannot usually be obtained in very pure form, and therefore platinum ($\theta_D \sim 225$ K) is chiefly used. The sensitivity $\partial\rho/\partial T$ of a typical platinum thermometer element is plotted in fig.4.8 as a function of temperature. The non-linearity below ~ 100 K makes this element inconvenient in the temperature range of most interest between 4 and 100 K; and the insensitivity below 10 K renders it relatively unsuitable for very low temperature determinations.

Sensitivity in the lowest temperature region can be increased by small impurity additions (a few ppm), usually of iron, to copper or gold; such doped materials then exhibit a resistivity minimum generally below 20 K followed by a further slow rise in resistivity with decreasing temperature.

Certain alloys, for which ρ_i is obviously high and for which we would presume temperature insensitivity, do exhibit anomalous resistivity behaviour below 200 K; constantan and manganin are two notable examples.

While their resistivity change is small in the range 0 - 200 K (typically 10%), these alloys do exhibit approximate linearity with temperature below 100 K.

4.5.1.2 Semiconducting elements

Conductivity in semiconductors is a function of the number of charge carriers and their mobility. In the intrinsic region, the resistance ρ varies nearly directly as $E_g/2kT$, where E_g is the band gap between conduction and valence bands. At low temperatures, $kT \ll E_g$, the presence of n or p type impurities contributes additional electrons or holes which may be excited across the band gap. A typical resistivity curve for a Ga + Sb doped germanium element is also plotted in fig.4.8. These elements are generally useful only below 50 K, where their sensitivity is high.

4.5.1.3 Carbon resistance

Crystalline graphite exhibits highly anisotropic resistivity behaviour, with $\rho \sim 10^{-4} \Omega \text{ cm}$ along the basal plane and $\rho \sim 1 \Omega \text{ cm}$ perpendicular to the basal plane. A single crystal behaves like a poor metallic conductor in one direction and a semiconductor in the other; if a polycrystalline aggregate is made, such as in a commercial carbon resistor, the resistivity behaviour with temperature might be expected to display an admixture of metallic and semiconductor characteristics. Clement and Quinell (1950, 1952) have found that commercial carbon resistors (for example 10Ω 1/10 w) manufactured by Allen-Bradley Company exhibit resistance which varies rapidly with temperature, especially

below 20 K. The behaviour of a $10 \Omega^{1/10}$ w resistor is also shown in fig.4.8.

4.5.1.4 Mounting

Resistance thermometers must be in intimate contact with the body whose temperature is to be measured; but, evidently, they must be nevertheless electrically insulated from metallic bodies. This is probably most conveniently done, for metallic or semiconductor elements, by a thin layer of low temperature varnish such as GE 7031. However the very high heat capacity of such cements ($\sim 2.5 \text{ mJ g}^{-1} \text{ K}^{-1}$ at 4 K; Phillips 1959) and their poor thermal conductivity affect the low inherent heat capacity and high thermal conductivity of metallic resistance elements. Carbon resistors suffer even more seriously from poor contact intimacy because of their cylindrical geometry and high heat capacity ($2 \text{ mJ g}^{-1} \text{ K}^{-1}$ or $100 \mu \text{ J K}^{-1}$ for an 0.05 g resistor at 4 K; Keesom and Seidel 1959) and very poor thermal conductivity ($100 \mu \text{ W cm}^{-1} \text{ K}^{-1}$ at 4 K; Johnson 1961). The heat flow from the centre of a small carbon resistor will be $\dot{q} \sim 10 - 100 \mu \text{ W K}^{-1}$ at 4 K, and since $m C_p / \dot{q} \sim 10 \text{ sec}$ such a resistor cannot be expected to follow accurately rapid variations in temperature. Additionally, the thermal conductivity and heat capacities of mounting cement are apt to be comparable or worse. Araldite, for example, has a thermal conductivity $\sim 100 \mu \text{ W cm}^{-1} \text{ K}^{-1}$ and a heat capacity of $2 \text{ mJ g}^{-1} \text{ K}^{-1}$ at 4 K (Parkinson and Quarrington 1954). A conducting cement, such as a colloidal suspension of silver, is probably thermally the best mounting compound but is structurally weak.

4.5.1.5 Self heating

Since the resistivity of resistance elements must be measured by passage of a current (for example, in a bridge circuit, etc.) the resultant heat can elevate the indicated temperature if it is not dissipated quickly enough. If the resistance of a 10 ohm carbon resistor at 4 K is $\sim 500 \Omega$ a current of 100 μA will raise the mean temperature by ~ 0.5 K assuming perfect thermal contact at the edge with a sink; a 10 μA current will lead to negligible rises. Metallic resistance elements, because of their lower resistivities, offer even less problem, although the bonding material (necessarily an insulator) will still be a poor thermal conductor.

4.5.1.6 Lead conductance

Unless connecting leads are also well cemented to thermal sinks, heat input along this source can lead to anomalous temperature readings. The mean thermal conductivity of copper leads is $\bar{\kappa} \sim 5 \text{ w cm}^{-1} \text{ K}^{-1}$, and assuming a wire diameter 0.1 mm and 10 cm lead length to a source at 300 K the heat input $\dot{q} \sim 5 \text{ mw}$, which is considerably more serious than self heating if these leads are not also cooled. A carbon resistor completely surrounded by a perfect sink can exhibit a thermal conductance no greater than $100 \mu\text{w K}^{-1}$ at 4 K or 5 mw K^{-1} at 30 K. We therefore expect that the resistor cannot possibly indicate a temperature lower than ~ 30 K under these conditions. The sinking of input leads, of course, entails the same precautions as the carbon resistor mounting. The best technique appears to be to wind at least several cm of enamelled wire lead around a post at sink temperature, cementing with a thin layer

of cryogenic varnish or colloidal silver (White 1968).

4.5.2 Thermoelectric thermometry

4.5.2.1 Thermoelectric effect

In a metal subjected to a thermal gradient the variation in the electron energy distribution function with temperature sets up a thermoelectric e.m.f. called the absolute thermoelectric force $E(T)$. The thermoelectric power, defined as dE/dT is then specific for any particular metals. If we have two junctions at T_1 and T_2 , fig 4.9a, between two dissimilar metals A and B, we may conveniently measure at M the difference in thermoelectric power and have a thermometric indication of the difference between their junction temperatures ($T_1 - T_2$). If it is inconvenient to bring B to the measuring instrument, we may select a suitable third metal C and form instead junctions AC and BC at a common temperature T_2 and measure across CC at M. Leads C are normally copper wire, T_1 an unknown temperature, T_R a known reference temperature whose choice will influence sensitivity in the range of interest; and B and C, called a thermocouple, are usually in wire form selected for their desired temperature response. If we wish the reference temperature point to be external to the unknown temperature point (for example, outside the microscope), we may have to add two further sets of junctions, usually a feed-through at ambient temperature, fig. 4.9b maintained at some ambient T_3 whose value is of no consequence so long as it is constant across all four junctions. If the reference junction is to be inside, a better configuration is illustrated in fig.

4.9c. Inhomogeneities, strains, lattice imperfections and impurities influence the value of thermoelectric power, so that care must be exercised in using the necessarily homogeneous well annealed thermocouple wires. Nevertheless, within reasonable limits of accuracy, thermocouples need not be individually calibrated, as must resistance thermometers, as their thermoelectric potentials are characteristic only of the material and not of the geometry as well.

4.5.2.2 Thermocouple response at low temperature

The thermoelectric power is a measure of the sensitivity at any temperature, and for most thermocouples is a function of the temperature, decreasing with decreasing temperature. The thermoelectric power ($\mu\text{V K}^{-1}$) of copper vs constantan, for example, is plotted in fig.4.8. (Powell, Bunch and Corruccini 1961); its usefulness clearly diminishes below ~ 30 K, and it is far from linear with temperature, implying that the lower temperature ranges are the least sensitive. Use of a low reference temperature (4.2 K) increases the sensitivity for measurements in the region below 10 K, but the extreme nonlinearity implies that a single reference temperature cannot serve for all ranges of interest. E.m.f. in the sub- μV region is also difficult to detect simply and reliably.

Small additions of magnetic solutes have been found to increase the low temperature sensitivity remarkably (Borelius et al. 1930; Dauphinee, MacDonald and Pearson 1953). Berman and Huntly (1963) and Berman, Brock and Huntly (1964) found gold-0.03% iron especially effective, and for gold-0.03% iron vs chromel a thermoelectric power varying

little with temperature. The latter is also plotted in fig.4.8 for comparison with Copper vs constantan, while the e.m.f. vs temperature is plotted in fig.4.10 for both liquid helium and liquid nitrogen reference temperatures. In the range 0-300 K the thermoelectric power varies only between 10 and 20 $\mu\text{V K}^{-1}$ resulting in a near linear response with temperature. Also, the same high sensitivity is retained in the lowest temperatures, enabling very accurate low temperature determinations. The junction can be most conveniently made by soldering the two thermocouple wires together with Wood's metal. E.m.f. is measured on a Phillips microvoltmeter using the 0-1, 0-3, and 0-10 mV ranges.

4.5.2.3 Reference junctions

Reference to fig.4.10 indicates that the maximum e.m.f. for the gold-0.03% iron vs chromel junction is ~ 5 mV between 0 and 300 K. If the microvoltmeter is readable to 0.5 divisions per cent, it is readable to 50 μV on the 0-10 mV scale, or between 2 and 5 degrees. Since greatest accuracy is desired in the 0-100 K region of typical cryogenic cooling, a liquid nitrogen reference temperature (77.36 K) will yield a minimum reading accuracy of 0.2 K - 0.4 K in the range 2 K - 150 K, which is certainly ample. The nitrogen reference junction is situated in a small external dewar of liquid nitrogen kept shielded from atmospheric contact using the configuration in fig.4.9b. If the nitrogen bath is permitted to absorb appreciable amounts of oxygen and water, its temperature can change.

A reference junction at liquid helium temperature can be afforded by joining the reference junction thermally to, but electrically

insulated from, a helium cryotube on the inlet side of and sufficiently removed from the cold stage. A convenient way to accomplish this feat is to drill a small hole in the cryotube, insert the junction as far as the central tube axis, and seal the hole again with cryogenic Araldite resin (AY 111 - HY 111); a length of each lead is then wound around the cryotube and cemented to sink the leads. Provided the normal enamel insulation is maintained right up to the junction, this procedure keeps the leads and junction electrically insulated and the junction in the liquid helium stream. This reference system cannot, of course, be used for cooling with gas flow of indeterminate temperature.

4.5.2.4 Lead conductance

The most convenient and effective way to fix the thermocouple junction thermally to the stage is to solder it with Wood's metal (melting point 353 K) directly to the cold stage. The other junctions and the microvoltmeter must then be electrically isolated from the microscope; earth protection can be maintained with a suitably high resistance ($\sim 10\text{ k}\Omega$). This method has the advantage that the thermal conductivity of junction/stage interface is considerably better than for insulated mountings, and a considerably larger heat input through the thermocouple leads can be tolerated. The mean thermal conductivities of gold and chromel are, respectively, $\bar{\kappa} = 3\text{ w cm}^{-1}\text{ K}^{-1}$ and $0.2\text{ w cm}^{-1}\text{ K}^{-1}$ over the range 4-300 K. Commercially available drawn wire is 0.3 mm diameter, so that the total heat input for 10 cm leads is $\sim 60\text{ mw}$. If we assume the junction is a ball $\sim 1\text{ mm}$ diameter, whose thermal conductivity is no worse than Wood's metal ($\kappa \sim 4\text{ mw cm}^{-1}\text{ K}^{-1}$ at 4 K; $120\text{ mw cm}^{-1}\text{ K}^{-1}$

at 10 K), the probable heat dissipation is $\sim 0.6 \text{ mw K}^{-1}$ at 4 K or 18 mw K^{-1} at 10 K. We might, therefore, expect an indicated temperature slightly high by $\sim 3 \text{ K}$ due to conductance of the leads, and some thermal sinking of the leads is found necessary. This, again, is most easily accomplished by wrapping and cementing a length of wire lead around an input cryotube. The heat input to the stage itself from the thermocouple leads, $\dot{Q} \sim 60 \text{ mw}$, is negligible compared with other losses.

4.5.3 Gas sublimation

Neither resistance nor thermoelectric thermometry is capable of measuring absolute temperature at the specimen under an illuminating beam unless the specimen itself is made a thermocouple junction or resistance element (Stojanowa and Belawzewa 1958; Watanabe, Someya and Nagahana 1962). The best that can be done with external thermocouples or resistance elements is to measure the temperature as close as possible to the specimen region, taking infinite care to sink the leads thoroughly; even then an additional thermal cooling path might be afforded by the sunked leads themselves and lead to an anomalously low indication.

Piercy, Gilbert and Howe (1963) have suggested a more reliable technique utilizing the sublimation point temperatures of gases introduced into the microscope column at known pressures, their solidification detected on a specimen substrate held below sublimation temperature. The useful range of pressure extends from 1 m torr (marginal for microscopy) to 10 μ torr when the deposition rate is inconveniently slow. Sublimation temperatures for various gases within this pressure range are listed in

Table 4.6. The temperature range 5-100 K is well covered, except for the gap between ~ 10 and ~ 30 K, which is unfortunately an area of major interest. Observed solidification, of course, only sets an upper limit for specimen temperature, but is nevertheless useful as positive proof of temperature attained. It is difficult to estimate the gas pressure in the region of the specimen; fortunately, the sublimation points do not vary greatly within the most probably pressure range. The solidified gas may be detected both in the image where growth islands are observed, and in the diffraction pattern, which can be indexed to the particular gas solidified.

For a specimen region well shielded from incidental contamination, the chief problem is presenting the specimen with a sufficiently large solid angle of gas to produce observable deposition rates (this is particularly true for the shielding precautions discussed in §4.6). A small capillary tube leading through the shielding to the region just below the specimen was found necessary to introduce sufficient gas; the tube is then fed via a fine needle valve to a source of pure gas at atmospheric pressure.

The specimen heating considerations introduced in §4.2.1 indicate that an evaporated carbon substrate may be expected to sustain an appreciable temperature rise from radiative and beam heating inputs and is not the best substrate to use for reliable indication of normally conducting specimen temperatures; unfortunately, all similar amorphous substrates suffer from poor thermal conductivity. Single crystal specimens are better than polycrystalline foils, because the ring patterns of polycrystalline solidified gas aggregates are readily separable from the

specimen diffraction pattern. Even without provision for gas introduction, nitrogen inevitably solidifies on a specimen during warming from low temperature as soon as the contamination shield (see §4.6.6) has warmed above ~ 30 K but before the weightier specimen holder (and specimen) have reached this temperature. This gas then sublimates when the indicated stage temperature is ~ 30 K, confirming that the specimen was indeed below this temperature.

4.6 Contamination

A surface maintained in an inert vacuum at a temperature below the sublimation point of any residual gas will have condensing upon it some fraction of the total number of molecules of that gas incident upon the surface. This fraction, which is a function of the molecular gas energy and surface temperature, is called the sticking coefficient, and for low energy molecular coincidence will be very close to unity. At high substrate temperatures hydrocarbon vapours adsorbed upon a surface may be cracked under action of the irradiating electron beam, and although sticking coefficients will be low, the adsorption followed by cracking will account for substantial deposition of amorphous carbon on the surface. These two phenomena constitute the contamination mechanisms responsible for degradation of thin foil specimen quality in the electron microscope. Our first consideration will be to determine the rate of gas molecules incident upon a surface, and our attention will subsequently be drawn towards evaluating the thickness of deposited contaminant layers and minimizing their agglomeration.

4.6.1 Molecular incidence

If we have a collection of different ideal gas molecules exerting a total pressure P , each collection of n_i gas molecules exerts a partial pressure p_i in proportion to the total pressure P as the total kinetic energy of the collection to the total molecular kinetic energy. When i gases are mixed at the same temperature, equipartition of energy states that the average kinetic energy of all molecules is the same and is a function only of the temperature T of the gas. The partial pressure p_i of any collection of n_i gas molecules of the same mass m_i in a unit volume is given by

$$p_i = n_i kT \quad (4.65)$$

where k is the Boltzmann constant. For the i 'th collection the energy distribution of the n_i molecules can be described by a Maxwellian distribution, for which an average molecular velocity $\bar{c}_i$ obtains, given by

$$\bar{c}_i = \sqrt{(8 kT/\pi m_i)} \quad (4.66)$$

The mean free path between molecular collisions $\bar{\lambda}_i$ is then given by

$$\bar{\lambda}_i = (1/\sqrt{2}) \pi n_i d_i^2 \quad (4.67)$$

where d_i is an effective molecular collision diameter.

The average molecular flux incident upon a surface of unit area may be deduced from the treatment of molecular effusion rates (see, for example, Jeans 1959). In cylindrical coordinates the flux $\phi(0, \psi)$ incident upon a unit surface from all directions $0, \psi$ above the surface is given by

$$\phi_i(0, \psi) = \int_0^{\pi/2} \int_0^{2\pi} n_i \bar{c}_i \cos \theta \sin \theta d\psi d\theta = \frac{1}{4} n_i \bar{c}_i \quad (4.68)$$

Substituting from (4.65) and (4.66) we obtain

$$\phi_i = p_i / \sqrt{2\pi m k T} \quad (4.69)$$

i.e. the flux is determined by the partial pressure, the mass and the temperature of the gas. Values for the parameters $\bar{c}$, n , $\bar{\ell}$ and ϕ for gases at 300 K and partial pressures of 10^{-5} torr are given in Table 4.7.

4.6.2 Accommodation and sticking coefficients

When molecules constituting an incident energy flux $\dot{E}_i$ strike a surface at temperature T_0 , they may either undergo specular reflection or be adsorbed for some time t before being diffusely re-emitted at some reflected energy flux $\dot{E}_r$. This situation arises in both considerations of rarefied gas dynamics and adsorption kinetics. The energy the incoming molecule has when it is on the solid surface depends on the rate at which excited phonon modes in the solid can take up energy from the incident molecule during the time of collision; the excitation of phonon modes in the solid will depend on the forces (Van der Waal's, polar, etc.) existing between the incident molecule and the solid at the time of collision. In dynamical equilibrium the molecular flux incident on the surface will be equal to the molecular flux leaving the surface. The number of molecules adsorbed on the surface at any one instant of time will depend on their average length of stay $\bar{t}$ before being re-emitted. This time will be proportional to the probability of acquiring the energy Q which they gave up upon being adsorbed, i.e.

$$\bar{t} = t_0 \exp (Q/k T_0) \quad (4.70)$$

where t_0 is related to the vibrational states of the molecule in its adsorbed state.

In a dynamical adsorption equilibrium we can describe the adsorption probability in terms of the energy flux balance by defining an accommodation coefficient a , first introduced by Knudsen (1930), defined as

$$a = \frac{\dot{E}_r - \dot{E}_i}{\dot{E}_o - \dot{E}_i}, \quad (4.71)$$

where $\dot{E}_o = \dot{E}_i - \dot{E}_r$. When $\dot{E}_r = 0$ we have unit adsorption probability, while $\dot{E}_r = \dot{E}_o$ defines a perfectly elastic collision probability.

Because the forces existing between an incoming molecule and a clean substrate are different from those existing between an incoming molecule and a substrate covered by many adsorbed layers, accommodation coefficients for monolayer adsorption and multilayer adsorption differ. The accommodation coefficient will also be specific for gas-substrate combinations, and will reflect surface condition (roughness etc.).

If the substrate temperature is below the sublimation point of the gas, in the presence of multilayer adsorption, Q is approximately the energy of sublimation Q_s of the gas from its own solid. If E_i is sufficiently small ($\sim Q_s$), there is little probability that the molecule will escape since in general $k T_o \ll Q_s$. In Table 4.7 we have additionally listed sublimation energies for the five gases we are most likely to encounter with any frequency in the microscope. We first note that their sublimation energies are comparable to or very much higher than the kinetic energy of the incoming gas (at 300 K), and we very reasonably expect that any such molecule striking a surface below its sublimation point will have a negligible chance of returning to its gas phase.

That is, we expect total adsorption.

In fact this behaviour is observed even for incident molecular energies several times the sublimation energy for surfaces just below the sublimation temperature. Since we are not interested in the energy of molecules leaving the surface, but only in whether they do leave the surface or permanently condense, we must define another coefficient, the sticking coefficient s , differing from the accommodation coefficient. If $\dot{n}_i$ is the total flux of molecules incident on a unit surface, and $\dot{n}_r$ is the total flux re-emitted, we define s such that

$$s = 1 - \dot{n}_r / \dot{n}_i . \quad (4.72)$$

If $\dot{E}_i \gg \dot{E}_0$, we could define the accommodation coefficient for condensation in a similar way, viz.

$$a_c = \frac{\dot{E}_i - \dot{E}_r}{\dot{E}_i} = 1 - \dot{E}_r / \dot{E}_i . \quad (4.73)$$

Sticking coefficients have been measured for molecular beams of N_2 (Arnold, Dawbarn and Busby 1970), A (Brown, Caldwell and Busby 1969), and CO_2 (Brown, Powell and Trayer 1968) with molecular energies between 0.3 and 0.9 eV incident upon cold copper substrates in high vacuum ($<10^{-10}$ torr). Flux rates employed were $\sim 10^{16} \text{ sec}^{-1} \text{ cm}^{-2}$ which defines a local pressure $\sim 100 \mu \text{ torr}$ at the substrate surface, and sublimation temperatures of 31 K, 36 K and 98 K respectively for N_2 , A and CO_2 . Just above the sublimation point, no condensation was observed ($s = 0$ but $a \neq 0$); below the sublimation point significant condensation was observed even for beams of high energy ($\sim 0.9 \text{ eV}$). We have extrapolated the N_2 data for a 23 K substrate to lower incident energies (the original data correspond to incident molecule temperatures between 1500 K and 4500 K), and find that for incident energies below 0.2 eV

(~ 1000 K), $s = 1.0$ over all incident angles on a substrate held 8 K below the sublimation temperature. Similar results are obtained for A and CO_2 . Kramers and Stemerding (1951) have similarly ascertained that there is no diffuse or specular reflection of water molecules from the surface of ice below 230 K at 100 m torr ($\sim$ the sublimation point). We may therefore conclude that, insofar as cryogenic contamination from residual gases in the microscope is concerned, we may safely assume a sticking coefficient of unity and calculate contamination rates on the basis of incident flux.

4.6.3 Contamination levels

Table 4.7 lists the fractional incidence of gases occurring in normal atmosphere in order of relative abundance. Several factors will alter this distribution for residual gases present within the microscope. First, the source of gases will be from small leaks and from outgassing of walls and particularly from surfaces with large specific adsorption capacity, such as photographic emulsions. As different gases diffuse at different rates through small orifices such as leaks, and are also adsorbed with differing efficiencies on surfaces within the microscope, we will expect some redistribution for gases initially present within the microscope. Second, the efficiency of pumping systems will vary for different gases, being generally more efficient for lighter gases for which the flux per unit area is high. Third, the pumping system may introduce additional gases, such as hydrocarbon or silicone vapours, in concentrations considerably higher than in normal atmosphere.

Generally, those gases diffusing most quickly through small leaks will be those most quickly removed by the pumping system, and we may expect little net redistribution from these sources. Adsorption of polar molecules is usually more efficient than adsorption of non-polar molecules, because of the induced dipole moments. Water vapour is particularly prone to adsorption, and, of course, condensation because of its low vapour pressure at room temperature in comparison with other atmospheric gases; and we expect the largest proportion of the residual gas content within the microscope to be water vapour. Simple precautions for avoiding adsorption of water vapour on microscope surfaces can lead to appreciably improved vacuum (see §4.6.7). Adsorbed water on photographic emulsions is by far the major source of poor vacuum in the microscope.

The presence of hydrocarbon vapours in the microscope can lead to considerable contamination on even room temperature substrates from the ionizing effect of the electron beam, which efficiently converts (cracks) hydrocarbon compounds to an irremovable amorphous carbon layer; this effect is well known in the electronmicroscopy of polymers (Grubb 1970). In this way the adsorption equilibrium is continually upset, the supply of molecules available for remission being continually depleted; the irradiated surface thus acts as a pump for hydrocarbons. Perfect efficiency only requires that the ionization time be shorter than the collision time ($\sim 10^{-12}$ sec). At very low temperatures the chemical changes necessary for reduction to carbon may proceed much less easily (Leisegang and Schott 1956), although low temperature polymer microscopy (Grubb 1970) suggests evidence to the contrary for many polymeric hydrocarbons. However, the hydrocarbon deposition rate is

considerably smaller than that of residual microscope gases at low temperatures.

4.6.4 Deposition rate

Since we can assume a unity sticking coefficient for multilayer condensation of room temperature gas molecules on substrates below sublimation temperatures, we may calculate the rate $\dot{d}$ directly from the incident flux by the relation

$$\dot{d} (p) = \frac{\Omega \phi M}{2\pi A_0 \rho_c} \quad (4.74)$$

where ϕ is the molecule flux from (4.69), M is the molecular weight, ρ_c the density of the condensed layer, A_0 Avogadro's number and Ω the total solid angle of the surfaces (both sides) exposed to the gas flux.

In Table 4.8 we have calculated the deposition rate from (4.74) for water between 10^{-4} and 10^{-7} torr partial pressure as a function of the solid angle for contamination. For the two other largest atmospheric constituents, N_2 and O_2 , we need only multiply the values by 1.1 and 0.87; so, in practice, the total residual gas pressure may be used in place of partial pressure regardless of contaminant species (H_2O , O_2 , N_2) with little error for cold stage temperatures below ~ 30 K.

The question next arises what to use as the pressure of condensable gases in the vicinity of the specimen. When the cold stage is operating, the pressure in the specimen chamber drops about an order or magnitude to 10^{-6} torr, as measured by an ion gauge, due to cryopumping by the cold surfaces. It has been erroneously assumed that the pressure near

the specimen will be at least at this level, without considering the operative gas effusion paths. Consider the configuration in fig.4.11 in which the cold stage sits in the objective pole piece bore. At pressures $\sim 10^{-5}$ torr, the mean free path $\bar{\lambda}$ (Table 4.7) is of the order of the internal dimensions of the microscope column. Therefore, we expect molecules to travel principally along straight line paths until they hit a wall. It is clear from fig.4.11 that if the cold stage is sufficiently close to the objective lens bore, all that concerns the bottom surface of the specimen is the effusion of gas through the objective lens bore from the column below together with outgassing from the top of the objective lens. Suppose the solid angle of exposure for the bottom specimen surface is reduced from 2π sterad to some value by a suitable shield. The pressure seen by the specimen will nevertheless still be that of the region below the objective lens bore, although that region is now collimated by a factor $\Omega/2\pi$. Unless the cryopump removes gas from the column below the specimen faster than it can be replaced by outgassing and/or leaks, the only improvement that can be made is by further collimation; this need not, however, be cold collimation: a $50\text{ }\mu\text{m}$ objective aperture, for example, further collimates the contamination solid angle for straight line molecular paths to $\sim 3 \times 10^{-4}$ sterad. A $400\text{ }\mu\text{m}$ aperture, large enough to embrace a substantial portion of the diffraction pattern (the aperture may then be left in at all times), still provides collimation $\sim 2 \times 10^{-2}$ sterad. While the cold shield effectively differentially pumps the region above the aperture, the specimen itself is nevertheless still exposed to that pressure below the aperture, suitably collimated. We must therefore use this pressure to calculate contamination

rates.

The pressure in this path is generally $\sim$ twice the pressure measured for the microscope as a whole, offering the poorest pumping path; for well outgassed photographic plates, we may expect (and indeed measure) a pressure no less than $2 - 5 \times 10^{-5}$ in the objective pole piece gap. While an objective aperture less than 400 μm diameter is in place, we can expect contamination rates $<$ a few tens of nm h^{-1} (less than with carbon contamination rates at room temperature with cold finger contamination protection, although all regions of the specimen are affected simultaneously), while without the aperture and with a cold shield collimation 0.2 sterad the rate is ten times this. (We have not included outgassing from the top of the objective lens, nor have we considered pressures $>10^{-4}$ torr for which straight line molecular propagation cannot be assumed). Additional measures for reducing contamination will be discussed in §4.6.7.

We may obtain a lower limit for the partial pressure of hydrocarbon vapours within the microscope by determining carbon contamination rates at room temperature. We may conveniently measure the rate of closure of holes in a holey carbon film substrate under the electron beam, and in this way measure contamination rates $\sim 0.1 \text{ nm sec}^{-1}$ (I L F Ray, private communication). If we assume that, in the extreme case, the electron beam manages to crack every arriving hydrocarbon, we may use the measured rate to calculate a flux ϕ of arriving carbon atoms; the former is a reasonable assumption, since the hydrocarbon flux is unlikely to be $>10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$ and the minimum electron flux is $>10^{16} \text{ cm}^{-2} \text{ sec}^{-1}$. If we assume an average of ten carbon atoms per hydrocarbon molecule (probably valid for

vacuum oils), we obtain a partial pressure $\sim 10^{-6}$ torr for hydrocarbon vapours which is small compared with other residual gases. Unlike room temperature contamination layers, cryodeposit layers can be made to evaporate from the specimen by elevating the specimen temperature.

4.6.5 Effect of contaminant layer

The effect of the residual gas contamination layers on the underside of the specimen on image contrast and absorption can be surmised from a treatment of electron scattering (Lenz 1954). Since the contamination layer is principally on the bottom (exit) surface of the specimen, it will contribute principally to the absorption and little alter the contrast information of the transmitted electrons. It will, however, affect the energy loss distribution, for example as measured along Kikuchi lines. The layer is usually sufficiently polycrystalline to be considered amorphous, and consists primarily of ice, as evidenced from indexable diffraction patterns of heavy contamination layers.

The elastic scattering length ℓ for 100 kV electrons scattered by amorphous ice is given by

$$\ell_{el} = \pi M/Z^{4/3} \lambda^2 \rho A_0 = 350 \text{ nm} \quad (4.75)$$

or three times larger than for the aluminium evaporated layer, §3.5.

Table 4.8 indicates that, within reasonable observation times (<1 hr), and with good microscope vacuum ($\sim 10^{-5}$ torr) and reasonable aperture collimation, the layer is not likely to exceed a few tens of nm. This thickness is a small fraction of the elastic scattering length, and one would not expect absorption due to the layer to exceed 10% of

total intensity. Fig.4.12 presents micrographs of the same area of a KI specimen taken at the beginning and the end of a one hour cold run at 10 K.

The corresponding elastic scattering lengths for solid nitrogen and solid oxygen are 388 and 272 nm respectively, which differ little from that of water. All these contaminant layers will have most effect on the clarity of Kikuchi line patterns whose contrast degrades most quickly in the presence of subsequent additional scattering.

4.6.6 Design of contamination shields

4.6.6.1 Solid angle

The thermal radiation shield discussed in §4.2.1.2 can be made to serve nicely as a contamination aperture as well. We can see from fig.4.11 that for a given desired viewing area on the specimen of radius $2s$ and solid angle of shielding Ω , parallel collimation, indicated by the broken lines in fig.4.11, is not necessary but only an aperture collimation of radius c , situated at some distance l' below the specimen. Since in general s ($\sim 100 \mu\text{m}$) will be very much smaller than c (this will be calculated below) we may calculate Ω as the solid angle subtended by a disc of radius c from a point situated distance l' above it. The maximum solid angle Ω_{max} will occur for the point situated on the symmetry axis of the disc for which case Ω_{max} is given by

$$\Omega_{\text{max}} = 2\pi \left\{ 1 - z / (1 + z^2)^{\frac{1}{2}} \right\} \quad (4.76)$$

where $z = l'/c$. The distance l' will be determined by the height we may safely raise the specimen from its normal focal position above the

upper plane of the objective pole piece bore without sacrificing resolution; this will be discussed in §4.8. If the shield is fixed rigidly to the specimen holder, the radius c will place limitations on the distance the thin area of the specimen is from the centre of the specimen disc. It is unreasonable to expect the thin specimen area to be produced within an area of radius less than $\sim 500 \mu\text{m}$ of the centre; on the other hand, there is no point in having an aperture diameter greater than the maximum translational travel of the cold stage, which will be limited by the presence of the shield to about $\pm 0.5 \text{ mm}$. The maximum value of Ω' is seen to be $\sim 2 \text{ sterad}$. Setting $c = 0.5 \text{ mm}$ we have $\Omega = 0.2 \text{ sterad}$.

The contamination rates in Table 4.8 were calculated with this total solid angle for contamination. The solid angle for contamination from above the specimen can, of course, be arranged to be very much smaller than that below, because more height is available above. If a 0.5 mm radius aperture is placed 15 mm above the specimen, the solid angle subtended is $\sim 10^{-2} \text{ sterad} \ll 0.2 \text{ sterad}$.

We have elected to use a shield rigidly fixed to the specimen holder and not to the specimen, because this enables the specimen to tilt through large angles independent of the contamination protection. If we had the same solid angle for contamination calculated above (0.2 sterad) and the shield fixed rigidly to the specimen, the maximum tilt angle would be $\pm$ the half apex angle α of the cone surrounding this solid angle, or

$$\alpha = \tan^{-1} \frac{1}{4} = 15^\circ \quad (4.77)$$

for the observed specimen area at the exact specimen centre. This is

not quite ample tilt, as described in §4.9, and assumes a collimating aperture of zero thickness.

If the observed specimen area is at a distance equal to the aperture radius from the specimen centre, the total tilt will still be 2α , but tilt on one side will be 0 and tilt on the other 2α ; if only a fixed tilt range $\pm\alpha$ is available, the total tilt in this case will be only $\alpha(+0 \text{ to } -\alpha)$ instead of $2\alpha(+\alpha \text{ to } -\alpha)$. If the shield is not fixed to the specimen the total tilt range $\pm\alpha$ will always be available.

4.6.5.2 Radiative shield heating

In the absence of any external nitrogen temperature shielding, for which there is little room within the confines of a narrow pole piece bore (~ 6.5 mm diameter) and which introduces a great deal of inconvenience, we are faced with a contamination shield fully exposed to room temperature radiation; we enquire whether this radiative heat input will result in significant heating of the contamination shield. The thickness of this shield will be limited by the space available, which limits thickness p to 0.1 mm, and its separation from the pole piece bore must be >0.5 mm, if we are to retain a translational facility of ± 0.5 mm. We may evaluate the maximum heating at the centre of the shield, the area of interest for specimen protection, using the approach of §4.2.1.2 in which specimen heating was calculated. We may approximate the geometry of the shield and its surroundings by two plane discs, area A_T at 300 K and A_O at 0 K, radius $s \sim 20$ mm where the shield is joined to the cold stage at s , separated by distance $\ell \sim 0.5$ mm. If ℓ is very much smaller than the radius of the discs, we may with little error

assume the configuration describes a complete enclosure, and we also have an angle factor of $f \sim 1$. The radiative exchange coefficient for two surfaces constituting an enclosure is

$$\frac{1}{F_{1-2}} = \frac{1}{f_{12}} + \frac{A_1}{A_2} \left(\frac{1}{\epsilon_2} - 1 \right) + \left(\frac{1}{\epsilon_1} - 1 \right); \quad (4.78)$$

or for the present case where $f_{12} = 1$, $A_1 = A_2$,

$$F_{1-2} = \left(\frac{1}{\epsilon_2} + \frac{1}{\epsilon_1} - 1 \right)^{-1}. \quad (4.79)$$

The maximum temperature rise at the centre of the disc is given by

$$T_m - T_s = \frac{F_{1-2} \sigma T_s^4}{4 \kappa p}. \quad (4.80)$$

The thermal conductivity κ for phosphorous-deoxidised copper (most convenient shield material) is $0.2 \text{ w cm}^{-1} \text{ K}^{-1}$ at 10 K (Powell, Rogers and Roder 1957), and we calculate the maximum temperature rise

$$T_m - T_s = 9.2 F_{1-2}. \quad (4.81)$$

Assuming $\epsilon_T = 1$ we have

$$T_m - T_s = 9.2 \epsilon_0 \quad (4.82)$$

and we recognise the importance of providing a polished finish on the contamination shield. For $\epsilon_0 \sim 0.1$ we can keep this temperature rise to $< 1 \text{ K}$. Usually the pole piece bore is also well polished, and we can expect a temperature rise $\sim 0.5 \text{ K}$.

4.6.7 Vacuum system

The severe dependence of cryocontamination levels on residual pressure as evidenced in Tables 4.7 and 4.8 indicates the necessity of

maintaining the best possible vacuum in the microscope. This entails improving the pumping system where it is insufficient, providing facilities for adequate desiccation of photographic emulsions, and maintaining the microscope free from unnecessary water vapour adsorbates. Additional measures can be provided to reduce specific contamination paths, such as that up the column from the photographic plate chamber.

4.6.7.1 The pumping system

The Siemens Elmiskop I microscope utilised in this study is supplied with a 125 l sec^{-1} oil diffusion pump, a mercury vapour diffusion pump, a large ballast tank and a single 50 l mn^{-1} rotary pump. The latter does double duty, backing the oil diffusion pump and roughing out the microscope column during initial pumpdown; the mercury vapour pump and ballast tank are meant to provide backing for the oil diffusion pump when the rotary pump is otherwise utilised.

This arrangement was considered both inconvenient and insufficient for cryogenic applications, and the following system was provided in its stead. The oil diffusion pump was replaced by a much larger 350 l sec^{-1} oil diffusion pump baffled above by a liquid nitrogen-cooled vapour trap. The mercury pump was dispensed with (in any event, the mercury would not cope with the larger amounts of oil vapour put out by the 350 l sec^{-1} diffusion pump) and replaced by two large single stage rotary pumps (150 l min^{-1}), one to permanently back the oil diffusion pump via the ballast tank and the second to rough out the microscope column, plate chamber, specimen lock or helium transfer tube. This system provides a larger pumping capacity, considerably more protection against back-

streaming oil vapours, and results in lower ultimate vacuum ($<5 \times 10^{-6}$). Initial pumpdown times are also much reduced, ~ 10 min from atmosphere to 10^{-5} torr with well desiccated photographic plates. Furthermore, the risk of inadvertently depriving the diffusion pump of adequate backing pressure was eliminated. Pirani gauges were installed in both rotary pump lines, while a Penning gauge was installed at the valve block level leading into the microscope chamber. Provision for mounting ionisation gauges at both the photographic chamber and specimen chamber levels was made. Several sliding seals in the gun pumping assembly were replaced with ones of more reliable design; all gaskets were initially replaced and regularly serviced. Finally, an airlock was installed in the photographic chamber to enable plate changing while the microscope remained under vacuum.

4.6.7.2 Plate desiccation

A previous system of rotary pump desiccation (to ~ 10 torr) was replaced by a unit incorporating an oil diffusion pump and water cooled baffle valve. Plate desiccation was carried out to a vacuum of 5×10^{-5} torr in about 12 hr in this unit; for plate retrieval air was admitted to the unit through a molecular sieve drying tube. Rapid transfer to the microscope chamber was facilitated by the cassette loading system integral to a 24-plate camera replacing the conventional 12-plate camera. Open plate holders (rather than the light-tight ones used in the 12-plate camera) reduced desiccation time. A set of 24 plates thus desiccated could be pumped in the microscope to $\sim 5 \times 10^{-5}$ torr within ~ 15 min after loading. This was very much in contradistinction to rotary pump

dessication, indicating the efficacy of the added diffusion pump.

4.6.7.3 Air admittance

The microscope was maintained free from unnecessary water adsorption by using very dry air for air admittance. Since the vacuum loading lock, described in §3.4 necessitated letting the whole microscope up to atmosphere during insertion, dry air admittance was deemed an absolute necessity. The requisite drying tube consisted of a 20 cm column of Union Carbide type 4A XW molecular sieve pellets, followed by a 5 cm layer of 4A XW powder; the powder served not only to complete drying but also to slow the rate of admittance to that which the drying tube could efficiently manage. Air admittance was achieved in about 5 min compared with the usual 30 sec. After this procedure re-evacuation to previous pressure was accomplished in less than 15 min. Admitting normal wet air necessitated repumping times of several hours. The efficacy of this technique, in particular, indicates the severity of water vapour adsorption and explains the predominance of water vapour in contamination layers.

4.7 Thermal Contraction

All materials undergoing cooling to very low temperatures will exhibit thermal contraction, resulting in a cumulative image drift and structural instability if proper account of it is not taken. In this section we examine the various sources of thermal contraction and evaluate their effect on image stability, cumulative image shift and

cold stage construction. Table 4.9 lists, among other properties, total fractional thermal contraction from 300 K to 4 K and expansion coefficient at 10 K, and it is with these properties that the following discussion will be concerned.

4.7.1 Specimen contraction

The specimen itself will contract with temperature, and we must evaluate this potential contraction contribution to instability. Consider an ideal specimen, with a 200 μm hole situated perfectly at the centre, the specimen centred perfectly in a symmetrically contracting cold stage. We shall be concerned with the movement of any feature under observation near the hole edge. From Table 4.9 we note that for a typical alkali halide (NaCl) the coefficient of expansion at 10 K is $\sim 10^{-6} \text{ K}^{-1}$ and the total fractional change in linear dimension upon cooling to 10 K is $\sim 10^{-2}$. An edge of the hole 100 μm from the centre will then undergo a total shift of $\sim 1 \mu\text{m}$ towards the centre in cooling. If the specimen is supported at one point on the perimeter only, and is $\sim 2 \text{ mm}$ diameter, the hole edge will then undergo a total shift of $\sim 10 \mu\text{m}$ depending slightly on which side of the hole the edge is situated with respect to the fixed point at the perimeter.

If we wish to resolve 3 nm in the image with a thermal contraction coefficient of 10^{-6} K^{-1} at 10 K equivalent to a translation with temperature at 10 K of $\sim 1 \text{ nm K}^{-1}$, we must confine temperature fluctuations to within $\sim 3 \text{ K}$.

4.7.2 Cold stage contraction

The total fractional contraction in cooling a copper cold stage to below 30 K is 3.25×10^{-3} . For a stage 2.5 cm diameter the shrinkage amounts to 81 μm . If we have designed the stage to accept a standard tapered specimen holder cartridge (1.4 cm diameter), the shrinkage at this position amounts to nearly 50 μm ; therefore we must construct the stage from the same material as the holder (in this case phosphorous-deoxidised copper) to avoid large stresses arising from differential contraction. If the stage and cartridge cool or warm at different rates, the resultant differential may lead to disastrous consequences: if the stage warms up more quickly than the cartridge, the cartridge will sink deeper into its taper and upon re-expanding will lodge fixedly in the stage. A thin coating of vacuum grease prevents this annoying occurrence, as well as improving conductivity at low temperatures.

The contraction coefficient at 20 K for copper is $\sim 5 \times 10^{-7} \text{ K}^{-1}$. If stage contraction responds to temperature unequally by 10% (for example, due to non-symmetrical assembly stresses), we will have drift at 1.3 nm K^{-1} and must therefore stabilise the temperature to within $\sim 2 \text{ K}$ for 3 nm resolution.

4.7.3 Cold stage supports

The problem of accommodating with stable stage supports a total stage contraction of nearly 100 μm is a difficult one, particularly as the supports may be expected to contract as well. One technique (Kitamura, Scrivastava and Silcox 1966; Hobbs 1970b) is to provide a

horizontal insultating support plane. A more stable approach (Venables, Ball and Thomas 1968) is to provide symmetrical support from a strong material of small thermal contraction and thermal conductivity. As discussed in §4.3.1.2, fused silica satisfied these criteria; in fact, fused silica actually undergoes a net thermal expansion below 100 K. The result is that, for a fused silica support bridging between 300 K and 10 K surfaces, the mean net contraction is near zero ($< 10^{-5}$); this may be compared with values for plastic supports (araldite, nylon, polystyrene, PTFE) listed in Table 4.9. The net contraction in a 2 mm diameter fused silica ball is < 20 nm. Because fused silica is also strong (yield stress $\sim 9 \text{ kg mm}^{-2}$) and undergoes little plastic deformation, support can be made with the minimum of material (viz. 3-point suspension with balls). Furthermore the mean thermal conductivity of fused silica is comparable with that of plastics.

The $81 \text{ }\mu\text{m}$ shrinkage in the copper stage may be taken up by elastic deformation of a ring supporting the three fused silica balls. The ring is made strong enough to prevent its deformation due to strain from the cryotubes during stage movement, but sufficiently weak that the copper stage does not deform appreciably first. Consider the ring in fig.4.13 made rigid at the three points marked P and exerting pressure on the balls at the points marked B. The ring then undergoes cantilever beam bending over length $L = \pi D/3$, where D is the ring diameter. The displacement y at $L/2$ is given by stress analysis as

$$y = - FL^3 / 192 Y I , \quad (4.83)$$

where Y is Young's modulus and I the moment of inertia of the beam;

$I = hd^3/12$ for a ring of height h and thickness d . Therefore,

$$|F| = 192 Y I y / L^3 = \frac{16 h d^3 Y}{L^3} y . \quad (4.84)$$

For a 22 mm diameter ring, height 4 mm, thickness 1 mm, $L = 2.3$ cm,

$h = 4$ mm, $d = 1$ mm, and $y = 81 \mu\text{m}/2 = 40 \mu\text{m}$, we find

$$F = 2.1 \times 10^{-6} Y \quad (4.85)$$

If we make the ring of stainless steel, $Y \sim 2 \times 10^{12}$ dynes cm^{-2} , we find we must exert a force

$$F = 4.2 \text{ kg} .$$

The maximum tensile stress σ in the beam is given by

$$\sigma = \frac{3 FL}{4 hd^2} = 13 \text{ kg mm}^{-2} , \quad (4.86)$$

well within the elastic limit of stainless steel. The corresponding deformation of the copper cold stage is an acceptable $1 \mu\text{m}$. Thus we see that the stage can be supported quite rigidly with little stage deformation and adequate elastic deformation of the support system to compensate stage shrinkage upon cooling. Since the crushing strength of fused silica is 9 kgmm^{-2} , if we assume the stress on 2 mm silica balls acts over an area of 1 mm^2 , we stand no danger of crushing the fused silica supports.

A compression test was made for a fused silica rod supported between stainless steel and phosphorous-deoxidised copper; this configuration exhibited perfectly elastic behaviour (fig 4.14) up to 20 kg (the limit of the test, not the elastic limit) with no evidence of silica failure.

4.8 Resolution

Since the cold stage must necessarily sit in the upper pole piece bore of the objective lens, and is bound to involve certain considerations of space in excess of normal requirements, we must know what changes in geometry, dimension and focal length may be made in the objective lens system without sacrificing acceptable resolution.

4.8.1 Objective lens design

Fig 4.15 illustrates typical pole piece geometry for the objective lens of the Siemens Elmiskop I electron microscope. Upper and lower pole piece bores, radii R_1 and R_2 are separated by a gap distance S . The object is located a distance z_o called the focal distance above the centre of the gap, and a distance f_o called the focal length from the principal plane of the lens. The lens is energized by NI ampere turns focusing relativistic electrons of energy $E_r = E(1 + 10^{-6} E)$ where E is the accelerating voltage.

Liebmann (1957) has shown that in an assymetrical lens with upper and lower bore radii R_1 and R_2 can be treated as a symmetrical lens with mean diameter $D = R_1 + R_2$ and that the quantity

$$\frac{f_o}{S+R_1+R_2} \left(\frac{NI}{E_r} \right)^2 = K \quad (4.87)$$

for an assymetrical lens is approximately constant to within a few per cent for $0.5 < S/(R_1 + R_2) < 2.0$ and weak lens excitation and low accelerating voltage. This representation enables focal properties for a useful range of lens geometry and excitation to be displayed in a series

of unified curves. Unfortunately, the region $S / (R_1 + R_2) < 0.5$ is the region of interest for pole pieces with increased accommodation space, and excitation is very high for 100 kV microscope lenses; substantial deviations from (4.87) occur in both cases. In other words, the focal properties of strong lenses, such as used in modern microscopes, do not lie on single curves, and cannot be accurately represented in unified presentations or by the simple formulation $f \propto NI^2$ often assumed. Discrepancies in spherical aberration coefficients are especially sensitive to changes in geometry and excitation.

Mulvey and Wallington (1969) have chosen to present, instead, "absolute" lens properties, by plotting focal data in units of $E_r^{1/2} / B_p$ as a function of the ratio NI / NI_A , where B_p is the magnetic flux density in the pole piece gap, NI the lens excitation, and NI_A the excitation for absolute minimum focal length. $NI_A / E_r^{1/2}$ is nearly a linear function of S/D alone for $0 \lesssim S/D \lesssim 2.0$.

4.8.2 Pole piece focal properties

The properties of two objective lens pole piece designs were calculated using the data of Mulvey and Wallington, for the Siemens Elmiskop I standard 6.5 mm upper bore high resolution pole piece. Properties of very wide 25 mm upper bore pole pieces were then determined to indicate the extreme result of widening the upper bore.

Siemens provides the following data for their objective lens:

normal excitation: 0.480 A, 7500 turns, $NI = 3600$;

maximum excitation: 0.530 A, 7500 turns, $NI_{\max} = 3980$.

The following geometric properties of the two pole pieces were assumed:

<u>6.5 mm</u>	<u>25 mm</u>
2 R ₁ 6.5 mm	2 R ₁ 25 mm
2 R ₂ 2.6 mm	2 R ₂ 2.6 mm
S 2.7 cm	S 2.7 mm
S/(R ₁ + R ₂) 0.59	S/(R ₁ + R ₂) 0.2
f 2.8 mm at 0.480 A	
NI _A 3579 A-turns	NI _A 3668 A-turns

The value of B_p was determined from a knowledge of f, NI and S/D for the 6.5 mm pole piece; the same value was assumed for the 25 mm pole piece for the same gap size S.

The results are presented graphically in figs. 4.16 and 4.17. The focal properties z₀, f₀ and the spherical and chromatic aberration constants C_s and C_c have been plotted as a function of objective excitation current.

4.8.3 Resolution

Electrons scattered from a point object through different scattering angles θ in passing through a lens give rise to a resolution limit due to spherical aberration

$$r_s = C_s \theta^3 \quad (4.88)$$

It is customary to assume for θ the optimum objective aperture semi-angle α_{opt} and to combine (4.88) with the expression for aperture diffraction-limited resolution to obtain

$$\alpha_{\text{opt}} = A C_s^{-1/4} \lambda^{-1/4}; \quad (4.89)$$

$$r_s = B C_s^{1/4} \lambda^{3/4}, \quad (4.90)$$

where A and B are constants ~ 1 and λ the electron wavelength ($\lambda = 0.0037$ nm for 100 keV electrons). While this approach may be partially valid for thick amorphous materials, it certainly does not represent the true resolution limit for diffraction contrast from crystalline specimens. In this case we must let θ represent the distribution of elastically and inelastically scattered electrons passing through the lens; of those electrons contributing to diffraction contrast, the elastically scattered ones describe nearly a δ function (broadened by finite incident divergence, shape and defect effects), while electrons undergoing low order plasmon scattering are scattered through very small angles only and likewise preserve diffraction contrast (see §3.6). The breadth of this scattering will be smaller than a typical objective aperture angle ($\sim 5 \times 10^{-3}$ rad) and it is this angular distribution which must be put into (4.88).

Crick and Misell (1971) have shown that even for the case of amorphous carbon films, the total scattering is strongly peaked in the forward direction at small angles, and the breadth of this distribution is considerably less than the aperture angle.

It is altogether probable that resolution is instead limited by chromatic aberration, since in a foil of moderate thickness ($\sim$ plasmon mean free path) nearly all electrons have lost energy, and electrons emerging from the specimen form a chromatic spread. The resolution by chromatic lens aberration is given by

$$r_c = \theta C_c \delta E/E, \quad (4.91)$$

where δE is the energy loss and E the electron energy. In very thin foils we must consider a δE equal to the difference between the zero loss and the mean energy loss, amounting to ~ 25 V. For thicker specimens, we must instead begin to consider the effective breadth of the energy loss distribution itself (Misell and Crick 1969). θ must again represent the principal angular distribution of the electrons passing through the aperture. In a thick foil an angular divergence of 10^{-3} rad and $C_s = 3$ mm produce a negligible resolution limit due to spherical aberration $r_s = 0.003$ nm; but an energy breadth 30 V and $C_c = 2$ mm for the same angular divergence lead to $r_c = 0.6$ nm.

In figs.4.16 and 4.17, we have also plotted the parameters $r_s = C_s^{1/4} \lambda^{3/4}$ and $r_c = \theta C_c \delta E/E$. For r_c we assume an angular divergence $\theta = 10^{-3}$ rad and an effective energy loss breadth $\overline{\delta E} = 20$ V for $E = 10^5$ V. Of course, r_s will be an absolute upper bound for resolution limited by spherical aberration r_s ; this limit can be realised if an objective aperture size $\alpha_o = A C_s^{-1/4} \lambda^{1/4}$ is used. The objective aperture diameter will be given by $d_o = 2 z_o \alpha = 2 z_o r_s^{-1} \lambda$ and is seen to actually increase with specimen height, although α_{opt} is decreasing. It is clearly seen that the principal effect of widening the upper pole piece bore is appreciable sacrifice of resolution due to increased chromatic aberration. There is very little sacrifice in resolution for specimen elevation by 1 mm in the normal 6.5 mm bore lens, and since the upper bore tapers outwards (fig.4.15), specimen elevation in a narrow bore pole piece appears the better way to obtain increased space for the helium stage without appreciable sacrifice of resolution.

The r_c curves incidentally illustrate the need to keep incident beam divergence small when using focussed illumination; this is most easily achieved using the smallest possible (50 μ m) condensor aperture, using higher beam currents (above the condensor aperture) if necessary to maintain sufficient image intensity.

4.8.4 Magnification changes with specimen height

If the Gaussian image plane of the objective lens is located at S' from the centre of an objective lens of focal length f_o , and if $S' \gg f_o$, the image magnification M_i is given by

$$M_i = \frac{S'}{f_o} . \quad (4.92)$$

In practice, $M \sim 25$ for a Siemens objective, so the assumption $S' \gg f_o$ is essentially valid. For a given intermediate lens excitation corresponding to focus at S' , the magnification M_i is seen to vary as f_o^{-1} . Raising the specimen height z_o results in a corresponding increase in f_o and decrease in magnification. The fractional change in magnification relative to magnification at normal focal length is plotted in figs. 4.16 and 4.17 for both 6.5 and 25 mm pole pieces. The magnification factor is conveniently nearly linear with objective excitation over the normal excitation range; this relationship, rather than the usually assumed I^2 proportionality, arises in strongly excited lenses (such as those used in the modern electron microscope); at lower excitations, where the thin lens approximation holds rather better, the magnification assumes a more parabolic shape. This is a point often overlooked when using the data of, for example, Liebmann (1955), and indicates the substantial deviations from (4.87) which occur for strongly excited lenses.

It will be seen that wider bore pole pieces result in a considerable decrease in magnification; one consequence is that accurate selected area diffraction must be accomplished at much lower values of image magnification, which is inconvenient when viewing, for example, small radiation damage loops. One alternative is to increase projector magnification in compensation. However, this also increases the size (and limits the field) of the diffraction pattern which is already enlarged for specimen position higher than normal.

The magnification of the diffraction pattern M_d with increasing specimen height, i.e. with decreasing lens excitation (a corresponding decrease in the image magnification M_i occurs as seen above), arises from the change of position of the back focal plane of the objective lens where the diffraction pattern is formed. As the focal plane moves farther from the central axis of the lens toward the intermediate lens (f_o increases as z_o increases), the diffraction pattern becomes increasingly magnified. Thus the magnification $M_d \propto f_o$ (cf. $M_i \propto f_o^{-1}$) if we neglect the small change in position of this diffraction plane relative to the intermediate lens. M_d has also been plotted in figs. 4.16 and 4.17.

4.8.5 Objective excitation in elevated positions

The Siemens Elmiskop I provides only a limited range of objective current control for each accelerating voltage step 40, 60, 80 and 100 kV. The current ranges appear in fig.4.18, and it is clear from fig 4.16 that the available excitation will only accommodate changes in specimen height less than ± 1 mm. To provide for further elevation, the

objective lens current controller circuit must be suitably modified to provide weaker lens excitation; the necessary modifications are summarised in fig. 4.18. Resistances $R_1 - R_4$ are normally progressively shunted across the objective controller as the accelerating voltage is raised to provide progressively stronger excitation ranges. It is sufficient simply to divorce switching of these additional resistors from the kilovoltage switch by providing a separate objective range switch, the system then providing 192 - 530 mA excitation in four overlapping ranges. In this way there is provision for specimen elevation up to nearly 10 mm above normal position for 80 and 100 kv accelerating voltages. An accurate milliammeter measuring objective lens current provides a sufficient indication of objective lens magnification factors.

4.9 Specimen Tilt

One feature of previous low temperature stages has been rather limited tilting capacity for the specimen. As it was intended in this study to perform on the alkali halides the sort of contrast experiments accomplished with metals, the minimum adequate tilting facility had to be determined.

4.9.1 Useful tilting range

Fig. 4.19 shows a standard stereographic triangle with the

principal poles containing useful low order reflections for the NaCl and CsCl alkali halides labelled.

It will be seen that from each of the low index poles 001, 011, 111, the next nearest useful poles are nearly 20° away. Therefore, we conclude that to be really useful, tilting facility must extend over at least 20° , and preferably $\pm 20^{\circ}$. The two sorts of tilting devices capable of attaining this range of tilt without obscuring the incident beam are the Valdrè (1962) double-lever tilting ball cartridge and the Ward (1967) platform-tilting cartridge. The Ward cartridge has been used occasionally for room temperature microscopy in these studies, but it presents considerably more bearing surface friction than the simpler Valdrè ball system and is far less reliable. Therefore, it was decided to adapt the Valdrè cartridge for use at liquid helium temperatures.

4.9.2 Use of tilting cartridges at low temperatures

The two problems that affect use of tilting cartridges intended for room temperature in cryogenic applications are sticking and provision of an adequate thermal path to the specimen.

With regard to sticking, small amounts of finger grease, hydrocarbon vapour, condensed water, etc., will solidify at low temperatures and cause the tilt to stick, the tilt return springs not being strong enough to overcome the increased friction. (No difficulty, however, is experienced with the elastic properties of the beryllium-copper springs which are usually used, since these improve at lower temperature.)

Obviously, scrupulous cleanliness must be practiced with the holder, which must be kept free from finger grease and out of oxidizing environments. A simple remedy decreases operating friction considerably: the bearing and sliding surfaces of the tilt pushers, which act on the first tilting lever, are coated with colloidal graphite ("Aquadag"), and likewise the lever surfaces on which they act. With this precaution no sticking has ever been experienced, even at 5 K.

As discussed in §4.3.1.2, mechanical contacts have been found to exhibit poor thermal paths at low temperatures. Accordingly, it is not sufficient to rely on the mechanical socket support of the tilting ball for adequate heat transfer: a direct thermal path through soldered joints must be provided. This is most easily accomplished by soldering the ends of a 0.1 mm diameter copper wire in the form of a 1-turn helix directly to the ball and to the bulk holder; such a spring exhibits adequate flexion and, additionally, serves to mechanically stabilize the ball which must be slightly free in its socket for smooth tilting. The thermal conductivity at 4 K of drawn copper is typically $\sim 1 \text{ W cm}^{-1} \text{ K}^{-1}$ (Johnson 1961), and the rate of heat transfer through this wire $\dot{q} \sim 100 \text{ } \mu\text{W K}^{-1}$. We have seen from §4.2.3 that radiative and beam heating inputs to the specimen are not likely to be $> 100 \text{ } \mu\text{W K}^{-1}$, so we conclude that the wire provides an adequate thermal path. Beryllium-copper would provide a more elastic helix, but its conductivity at 4 K is $\sim 20 \text{ mW cm}^{-1} \text{ K}^{-1}$ and provides a thermal path only $\dot{q} \sim 1 \text{ } \mu\text{W K}^{-1}$ which is less than adequate.

The tilting ball weighs $\sim 0.1 \text{ g}$, with an enthalphy $\sim 8 \text{ J}$ at 300 K. Since the mean conductivity $\bar{\kappa}$ of the copper wire is $\sim 1 \text{ W cm}^{-1} \text{ K}^{-1}$, we

expect on cooling an average heat transfer rate $\sim 15 \text{ mJ sec}^{-1}$ or a cooling time of $600 \text{ sec} = 10 \text{ min}$. This is comparable to the time allowed for the stage to cool and stabilize at low temperature.

An adequate thermal path to the cartridge itself is maintained by a thin film of silicone vacuum grease spread on the cartridge body; this substance transforms at low temperatures to a glass with a thermal conductivity $\sim 100 \text{ } \mu\text{W cm}^{-1} \text{ K}^{-1}$ at 5 K (Reese and Tucker 1965), which is adequate given the large surface area and a thin film. If the cartridge body presents a surface area of 3 cm^2 , a grease film thickness of $10 \text{ } \mu\text{m}$ still permits heat transfer at the rate 3 W K^{-1} , which is better than the phosphorous deoxidized copper in stage and cartridge. The silicone grease also prevents the cartridge inextricably lodging in the stage due to the stage temperature gradient in warming, a very serious problem in the absence of the grease film.

4.9.3 Tilt drives

Thermal conductivity through the tilt push rod - cartridge pusher interfaces is unlikely to present a serious heat leak, even at low temperatures, because of the poor thermal conductivity of pressed contacts under light loads. Dimensional stability at the push rod tip is a far greater concern; to ensure both stability and thermal isolation, tilt pushers are tipped with fused silica rod. These terminations are typically $\sim 1 \text{ mm}$ diameter and offer considerably less thermal path than the ball stage supports, as well as exceptional dimensional stability under the sudden temperature changes induced by variable loading during tilting.

4.10 Liquid Helium Stage Design

4.10.1 Previous helium stage designs

A variety of electron microscope helium temperature stages of varying sophistication and capability has appeared during the past ten years, providing some basis for comparison with a design developed in the present study and delineated in §4.10.2. These stages are of two basic types: reservoir systems and continuous coolant flow systems.

The points of comparison, in approximate order of importance, are:

- (1) resolution/stability
- (2) minimum temperature capability
- (3) tilt
- (4) specimen exchange facility
- (5) coolant consumption
- (6) complexity (additional shielding, etc.).

We briefly indicate these relevant features of each stage design in Table 4.10. The small latent heat of liquid helium means that reservoir stages are accompanied by appreciable nucleate boiling unless extensive thermal shielding (usually liquid nitrogen- or exhaust gas-cooled) is employed and conductive losses reduced to the bare minimum. The latter condition is somewhat at variance with the support requirement for a large reservoir. Reservoir systems are relatively inconvenient because specimens cannot usually be removed until the reservoir is exhausted and warmed to room temperature, and they are uneconomical because of the initially large heat capacity of the reservoir and the wastage when an experiment is terminated before the reservoir is exhausted.

Extreme stability has been demonstrated when the helium stage is integral with a superconducting objective lens, but helium consumption for such a system is prohibitively high for routine studies.

By comparison, continuous coolant flow designs offer considerably more flexibility and far less complexity. As was shown in §4.2, the thermal radiation shielding required may be dispensed with because of the much higher heat exchange efficiency of flowing cryofluids. There is little waste in terminating experiments, and consumption is generally lower because the stage support requirements are considerably less stringent. Intermediate temperatures are obtained with even larger economy, in comparison with reservoir systems where additional heat must be applied (and thus increased consumption) to elevate the specimen temperature.

The resolution attained with either system is directly related to the thermal stability of the insulating supports; the use of fused silica supports, in preference to plastic supports, by a number of workers (Venables et al. 1968; Colliex and Jouffrey 1968; Hobbs 1970b) has provided consistent thermal and mechanical stability. Of considerable importance to routine work is provision for rapid and straightforward specimen exchange, without the necessity of breaking the microscope column or disassembling the helium stage. Finally, simple and straightforward design is a necessity when a stage must be frequently installed and removed from a microscope in demand by other users.

4.10.2 Present design

Fig.4.20 through 4.22 illustrate a simple and straightforward liquid helium stage conforming to the principles outlined in previous sections and designed for rapid installation on a Siemens Elmiskop I microscope.

Fig.4.20 is a cross-section diagram of the stage. The modified Valdre double-tilt cartridge, lightly greased with silicone vacuum grease, seats in a phosphor-bronze helium flow chamber supported from a stainless steel ring by three fused quartz balls Q riding in stainless steel screw sockets. An integral 0.25 mm thick cold shield is soldered to the bottom of the helium chamber, centrally bored with an 800 μ m diameter hole. A similar 800 μ m cold aperture is placed in the screw-in withdrawal holder. A 0.1 mm copper spring spirals around the cartridge tilting ball and is soldered to the ball at one end and to the cartridge body at the other.

The stainless steel ring anchors in the brass stage block illustrated in fig.4.21 by means of four stainless steel screws. The quartz-tipped threaded tilt rods screw into this stage block and are driven by standard Siemens tilt drives. A special dog-leg drive assembly, shown installed in fig.4.22, was installed for the right hand tilt drive in order to clear the specimen loading lock. Helium gas or liquid is supplied to the stage through a flexible brass bellows in each helium line. The entire assembly is accommodated in the standard 6.5 mm diameter high resolution objective pole piece, the specimen elevated 1 mm above normal specimen height. Specimen translation is maintained over nearly a 1 mm area.

Fig.4.22 shows the stage installed in a special steel chamber in the column of the Siemens Elmiskop I microscope. A viewing window in the chamber and an internal light source aid in loading the specimen cartridge from the specimen loading lock. Helium is supplied via a standard 17 litre dewar and a removable evacuated transfer tube. Pressurisation is maintained by the helium gas cylinder and pressure regulation is monitored by a 1 m alcohol manometer (not shown). The exit line, obscured by the electron gun adjustments, is left open to the atmosphere. A microvoltmeter indicates thermocouple e.m.f., referenced to the liquid nitrogen reference bath shown. The external objective lens current range controlling switch and monitoring milliammeter are also shown. A timer is used for estimating total helium consumption and for gauging cool-down rates.

The specimen cartridge is loaded into the stage with the removable vacuum loading lock described in §3.4.2. For specimens to be loaded or removed under maintained vacuum, the microscope column must be let down to air, though as indicated in §4.6.7.3 this is no inconvenience provided dry air is admitted. If the vacuum transfer facility is not essential, the loading lock may be utilised as a normal evacuable specimen loading airlock into the evacuated microscope column.

A particular advantage in this stage and its integral cold shield is that it will accept any Siemens specimen cartridge (non-tilting, stereo, magnetic, raised position, Valdrè double-tilt, in-situ straining, even heating) with no modification.

4.11 Special Problems in Cryomicroscopy of Alkali Halides

Difficulties in cryomicroscopy of alkali halide foils have mainly to do with thermal stresses arising from thermal shock and differential thermal expansion during cooling. Since the alkali halides easily cleave under sudden stresses and yield easily under small prolonged stresses, the rather large thermal contractions and poor thermal conductivity peculiar to alkali halides may result in considerable specimen degradation (for example, cleaving off of thin areas or considerable plastic flow) during cooling unless adequate precautions are taken to minimise cooling rates and eliminate differential mounting stresses.

4.11.1 Quenching stresses

Fig.4.23 shows the stress birefringence pattern exhibited by an NaCl crystal dropped into liquid nitrogen, illustrating the extent of deformation introduced by thermal stresses arising during rapid cooling. These stresses have been noted by Kear and Pratt (1959) but have not been subjected to analysis. It is significant that the propagation of slip bands extends throughout the crystal. Since rather similar, though less drastic, imposed temperature and stress conditions will occur during the cooling of thin foil specimens supported and cooled from their outer edges, it is particularly important to analyse the extent and magnitude of these stresses and to ascertain the conditions under which they may be rendered negligible. There are two specific aspects to be considered: the first is that a temperature differential is established across the foil with different parts of the foil contracting at different rates; the second is that both thermal expansion

coefficient and thermal conductivity are functions of temperature with cooler areas expanding more slowly and conducting rather better than warmer regions under the same temperature gradient. To an extent, the temperature dependence of the thermal expansion coefficient and conductivity will tend to mitigate the severity of differential expansion along a temperature gradient. However, since the expansion coefficient of a typical alkali halide (fig 4.24) reduces by only one-third between 300 K and 100 K, the range over which most of the contraction takes place, and the conductivity increases very little until ~50 K, this counter effect is small and we shall assume the expansion coefficient and conductivity temperature independent.

If a cylinder of radius s , conductivity κ , specific heat C_p , density ρ , and expansion coefficient α is initially at constant temperature T_o , and its outer surface is suddenly maintained at temperature $T' < T_o$ at time $t = 0$, the temperature at radius r at any time t is given by the series

$$T(r,t) - T' = (T_o - T') \sum_{n=1}^{\infty} \frac{J_o(B_n r/s)}{B_n J_1(B_n)} \exp(-a_n t) \quad (4.93)$$

where J_o and J_1 are first and second order Bessel functions, B_n are the zeroes of J_o , and a_n are given by

$$a_n = \frac{\kappa}{C_p \rho} \frac{B_n^2}{s^2} \quad (4.94)$$

Since the B_n are 2.4, 5.5, 8.7, and the B_n^2 appears in a negative exponential, we shall neglect terms of the series higher than order 1. Substituting typical values for an alkali halide foil into (4.94) we obtain from (4.93)

$$T(r,t) - T' = (T_0 - T') 1.67 \exp(-3.6 t) \quad (4.95)$$

and we note that there will be a negligible temperature difference between specimen edge and specimen centre after about 1 - 2 sec, even for $T' = 0$ K. We therefore conclude that approximate thermal equilibrium is achieved rather more rapidly than we can cool the cold stage.

The thermal stresses arising from this established temperature gradient are derived by Timoshenko and Goodier (1970) considering only first order series terms

$$\begin{aligned} \sigma_r &= \frac{2 \alpha Y (T_0 - T')}{1 - \nu} \exp(-\alpha t) \left\{ \frac{1}{B_1^2} - \frac{1}{B_1} \frac{J_1(B_1 s/r)}{B_1 s/r J_1(B_1)} \right\} \\ \sigma_\theta &= \frac{2 \alpha Y (T_0 - T')}{1 - \nu} \exp(-\alpha t) \left\{ \frac{1}{B_1^2} + \frac{1}{B_1} \frac{J_1(B_1 s/r)}{(B_1 s/r) J_1(B_1)} - \frac{J_0(B_1 s/r)}{B_1 J_1(B_1)} \right\}, \end{aligned} \quad (4.96)$$

where Y is Young's modulus ($= 1/S_{11} \sim 5 \times 10^{11}$ dynes cm^{-2}), ν is Poisson's ratio (~ 0.25) and $\alpha \sim 4 \times 10^{-5}$. In the centre of the foil we have

$$\begin{aligned} \sigma_r &= -470 (T_0 - T') \exp(-3.6t) \text{ g mm}^{-2} \text{ (compressive)} \\ \sigma_\theta &= +97 (T_0 - T') \exp(-3.6t) \text{ g mm}^{-2} \text{ (tensile)}. \end{aligned} \quad (4.97)$$

If our cooling temperature decrement ($T_0 - T'$) is made over a period of 1 sec, we have stresses

$$\begin{aligned} \sigma_r &= -13 (T_0 - T') \text{ g mm}^{-2} \\ \sigma_\theta &= +2.7 (T_0 - T') \text{ g mm}^{-2} \end{aligned} \quad (4.98)$$

and we note that cooling rates must be restricted to a few K sec^{-1} if the yield stress in undeformed crystals ($\sim 20\text{-}30 \text{ g mm}^{-2}$) is not to be exceeded. Consequently a cooling rate $\sim 1 \text{ K sec}^{-1}$ is maintained throughout cooling to preclude such plastic deformation.

4.11.2 Differential contraction stresses in mounting

If an alkali halide foil is firmly fixed about its perimeter to a material of different thermal expansion coefficient (not to say differing conductivity), differential contraction stresses will arise upon cooling, increasing with increased cooling. This problem was briefly indicated in §3.4.3 and an alternative mounting procedure described. We shall here demonstrate the severity of these induced stresses via the magnitude of the virtual strains.

In fig.4.24 the thermal expansion coefficient for NaCl (other alkali halides are very similar) has been plotted as a function of temperature; more to the point, the total fractional contraction in cooling has been plotted for NaCl and two metals, Zn and Cu. (Zn was initially chosen as a mounting ring because (of all machinable metals) its contraction characteristics most closely approach those of alkali halide crystals.) If either of these metals is used as a mounting ring (together with a very thin layer of cement) the difference between their fractional contraction and that of the alkali halide specimen is a direct indication of the strain that must be accommodated by nucleation and movement of dislocations or crack propagation. It is apparent that strain of the alkali halide will be positive, i.e. a tensile stress, since alkali halides contract more

than metals. The magnitude of the radial strain to be accommodated will be, from fig 4.24

$$\epsilon_r \sim 6 \cdot 10^{-4} \quad \text{for zinc}$$

$$\epsilon_r \sim 5 \cdot 10^{-3} \quad \text{for copper.}$$

This strain may be accommodated by the passage of dislocations across the foil, leaving behind observed slip traces and a kinked foil; the process is illustrated schematically in fig 4.25. If the foil is an (001) section, the slip geometry will be as indicated in fig.4.25(a), or for a (101) section in fig 4.25(b). The elongation accommodated by passage of one dislocation will be respectively $b\sqrt{2}/2$ and $b\sqrt{3}/2$, or ~ 0.3 nm.

Consider a uniformly thin foil cemented to a Cu mounting ring 2 mm diameter. The total radial elongation normal to each set of slip planes is $10 \mu\text{m}$ upon cooling from 300 K to below 50 K; therefore, passage of $\sim 2 \times 10^4$ dislocations is required, or a separation ~ 100 nm between slip traces in each slip system. Fig 4.26 illustrates micrographs taken from two thin specimens of (001) and (101) orientations, mounted on Cu rings and cooled slowly to 10 K; the slip systems are clearly evident, and the slip trace separation is ~ 100 nm as expected. When a Zn ring is used, the slip trace spacing is on average 5-10 times larger.

In a heavily dished specimen, where there is considerable thickness disparity between the specimen perimeter and the thinned region, the maximum stress will occur in the central thin areas, and it is high enough to initiate cleavage cracks. These propagate across the entire specimen and fracture off most of the thinned area. However, extensive initial cleavage does preclude further plastic deformation by slip.

Clearly, neither mode of strain accommodation is particularly desirable, and a single point mounting system free from differential strains, as described in §3.4.3, is to be preferred.

TABLE 4.1

CRYOGENIC FLUID PROPERTIES

	T_b (K)	C_p (J g ⁻¹)	λ_v (J g ⁻¹)	κ (mw cm ⁻¹ K ⁻¹)	ρ (g cm ⁻³)	μ (μ poise)	COST (UK £ 1 ⁻¹)
He	1 4.21	4.5	21	0.27	0.126	36	2.0
	g -	7.0 (4K) 6.0 (10K)	-	0.1 (4K) 0.17 (10K)	0.01 (4K) 0.005 (10K)	10.4 (5K) 22.3 (10K)	
H ₂	1 20.39	9.8	455	1.19	0.07	132	1.0
	g -	12.7	-	0.16	0.07	10.5	
N ₂	1 77.36	2.25	213	1.38	0.81	1580	0.05
	g -	1.05	-	0.07	0.0045	60	
O ₂	1 90.18	1.7	209	1.47	1.14	1900	0.10
	g -	0.92	-	0.084	0.0045	70	
A	1 87.4	1.13	159	1.22	1.40	2520	
	g -						

TABLE 4.2

Flow Properties of Cryogenic Helium in Forced Convection

It is assumed the cold stage has an internal surface area 10 cm^2 , cross section for flow 0.1 cm^2 and an equivalent flow diameter 0.25 cm . The transfer tube or exit pipe is assumed to have an internal diameter 0.25 cm .

	gas, 4K	gas, 10K	liq, 4K (1 lh^{-1})	liq, 4K (10 lh^{-1})	liq→10% gas	liq→50% gas	Exit gas, $T = 150\text{K}$
$\dot{m}$ (g sec^{-1})	0.035	0.035	0.035	0.35	0.035	0.035	0.035
G ($\text{g sec}^{-1} \text{cm}^{-2}$)	0.35	0.35	0.35	3.5	0.35	0.35	0.35
ρ (mg cm^{-3})	10	5	126	126	37 (ρ_f) 58 (ρ_g)	9.6 (ρ_f) 19 (ρ_g)	30
κ ($\text{mw cm}^{-1} \text{K}^{-1}$)	0.10	0.17	0.27	0.27	0.17 ($\kappa_{f,v}$)	0.17 ($\kappa_{f,v}$)	
C_p ($\text{J g}^{-1} \text{K}^{-1}$)	7	5.5	4.5	4.5	5.5 ($C_{p_{f,v}}$)	5.5 ($C_{p_{f,v}}$)	
μ ($\mu \text{ poise}$)	10.4	22	36	36	22 ($\mu_{f,v}$)	22 ($\mu_{f,v}$)	130
Re	8420	3950	2430	24300	2780 (Re_f)	2200 (Re_f)	1230 (pipe)
Pr	0.73	0.71	0.60	0.60	0.72 ($\text{Pr}_{f,v}$)	0.72 ($\text{Pr}_{f,v}$)	
Nu	30.4	$\begin{Bmatrix} 8.5^1 \\ 16.6^t \end{Bmatrix}$	$\begin{Bmatrix} 6.9^1 \\ 11.6^t \end{Bmatrix}$	73	8.3	17.7	
h ($\text{w cm}^{-2} \text{K}^{-1}$)	0.012	$\begin{Bmatrix} 0.006^1 \\ 0.011^t \end{Bmatrix}$	$\begin{Bmatrix} 0.008^1 \\ 0.013^t \end{Bmatrix}$	0.079	0.0056	0.0012	
q_f (w K^{-1})	0.12	$\begin{Bmatrix} 0.057^1 \\ 0.11^t \end{Bmatrix}$	$\begin{Bmatrix} 0.075^1 \\ 0.13^t \end{Bmatrix}$	0.79	0.056	0.012	
Q (λ) (w)	-	-	-	-	0.06	0.33	
Q, 5K (w)	0.12	0.11 ^t	0.13 ^t	0.79	0.12	0.34	

1, laminar t, turbulent

•

Table 4.2 (contd)

	Gas, 4K (1 lh ⁻¹ liq)	liq, 4K (1 lh ⁻¹)	liq, 4K (10 lh ⁻¹)	Exit gas, $\bar{T} = 150K$ (1 lh ⁻¹ liq)
f, stage	0.033	0.047	0.025	-
f, pipe	0.029	0.040	0.022	0.052
P _M (dynes cm ⁻²)	12.2	1.0	100	408
P _e , 3m (dynes cm ⁻²)	980 (0.07 torr)	12000 (9.1 torr)	12000 (9.1 torr)	-
P _f , stage (dynes cm ⁻³)	5.7	0.091	4.9	-
P _F , stage (dynes cm ⁻²)	41 (negligible)	0.65 (negligible)	35 (negligible)	
P _f , pipe (dynes cm ⁻³)	2.4	0.26	4.3	42
P _F , 3m pipe (dynes cm ⁻²)	713 (0.05 torr)	78 (0.005 torr)	1300 (0.1 torr)	13000 (9.9 torr)

Table 4.3

Momentum Pressure Changes for Helium Flow

χ (%)	R_l (%)	R_g (%)	Δp_M (dynes cm ⁻²)	p_M (dynes cm ⁻²)	Pressure Change	
0	100	0	0	1.0		↑
1	64	35	0.54	1.5	} 54%	unstable
5	40	60	1.3	2.3	} 53%	
10	32	68	1.7	2.7		
15	26	74	2.1	3.1	} 16%	
20	23	77	2.35	3.4	} 8%	↓
25	21	79	2.6	3.6	} 7.5%	
30	19	81	2.9	3.9	} 7.5%	
35	17	83	3.1	4.1	} 7.5%	
90	3	97	9.5	10.5		stable
95	2	98	10.3	11.3	} 7.5%	
					} 8.0%	
100	0	100	11.2	12.2		

Table 4.4

Dynamic Cooling Parameters for Cryogenic Helium

	T, K				
Helium	300	150	50	20	10
ρ (mg cm ⁻³)	0.15	0.35	1.0	2.5	5.0
κ (mw cm ⁻¹ K ⁻¹)	1.5	0.97	0.47	0.26	0.17
C_p (J g ⁻¹ K ⁻¹)	5.8	5.8	5.8	5.8	5.5
μ (μ poise)	205	130	65	36	22
Stage					
$\dot{m}$			0.035 g sec ⁻¹		
G			0.35 g sec ⁻¹ cm ⁻²		
Re	428	675	1350	2430	3950
Pr	0.79	0.78	0.80	0.80	0.71
Nu	4.3	4.9	6.3	7.6	16.6
$\dot{q}$ (w K ⁻¹)	0.25	0.19	0.12	0.08	0.11
f	0.146	0.095	0.047	0.026	0.035
$C_{p, \text{Copper}}$ (J g ⁻¹ K ⁻¹)	0.35	0.3	0.1	0.007	0.00086
$C_{p, \text{Stage}}$ (J K ⁻¹)	14.0	12.0	4.0	0.28	0.034
Q, input (w)	0	0.38	0.65	0.70	0.72
$\dot{T}_s$ (λ) (Ksec ⁻¹)	0.052	0.061	0.184	1.05	
$\dot{T}_s$ (f) (Ksec ⁻¹)	2.0	1.15	1.17		

Table 4.4 (contd)

	300	150	50	20	10
<u>Transfer tube</u>					
$\frac{\sigma}{G(\text{g sec}^{-1}\text{cm}^{-2})}$	0.11	0.42	0.70	2.0	3.0
Re	134	810	2700	12500	33500
f	0.48	0.079	0.024	0.030	0.023

Table 4.5

Flow Properties of Cryogenic Nitrogen in Forced Convection

	gas, 77K (1 lh ⁻¹ liq eq.)	liq, 77K (1 lh ⁻¹)	gas, 77K (10 lh ⁻¹ liq eq.)
$\dot{m}$ (g sec ⁻¹)	0.225	0.225	2.25
G (g sec ⁻¹ cm ⁻²)	2.25	2.25	22.5
ρ (mg cm ⁻³)	4.5	810	4.5
κ (mw cm ⁻¹ K ⁻¹)	0.07	1.38	0.07
C_p (J g ⁻¹ K ⁻¹)	1.05	2.25	1.05
μ (μ poise)	60	1580	60
Re	9400	355	94000
Pr	0.9	2.6	0.9
Nu	33.8	5.9	213
h (mw K ⁻¹ cm ⁻²)	9.5	330	60
$\dot{q}_f$ (w K ⁻¹)	0.1	0.33	0.6
$\dot{Q}$ (λ)(w)(total conversion)		48	
f , stage	0.032	0.18	0.019
f , pipe	0.028	0.09	0.016
p_f , pipe (dynes cm ⁻³)	254	4.5	14500
p_f , 3m pipe (torr)	58	1	3140 (4 atm!)
p_e , 3m (torr)	13.2	180	13.2

Table 4.6

Gas Sublimation Temperatures*

Gas	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}
H ₂ O	162.0	173.0	185.0	198.5	215.0
CO ₂	85.7	91.5	98.1	106.0	114.5
Xe	58.2	62.7	68.1	74.4	82.1
Kr	42.2	45.5	49.4	53.9	59.4
O ₂	31.9	34.1	36.7	39.8	43.3
A	30.6	33.1	35.9	39.2	43.2
N ₂	27.0	29.0	31.4	34.1	37.5
Ne	8.5	9.2	10.1	11.1	12.3
H ₂	4.4	4.8	5.4	6.1	6.9

* Honig and Hook (1960)

Table 4.7

Molecular Kinetics at 300 K and 10^{-5} torr Partial Pressure

gas	occurrence %	E_K (eV molecule ⁻¹)	n (cm ⁻³)	$\bar{c}$ ($\times 10^4$ cm sec ⁻¹)	$\bar{x}$ (cm)	ϕ ($\times 10^{15}$ cm ⁻² sec ⁻¹)	Q_{subl} (eV molecule ⁻¹)
N ₂	75.5			4.75	4.8	3.90	0.0703
O ₂	20.3			4.44	5.2	3.64	0.0814
H ₂ O	3.4			5.93	3.2	4.87	0.528
A	0.9			3.98	5.1	3.27	0.0867
CO ₂	0.029	0.0328	3.2×10^{11}	3.78	3.2	3.11	0.293
Ne	18×10^{-4}			5.60	10.0	4.60	
He	5.2×10^{-4}			12.5	14.2	10.3	
Kr	1.0×10^{-4}			2.74	3.9	2.25	
H ₂	0.5×10^{-4}			17.7	8.9	14.5	
X _e	0.08			2.19	2.9	1.80	

Table 4.8

Contamination Rates

Rates are for H₂O, assuming unity sticking coefficient
 for N₂, multiply by 1.1
 for O₂, multiply by 0.87

Ω	$\frac{2\pi \text{ sterad}}{\text{nm sec}^{-1}}$		$\frac{1 \text{ sterad}}{\text{nm sec}^{-1}}$		$\frac{0.2 \text{ sterad}}{\text{nm sec}^{-1}}$		$\frac{0.02 \text{ sterad}}{\text{nm sec}^{-1}}$	
$P \text{ (torr)}$	nm hr^{-1}	nm hr^{-1}	nm hr^{-1}	nm hr^{-1}	nm hr^{-1}	nm hr^{-1}	nm h	nm h
10^{-7}	3.2×10^{-2}	115	2.5×10^{-3}	45.6	5.1×10^{-4}	1.8	5.1×10^{-5}	0.18
10^{-6}	0.32	1145	2.5×10^{-2}	91.1	5.1×10^{-3}	18.3	5.1×10^{-4}	1.83
5×10^{-6}	1.6	5740	0.13	456	2.5×10^{-2}	91.8	2.5×10^{-3}	9.2
10^{-5}	3.2	11450	0.25	911	5.1×10^{-2}	183	5.1×10^{-3}	18.4
5×10^{-5}	15.9	5.74×10^4	1.3	4555	0.25	9.8	2.5×10^{-2}	91.8
10^{-4}	31.8	1.14×10^5	2.5	9110	0.51	1836	5.1×10^{-2}	184

Table 4.9

Thermal Properties of Cold Stage Materials

Fractional Thermal Contraction ($\times 10^{-4}$) from 293 K.

	$\alpha, 20\text{K}$ ($\times 10^{-7}$)	0	20	40	60	80	100	150	200	250
Cu	3.0	32.6	32.6	32.4	31.6	30.2	28.3	22.2	14.9	7.1
Stainless Steel	<5	-	29.7	29.6	29.0	27.8	26.0	20.3	13.8	6.6
Pyrex	<50	5.6	5.6	5.7	5.6	5.4	5.0	3.9	2.7	0.8
Fused Silica	$7.5^{\dagger}$	-0.7	-0.65	-0.5	-0.3	-0.1	0.0	0.1	0.2	0.1
Araldite	$50^{\dagger}$	106	105	102	98	94	88	71	50	25
Nylon	$50^{\dagger}$	139	138	135	131	125	117	95	67	34
Polystyrene	$150^{\dagger}$	155	152	147	139	131	121	93	63	30
PTFE	$150^{\dagger}$	214	211	206	200	193	185	160	124	75
NaCl	~ 6	76	76	76	74	71	66	52	34	15

$\dagger$ estimated from 0 - 20 K contraction data

Table 4.9 (contd)

Thermal Conductivity κ ($\text{mw cm}^{-1}\text{K}^{-1}$, except † $\text{w cm}^{-1}\text{K}^{-1}$)

T, K

	5	10	20	40	80	100	200	300
Cu (high purity)	$85^\dagger$	$135^\dagger$	$89^\dagger$	$20^\dagger$	$5.6^\dagger$	$4.7^\dagger$	$4.6^\dagger$	$4.6^\dagger$
• Phos. deox. Cu	90	200	430	800	$1.25^\dagger$	$1.4^\dagger$	$1.9^\dagger$	$2.3^\dagger$
Beryllium Cu	24	58	105	210	370			
Wood's metal	55	120	170	200	230	240		
Stainless steel	3.0	7.0	20	45	83	94	130	150
Fused silica/Pyrex	1.0	1.2	1.5	2.4	4.5	5.5	9.0	10
Nylon	0.06	0.4	1.0					
Perspex	0.6	0.6	0.75					
Polyethylene	2.0							
PTFE	0.5	0.95	1.4	2.0	2.3			
Carbon resistor	$<<1$	1	3	7	12	13		
NaCl	$6^\dagger$	$10^\dagger$	$3^\dagger$	$1^\dagger$	300			

Table 4.10

Liquid Helium Temperature Microscope Stages

Design	Microscope	(a) Reservoir Stages					Additional Shielding, etc.
		Resolution; Stage Support	Min.T; Coolant	Tilt	Specimen Exchange Facility	Consumption	
Piercey, Gilbert & Howe (1963)	Siemens Elmiskop I	not stated; plastic	20 K LHe	none	normal air-lock; solder cold finger in situ	not stated	none
Boersch et al (1966)	Siemens Elmiskop I	not stated	2.5 K LHe	none	break column	not stated	extensive thermal shield cooled by exhaust gas
Kitamara, Scrivastava & Silcox (1966)	Hitachi HU 11	~ 3 nm; PTFE, nylon pins	4.4 K LHe	$\pm 12^\circ$ double tilt	break column	not stated	extensive LN ₂ thermal shielding
Fernandez-Moran (1966, 1970)	Hitachi HU 11B	0.5-1 nm; superconducting objective lens	1.9 K LHe	none	break column	5-8 l hr ⁻¹	extensive LN ₂ thermal shielding
Berjot et al (1966)	not stated	not stated; superconducting objective lens	4 K LHe	none	break column	not stated	not stated

Table 4.10 (contd)

(b) Continuous Flow Stages

Design	Microscope	Resolution; Stage Support	Min.T; Coolant	Tilt	Specimen Exchange Facility	Consumption	Additional Shielding etc.
Venables (1963)	Siemens Elmiskop I	poor; plastic	15 K LHe	single tilt	normal airlock	not stated	none
Cotterill (1964)	Siemens Elmiskop I	not stated; PTFE socket	not stated He gas	none	break column	not stated	none
Valdrè (1964) Valdrè & Goringe (1965)	Siemens Elmiskop I	fair; nylon socket	5 K L He	$\pm 7^\circ$ double tilt	break column	$3-5 \text{ hr}^{-1}$	none
Valdrè & Goringe (1970)	Cambridge 650 kV	fair; nylon socket	5 K LHe	$\pm 7^\circ$ doubt tilt	special airlock	$3-5 \text{ hr}^{-1}$	none
Watanabe et al. (1966) Watanabe & Ishikawa (1967)	Hitachi 500 kV	not stated; stainless steel points	3 K LHe		normal airlock	2 hr^{-1}	
Schulze & Schimmel (1966)	Siemens Elmiskop I	not stated PTFE pads	15-20 K L He	$\pm 20^\circ$ double tilt	normal airlock	not stated	small cap on end of Valdrè cartridge
Venables (1966) Venables, Ball & Thomas (1968)	Hitachi HU 11B	2.5 nm fused silica	$< 8 \text{ K}$	$\pm 8^\circ$ double tilt	normal airlock	$< 0.5 \text{ hr}^{-1}$ at 10 K	extensive LN_2 thermal and contamination shielding

Table 4.10 (contd)

(b) Continuous Flow Stages (contd)

Design	Microscope	Resolution; Stage Support	Min.T; Coolant	Tilt	Specimen Exchange Facility	Consumption	Additional Shielding etc.
Colliex & Jouffrey (1968)	Hitachi HU 11B	3 nm ; fused silica insu- lation at tilting ball	<8.5 K LHe	$\pm 7^\circ$ double tilt	break column	2.5 lhr ⁻¹	none
Heidl & Urban (1970)	Hitachi 650 kV	not stated; circular PVC	4-300 K auto temp. control, He gas	$\pm 30^\circ$ double tilt	normal airlock	1 lhr ⁻¹ at 18 K	extensive thermal and contamination shielding cooled by exit gas
Honjo et al (1970)	JEM 150	1.7 nm; PTFE	8 K	$\pm 10^\circ$ double tilt	normal airlock	not stated	extensive LN ₂ shielding and constant temperature water cooling for all room temperature parts
Rudman & Flewitt (1970)	AEI 802	poor; cantilever mounting	20 K; Air Products N ₂ gas Joule- Thompson cryotip	$\pm 25^\circ$ single tilt 30° rota- tion	remove cryotip	-	none
Hobbs (1970b) this study	Siemens Elmiskop I	<2.5 nm over 15 sec; fused silica	5 K; LHe or He gas	$\pm 22^\circ$ double tilt; accepts any Siemens cartridge	double vacuum loading lock	1 lhr ⁻¹ at 10 K	integral LHe contamination shield

Fig. 4.1. Warming curve for the liquid helium stage described in §4.10. Broken curve shows the initial low temperature behaviour; dotted line is the specific heat of the (predominantly) Cu stage material for comparison. Note that some external heat source is realistically necessary for warming unless one has considerable patience.

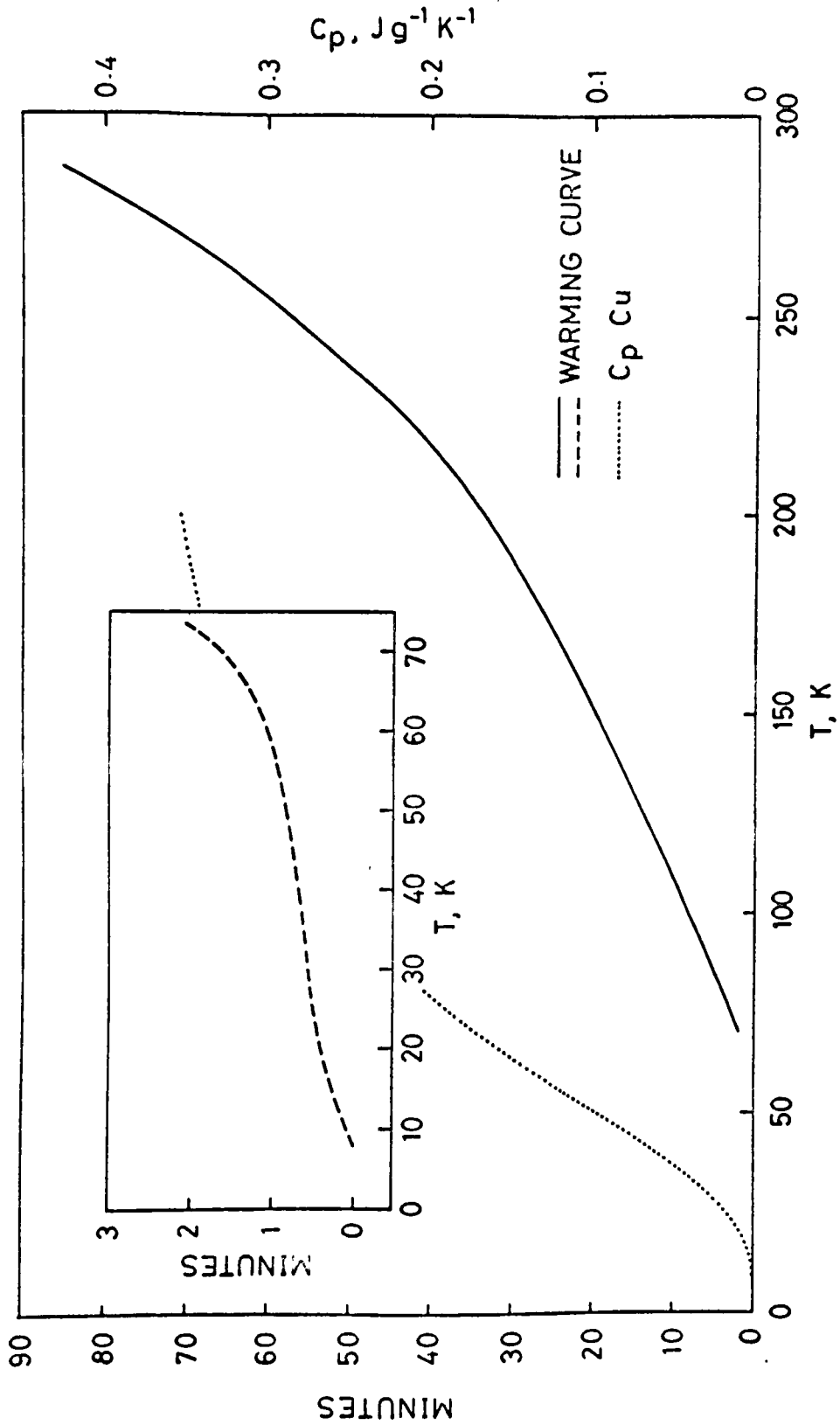


Fig. 4.2. Transfer-tube-to-cold-stage demountable coupling arrangement.

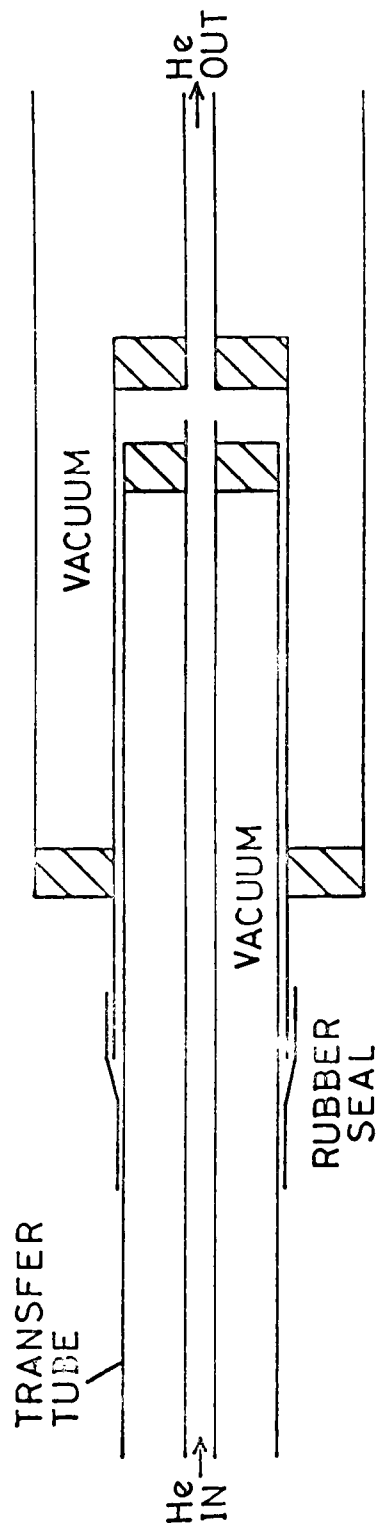
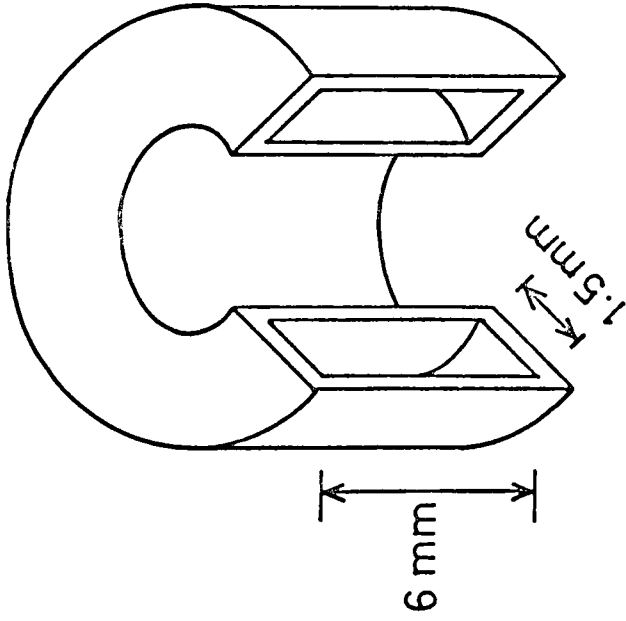
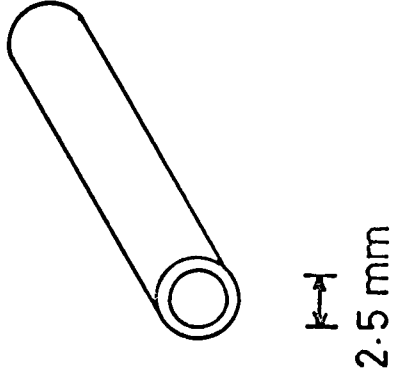


Fig. 4.3. Flow geometries for forced convection. Both transfer tube and cold stage have equivalent flow diameters $D_h = 2.5$ mm, but differ in cross sectional area by a factor of 2.

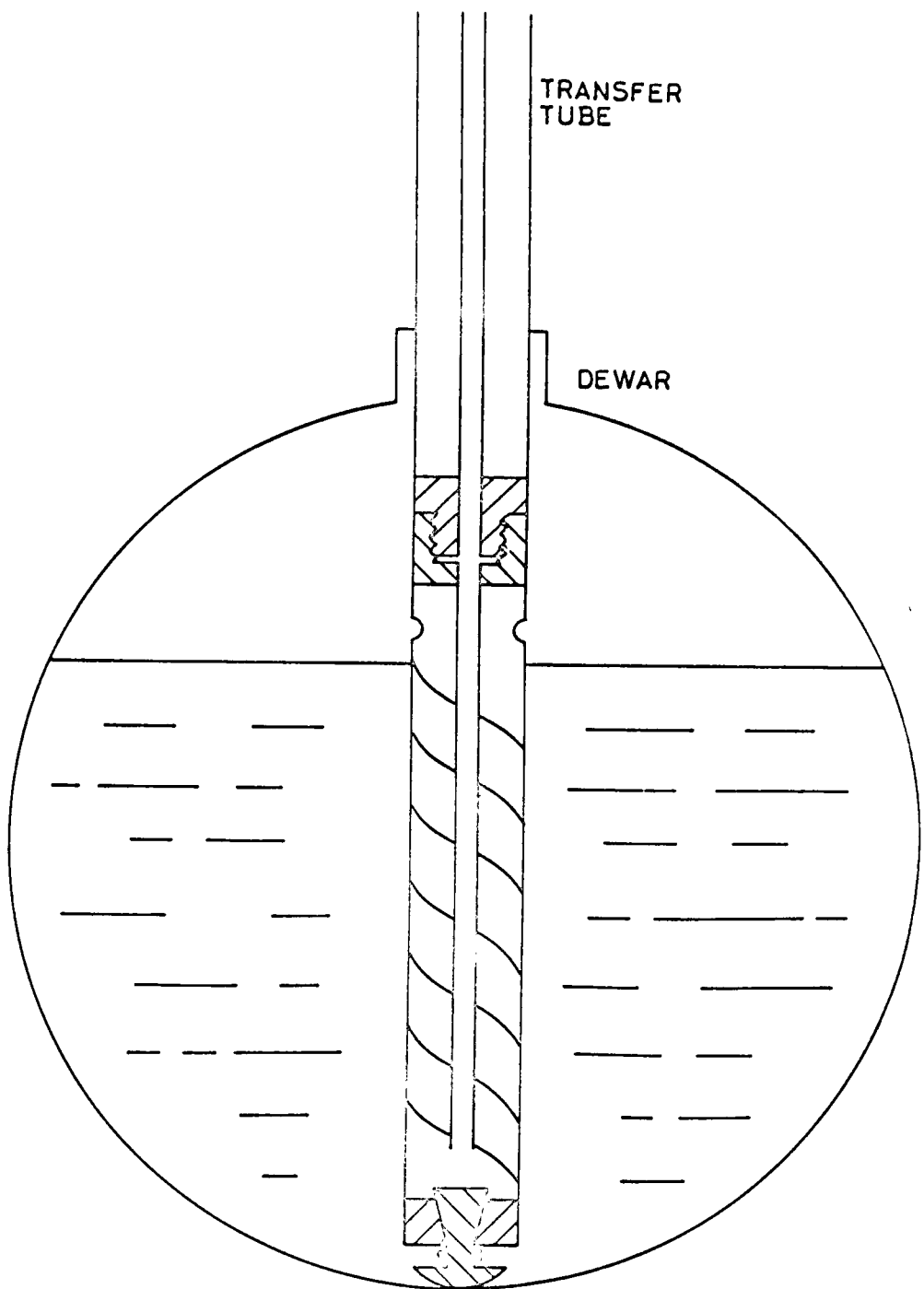


COLD STAGE



TRANSFER TUBE

Fig. 4.4. System for ensuring pure cold gas flow from a dewar filled with liquid, after Klipping, Schönherr and Schultz (1970). Gas is drawn from just above the liquid level and spiralled through a heat exchanger to the transfer tube inlet. A spring-loaded valve at the bottom enables liquid to be drawn for the lowest temperature work.



TRANSFER
TUBE

DEWAR

Fig. 4.5. Schematic representation of the efficiency and stability of cryogenic helium flow. The region of unsteady liquid flow is to be avoided, and can be attained instead with gas cooling with an acceptable increase in consumption.

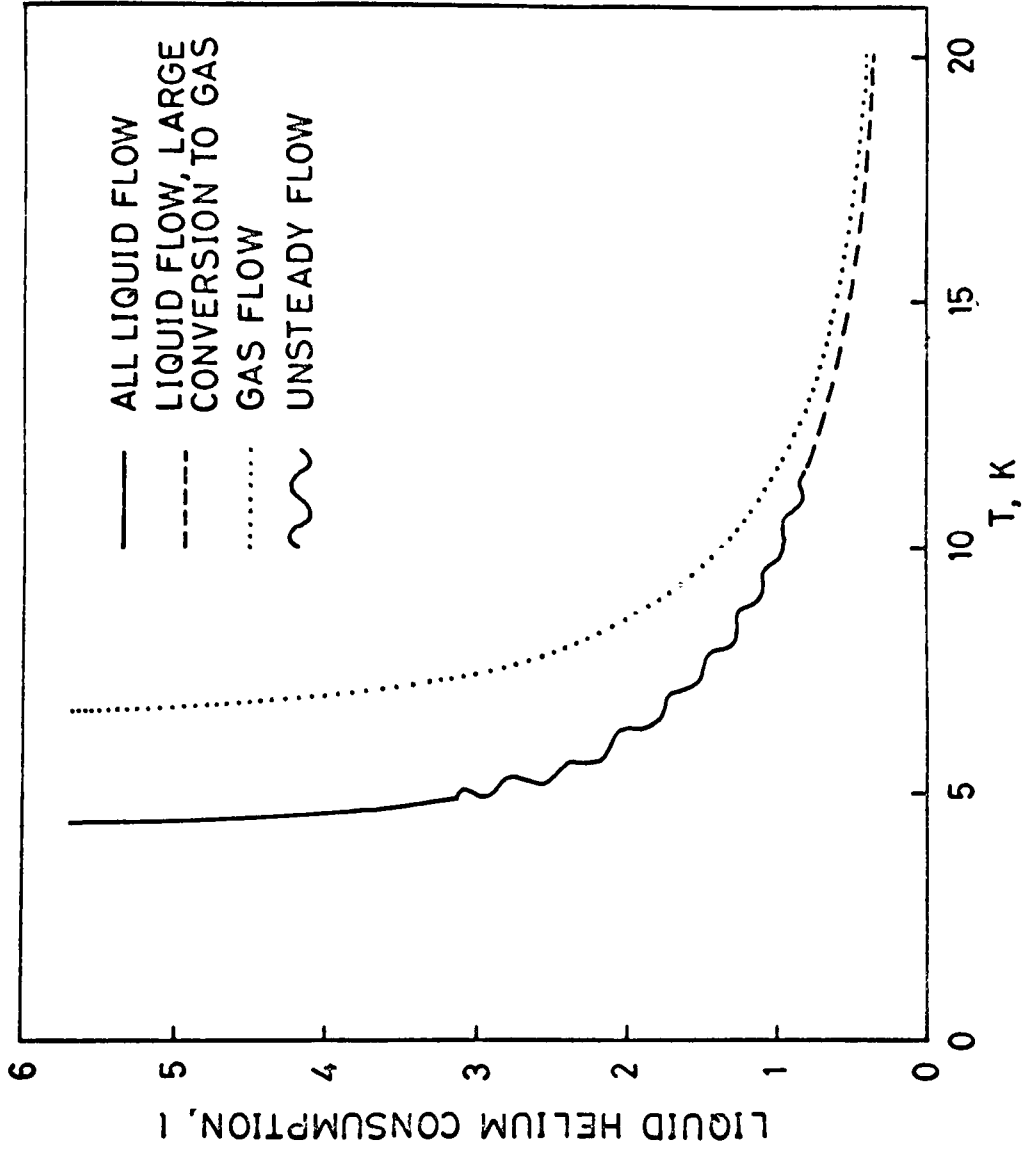


Fig. 4.6. Calculated and measured cooling rates for the helium stage described in §4.10, using liquid helium and a total maintained pressure of 9 torr. The calculated cooling rate neglects heat input to the stage, and so remains higher than the experimental curve in the low temperature region. A cooling rate $\sim 2 \text{ K sec}^{-1}$ is sufficiently slow to prevent serious differential cooling stresses in the specimen.

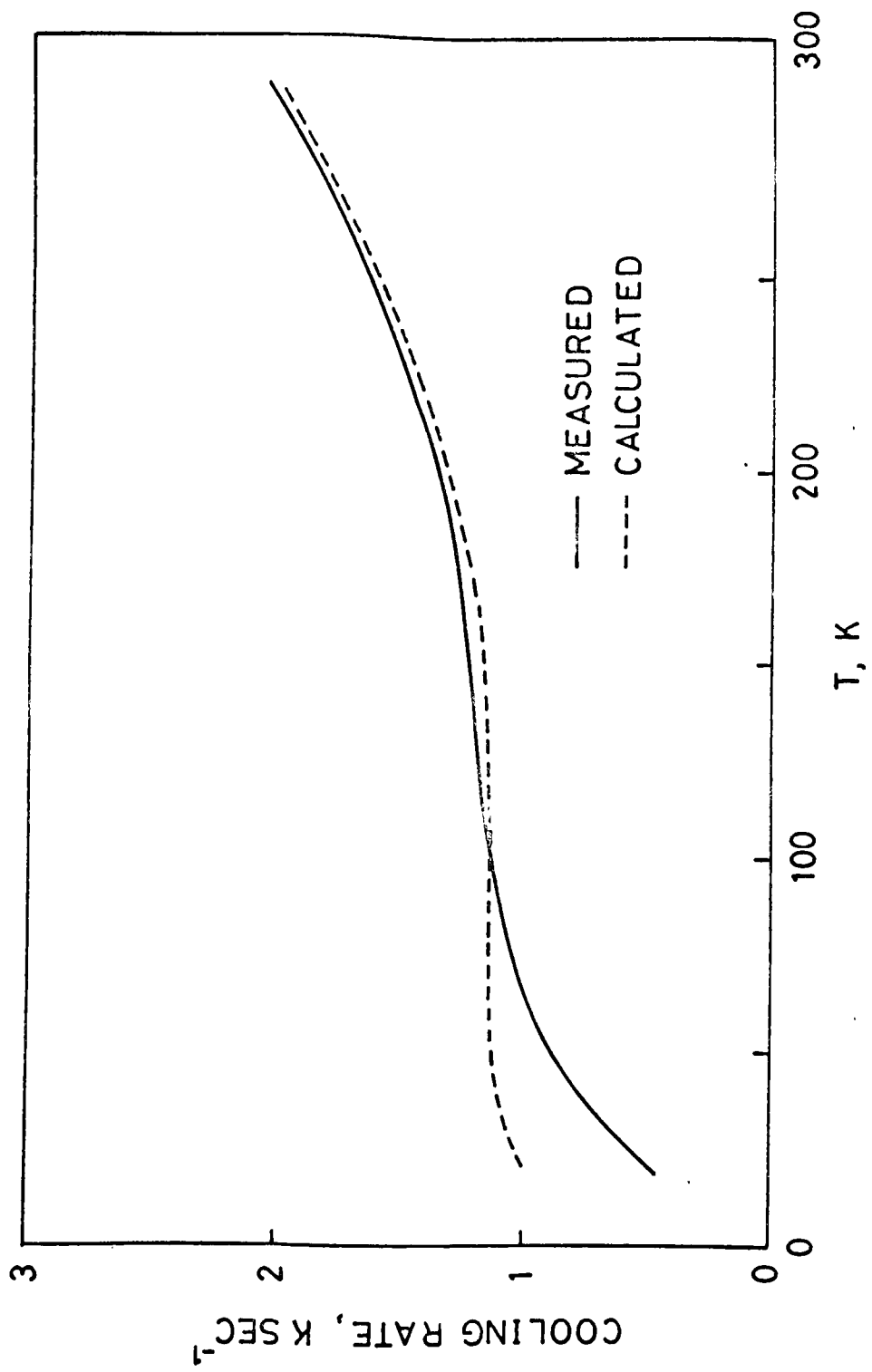
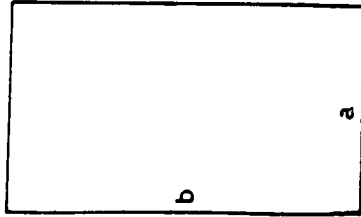


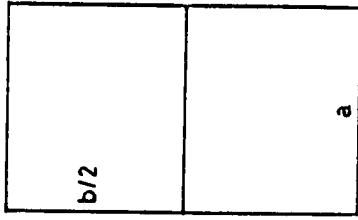
Fig. 4.7. Possible subdivisions in the flow channel of the helium stage described in §4.10 to increase heat transfer. Subscripts p and s refer to parallel or sequential flow, and indicated heat transfer rates $\dot{q}$ are relative to the undivided configuration (1). Configuration (5) is a double screw-cut helix, the equivalent of configuration (4) sequentially fed.

(1)



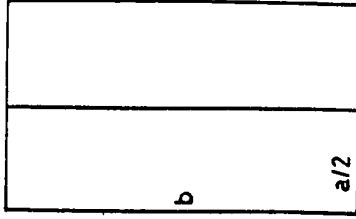
$$\begin{aligned} A &= ab \\ u &= 2a + 2b \\ \dot{q} &\approx 1.0 \end{aligned}$$

(2)



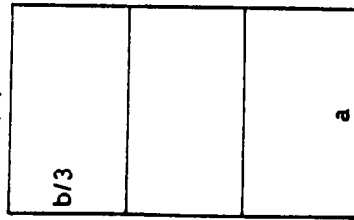
$$\begin{aligned} A &= ab/2 \\ u &= 2a + b \\ \dot{q}_p &= 1.2 \\ \dot{q}_s &= 2.2 \end{aligned}$$

(3)



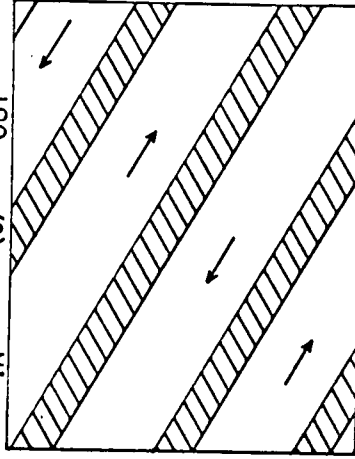
$$\begin{aligned} A &= ab/2 \\ u &= a + 2b \\ \dot{q}_p &= 2.0 \\ \dot{q}_s &= 3.5 \end{aligned}$$

(4)



$$\begin{aligned} A &= ab/3 \\ u &= 2a + 2b/3 \\ \dot{q}_p &= 1.5 \\ \dot{q}_s &= 3.6 \end{aligned}$$

IN (5) OUT



$$\dot{q} = 3.6$$

Fig. 4.8. Comparison of the response of temperature measuring devices. The parameter $d\theta/dT$ refers to the differential change in some thermometric property with temperature, i.e. the sensitivity. For the Pt resistance thermometer $d\theta/dT$ is in units of $\Delta\{(R_T - R_{4K})/(R_{273K} - R_{4K})\}/\Delta T \times 10^{-3} \text{ ohm K}^{-1}$; for the carbon and Ge resistance thermometers, in units of 10^1 ohm K^{-1} ; for the Cu vs constantan and Au/Fe vs chromel thermocouples, in units of $\mu\text{V K}^{-1}$. The Au/Fe vs chromel thermocouple is the only device which maintains a nearly constant measurable sensitivity over the whole temperature range 0-300 K. This leads to a nearly linear e.m.f. vs T calibration, fig. 4.10.

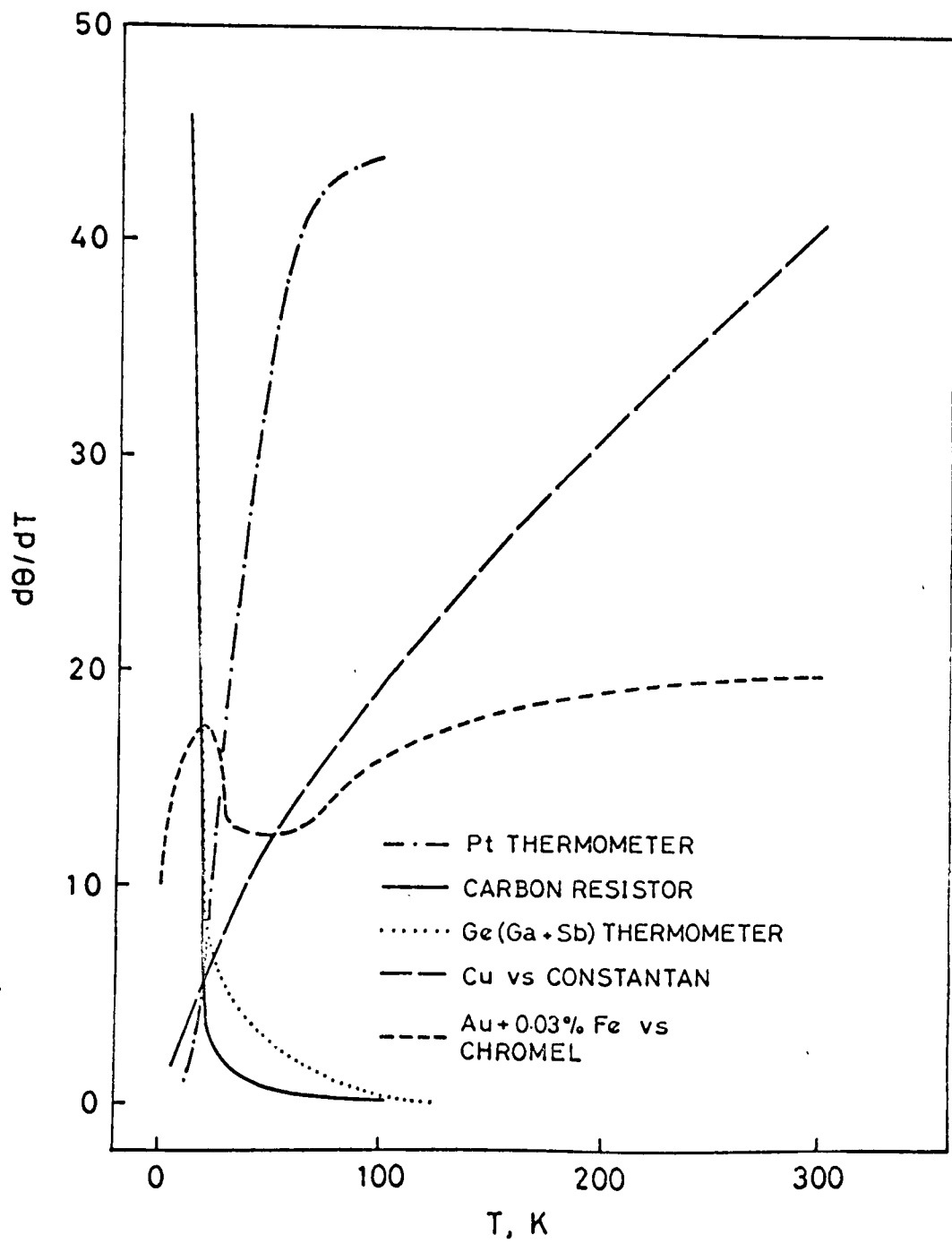


Fig. 4.9. Three possible thermcouple configurations. (a) is suitable where both measuring and reference junctions are easily accessible, for example external to the microscope. (b) is suitable for cold stage measurements with an external reference junction. (c) is suitable for use with an internal reference junction.

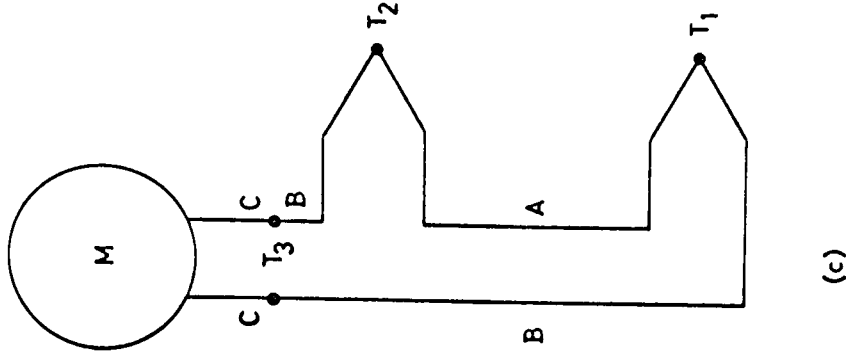
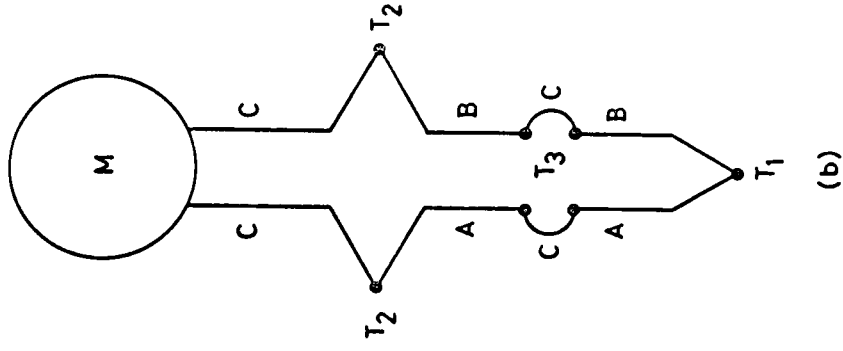
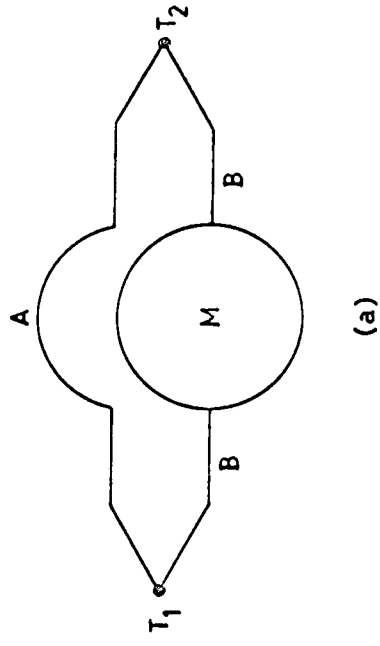


Fig. 4.10. Thermocouple e.m.f. vs temperature calibration for a Au-0.03% Fe vs chromel thermocouple for both liquid helium and liquid nitrogen reference temperatures. A single microvoltmeter with 0-1, 0-3 and 0-10 mV ranges is sufficient for measurements in the range 0-300K with accuracy better than 1K for temperatures below about 150K.

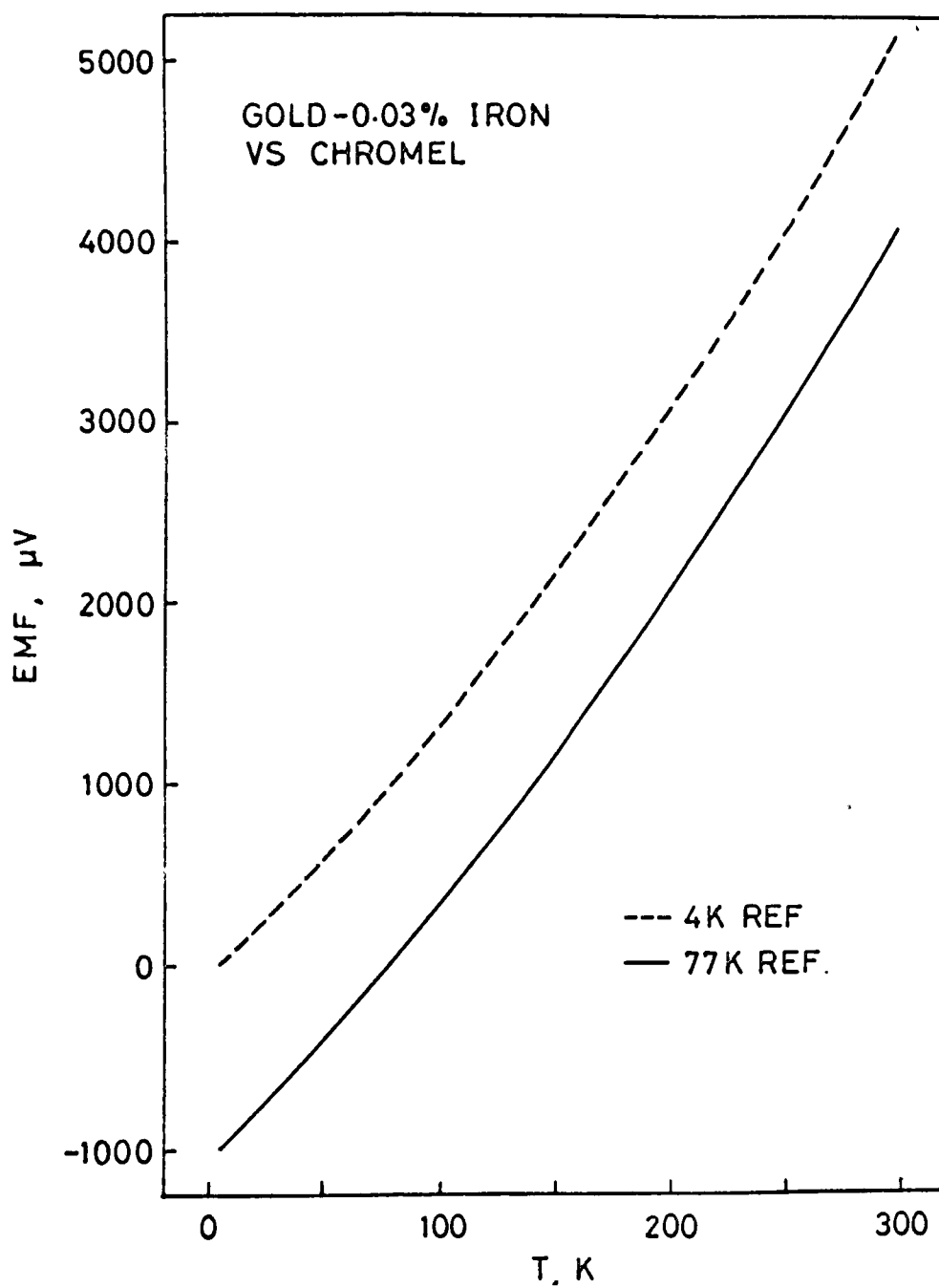


Fig. 4.11. Gas diffusion paths in the vicinity of the cold stage. Ω_1 and Ω'_1 are the solid angles for specimen contamination respectively without and with the objective aperture in place. A_2 is the area of the condensor aperture, A_3 the area of the major pumping port. Although the specimen chamber may reach a pressure $< 10^{-6}$ torr during helium flow, the operative contamination path is that from the column below the specimen through solid angles Ω or Ω' . The source of most residual gas diffusing along this path is outgassing from photographic emulsions.

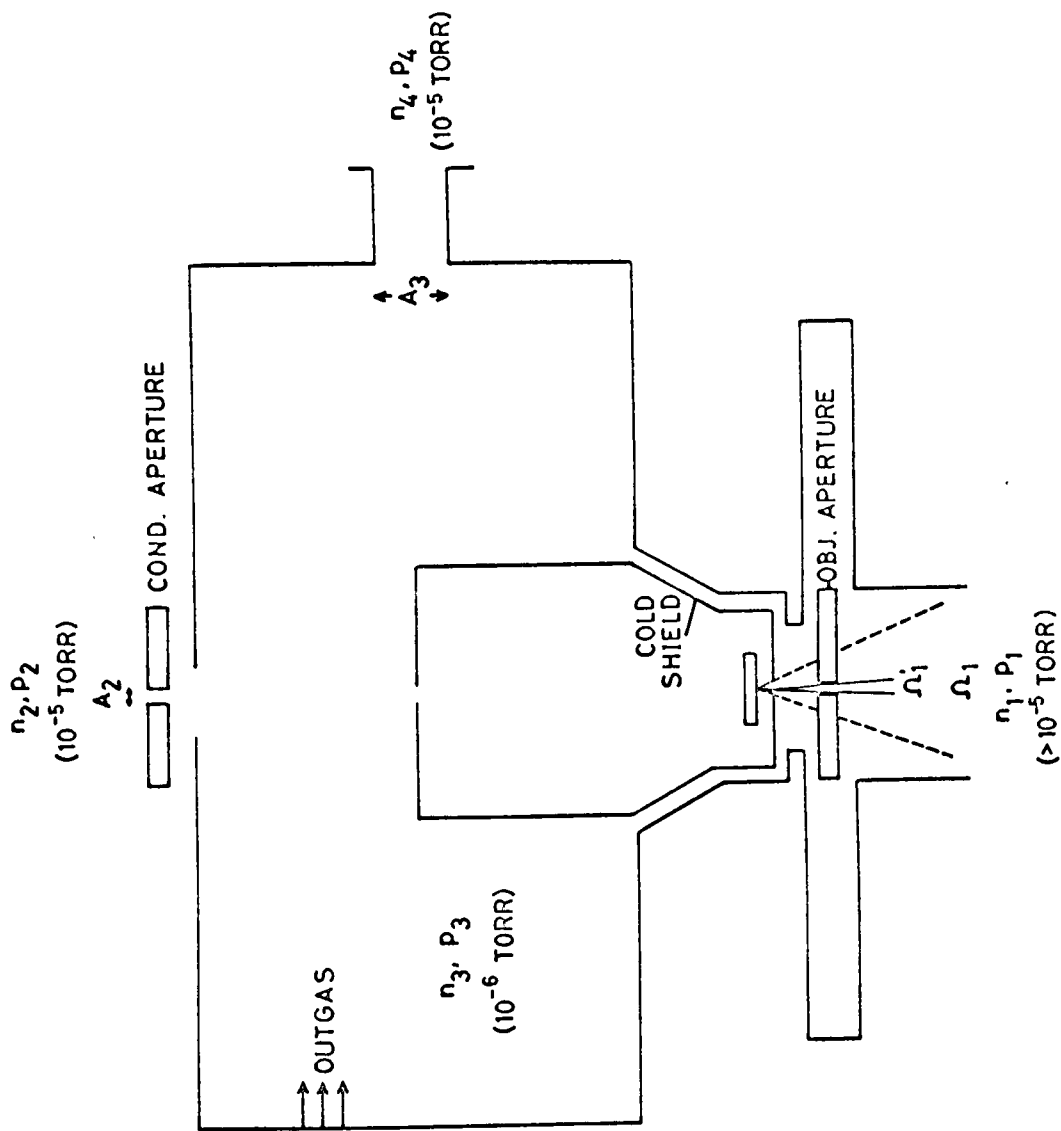


Fig. 4.12. Two micrographs of the same area of a KI foil separated by one hour's observation at 10K, illustrating the contamination protection afforded in the cold stage described in §4.10.

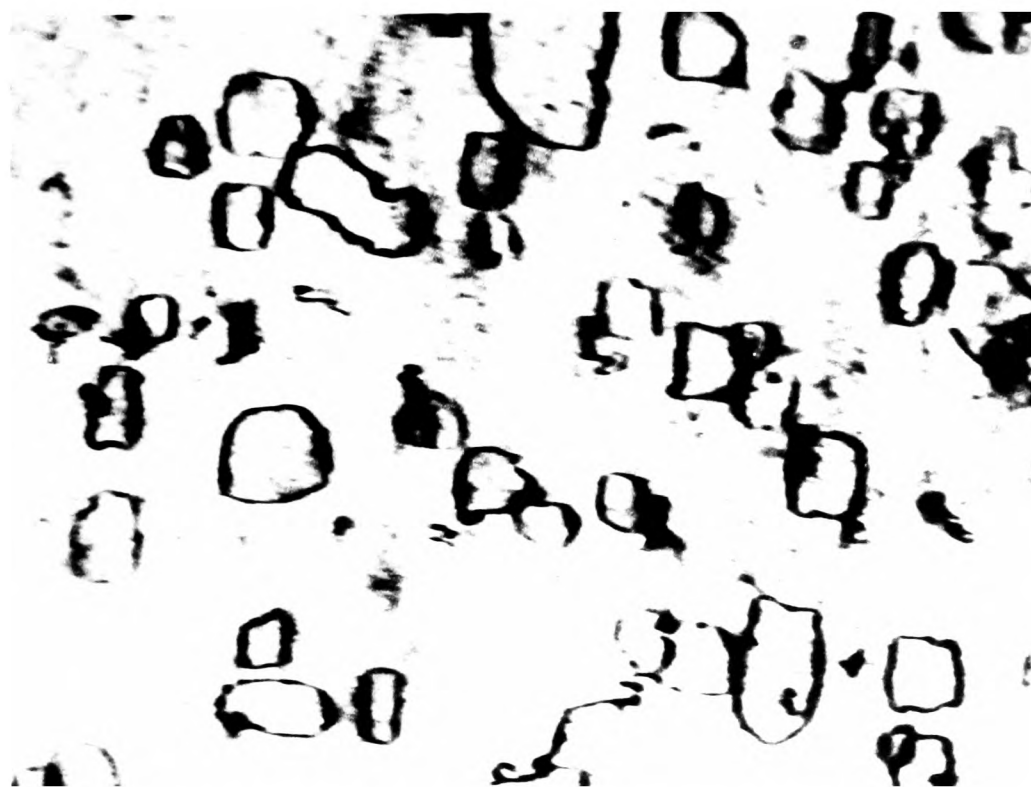


Fig. 4.13. The cold stage mounting ring (above) incorporating quartz ball suspension maintained with a force F by the elastic deformation of the stainless steel mounting ring. The beam bending analogue (below) is used for determining F from ring dimensions and displacement. Points P on the ring remain fixed.

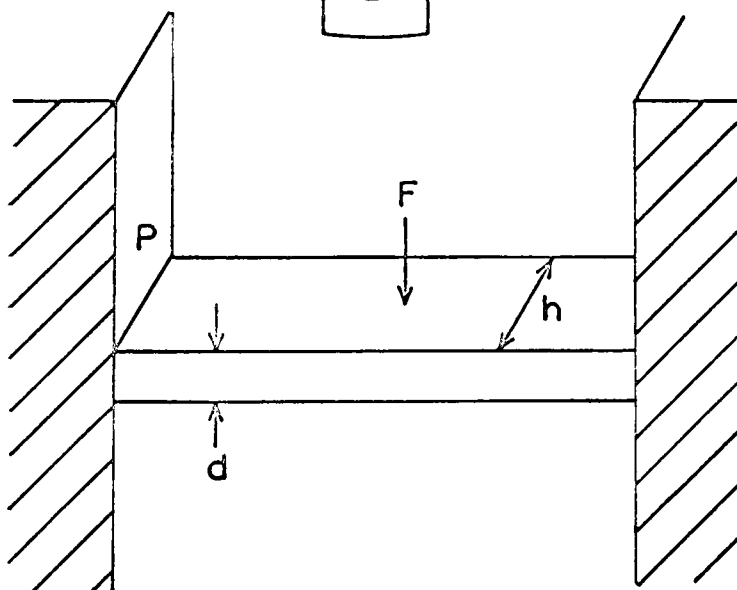
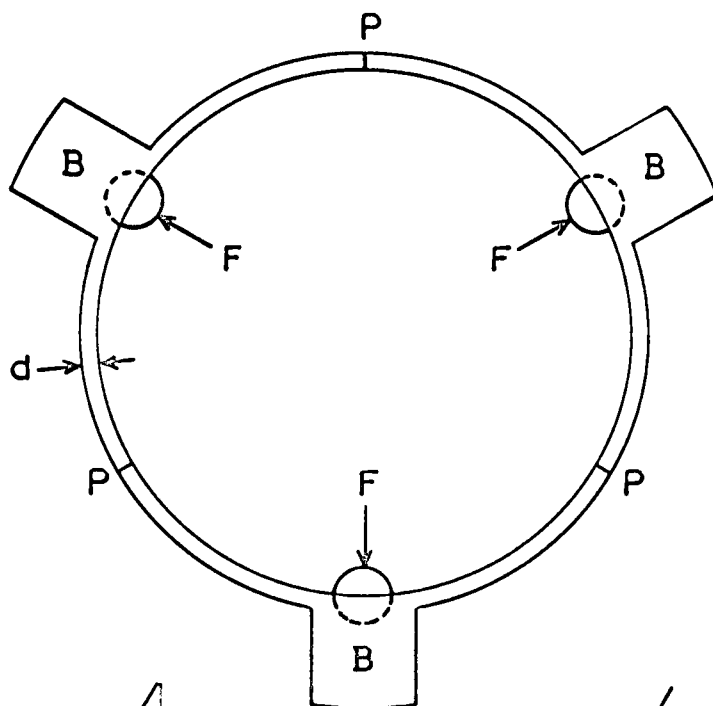


Fig. 4.14. Elastic behaviour of a fused quartz suspension system. Curves represent loading (solid line) to 1% deformation and unloading (broken line). The cross sectional area of the quartz was $\sim 3 \text{ mm}^2$, showing that a constraining stress at least 6 Kg mm^{-2} can be sustained.

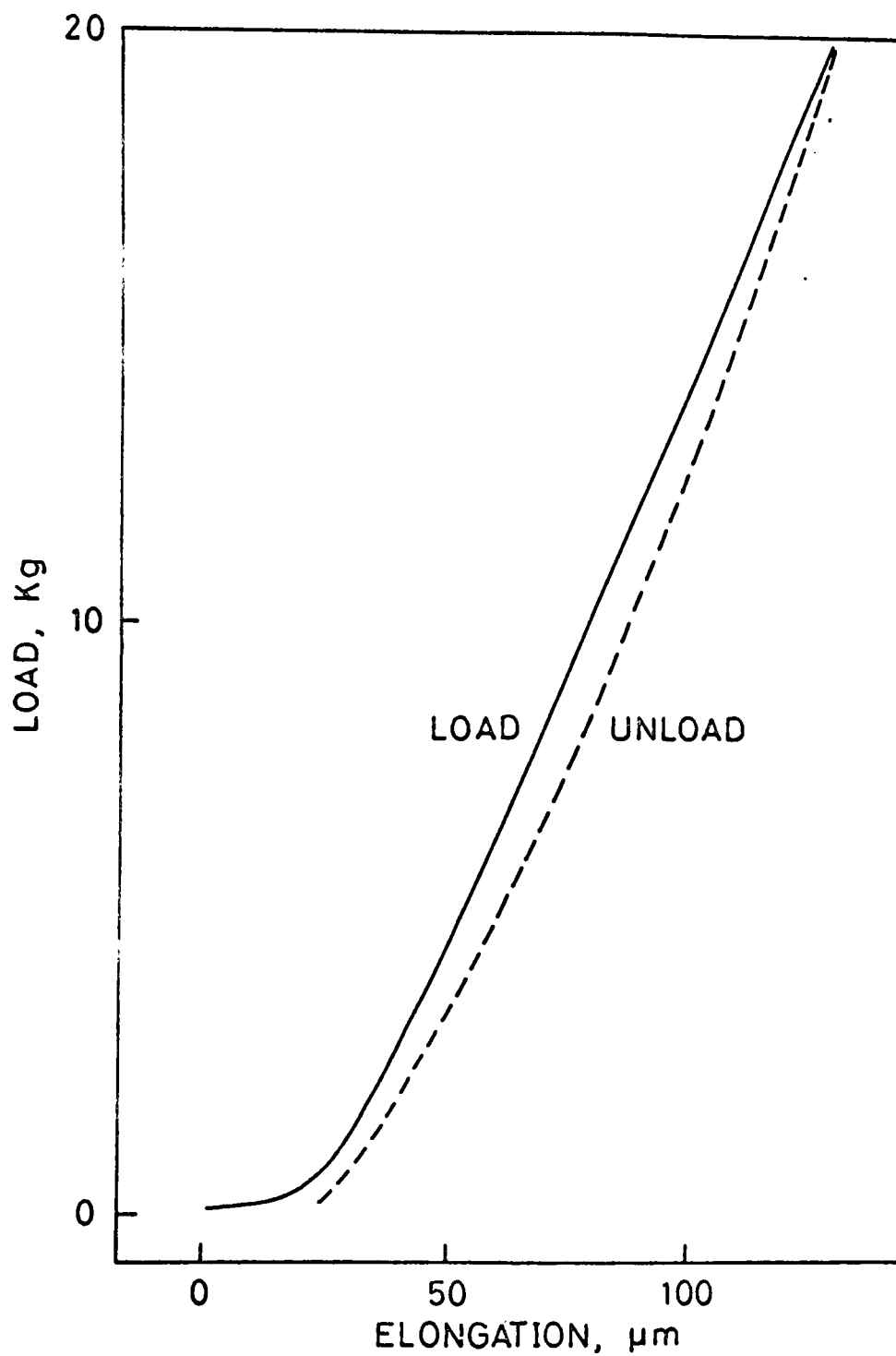
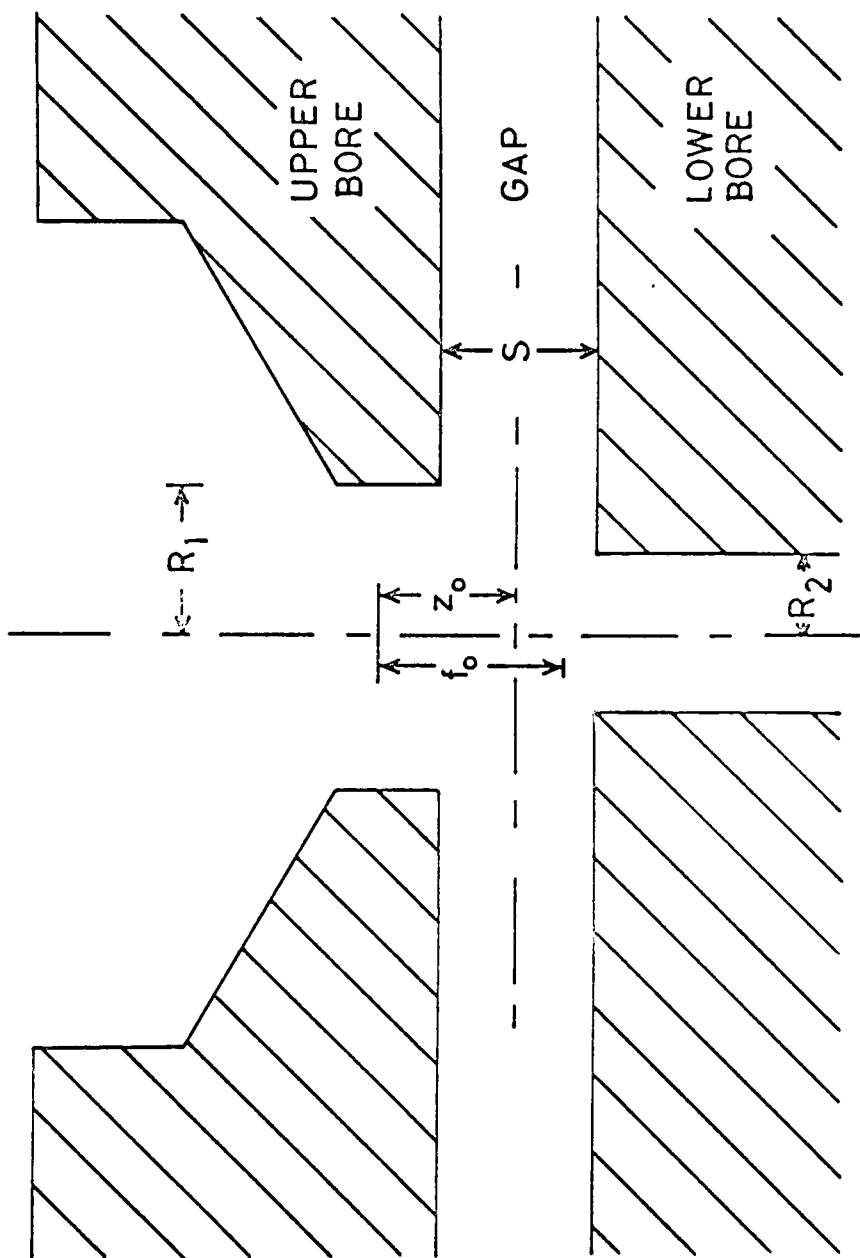


Fig. 4.15. Objective lens pole piece geometry. Upper and lower lens bores, radius R_1 and R_2 , are separated by gap distance S . f_0 is the distance from specimen to focal point of the lens, z_0 the distance from specimen to geometric centre of the lens.

○ ○ ○ ○ ○ ○ ○ ○ ○ ○



○ ○ ○ ○ ○ ○ ○ ○ ○ ○
N TURNS

Fig. 4.16. Focal properties of the 6.5 mm diameter upper bore objective pole piece as used in the Siemens Elmiskop I. f_0 and z_0 are the focal length and focal distance (in mm); C_s and C_c are the spherical and chromatic aberration constants (in mm); r_s and r_c are the resolution limits (in Angstrom units) from spherical and chromatic aberrations as defined in §4.8.3; α_0 is the optimum aperture size (in μm) for minimum spherical aberration. M_i is the image magnification and M_d the magnification of the diffraction relative to that for a specimen in the normal specimen position (specimen elevation = 0). For crystalline specimens, r_c is the effective limit to resolution.

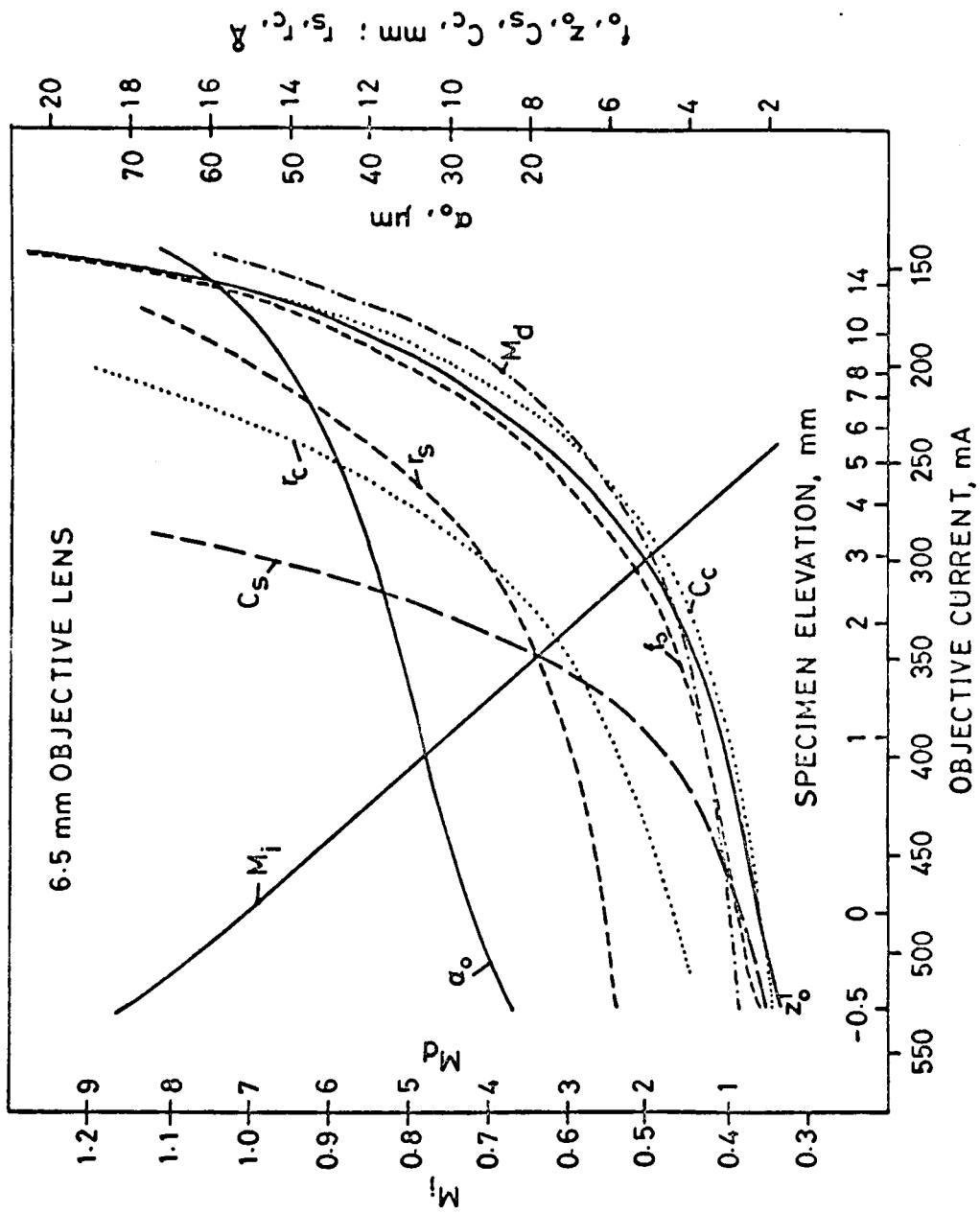


Fig. 4.17. Focal properties of a fictitious 25 mm diameter upper bore objective pole piece for use in place of the normal 6.5 mm pole piece. f_o , z_o , C_s , C_c , r_s , r_c and α_o are as defined in fig. 4.16. M_i and M_d are relative to magnifications for specimens in the normal position in the 6.5 mm pole piece. Note the decreased resolution from chromatic aberration relative to the 6.5 mm pole piece.

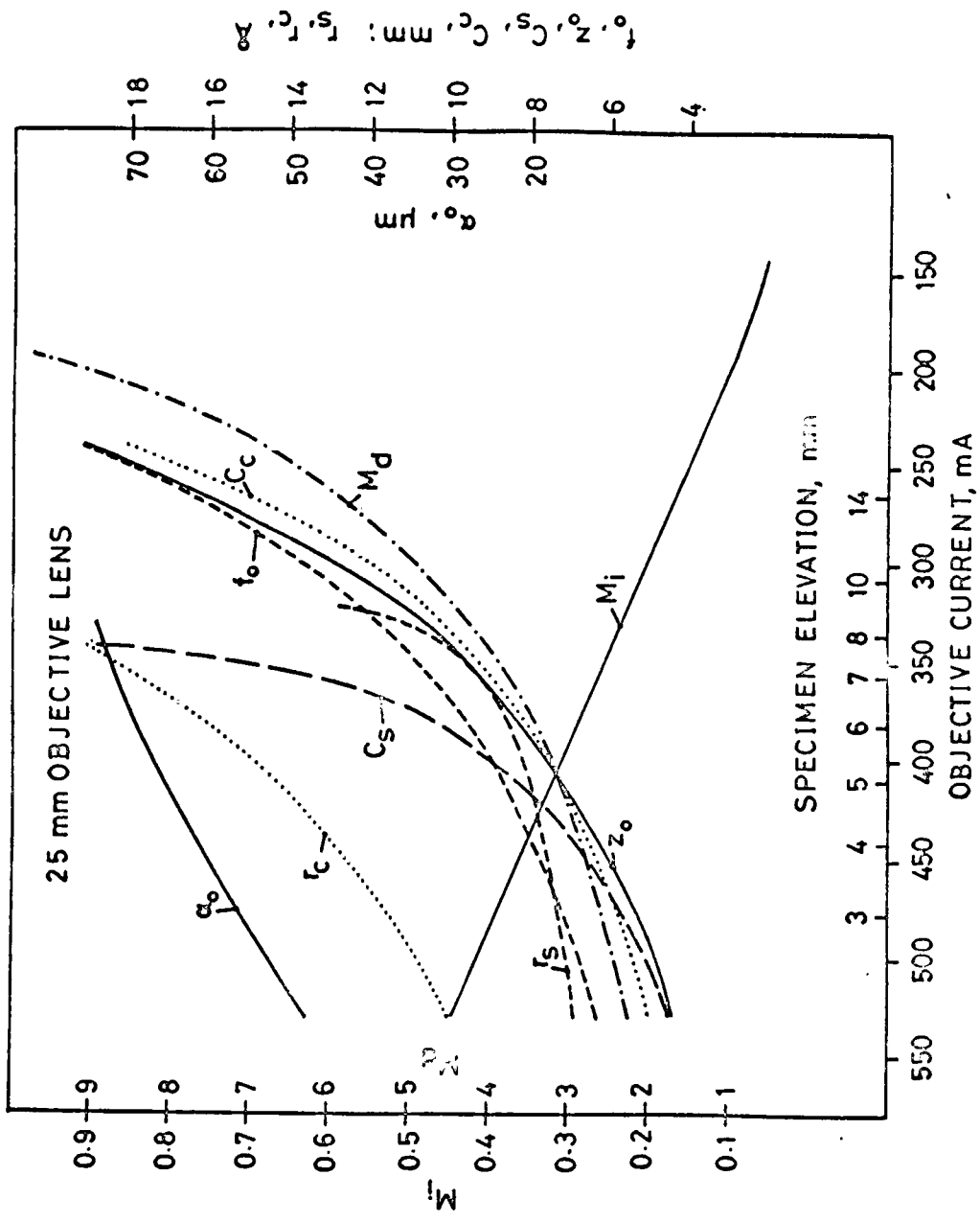


Fig. 4.18. Circuit modifications to the objective lens controller to provide a continuously variable excitation from 192-530 mA in four overlapping ranges: 192-341 mA, 253-410 mA, 322-479 mA and 373-530 mA.

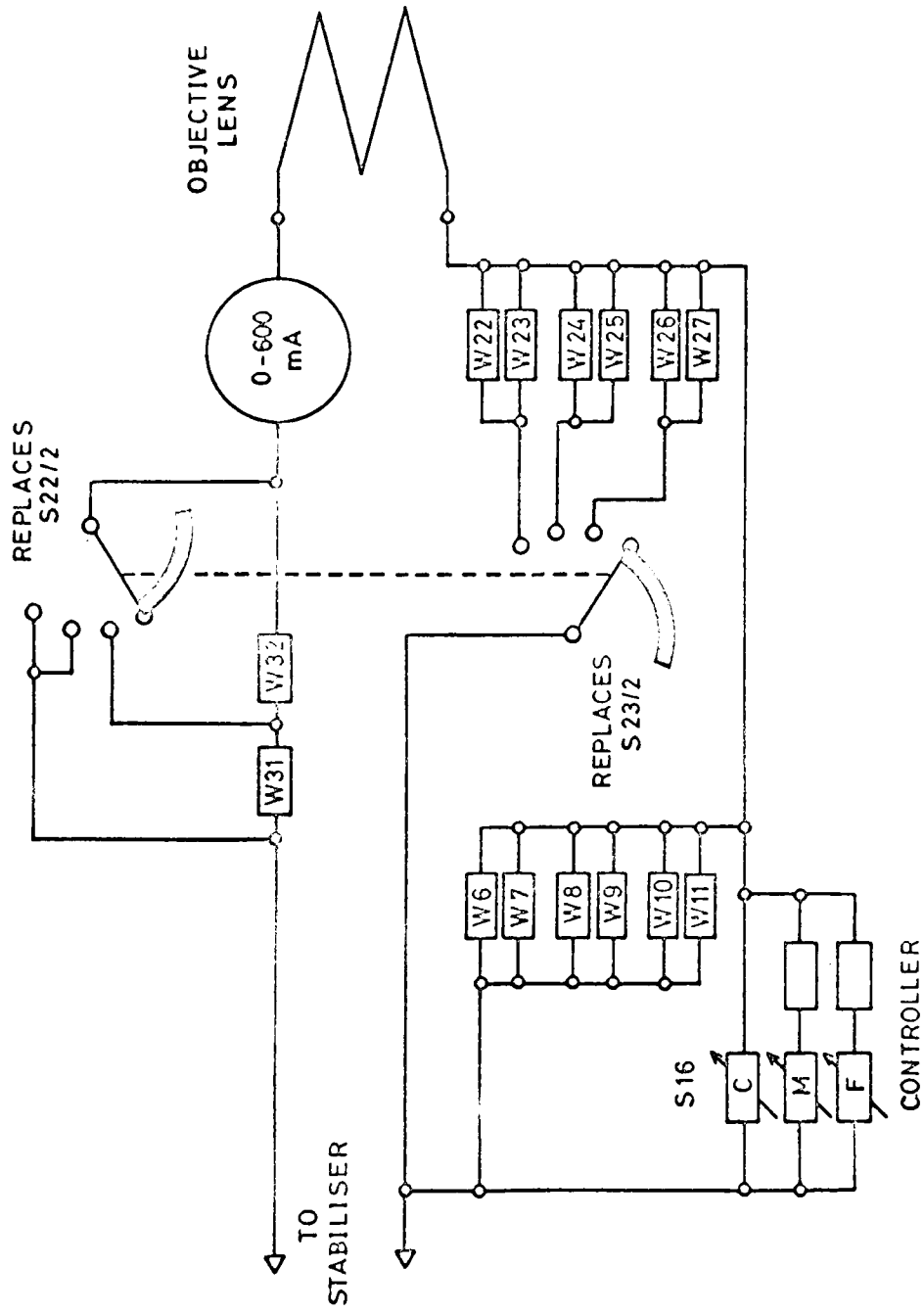
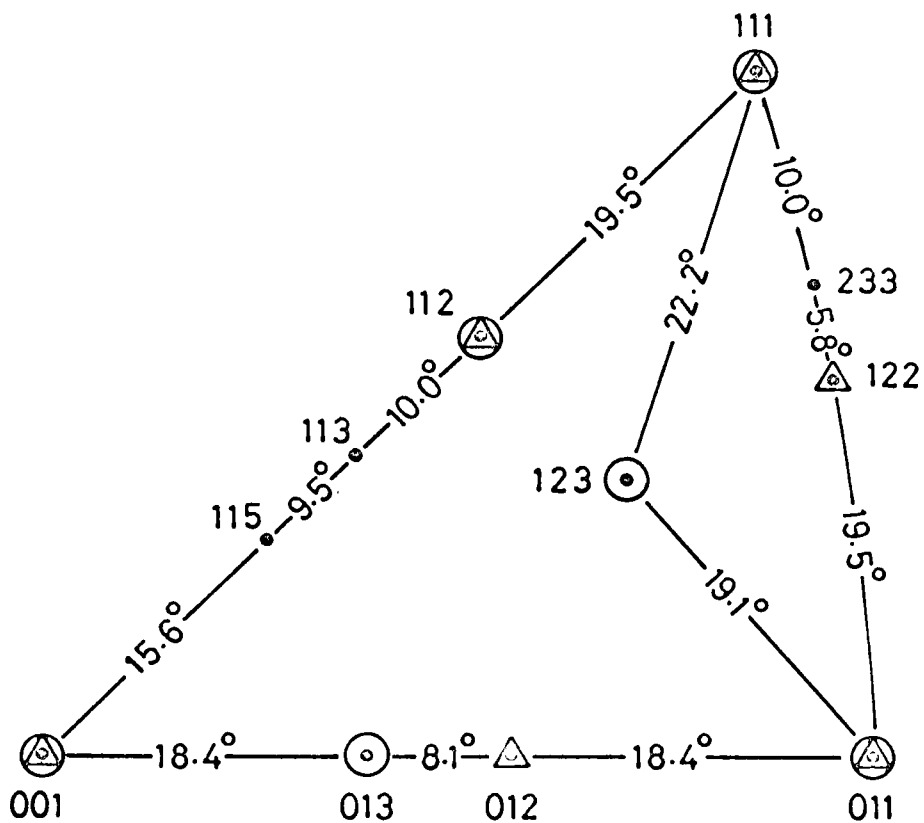


Fig. 4.19. Stereographic plot showing principal reciprocal lattice planes available with $\sim 20^\circ$ specimen tilt for NaCl and CsCl structures.



PRINCIPAL RECIPROCAL LATTICE PLANES

⊙ NaCl

△ CsCl

Fig. 4.20. Cross sectional view of the liquid helium cold stage described in §4.10. The contamination shield is 0.5 mm thick and has a central 800 μm aperture. The Valdrè tilting cartridge seats 1 mm above normal position in the objective lens pole piece bore.

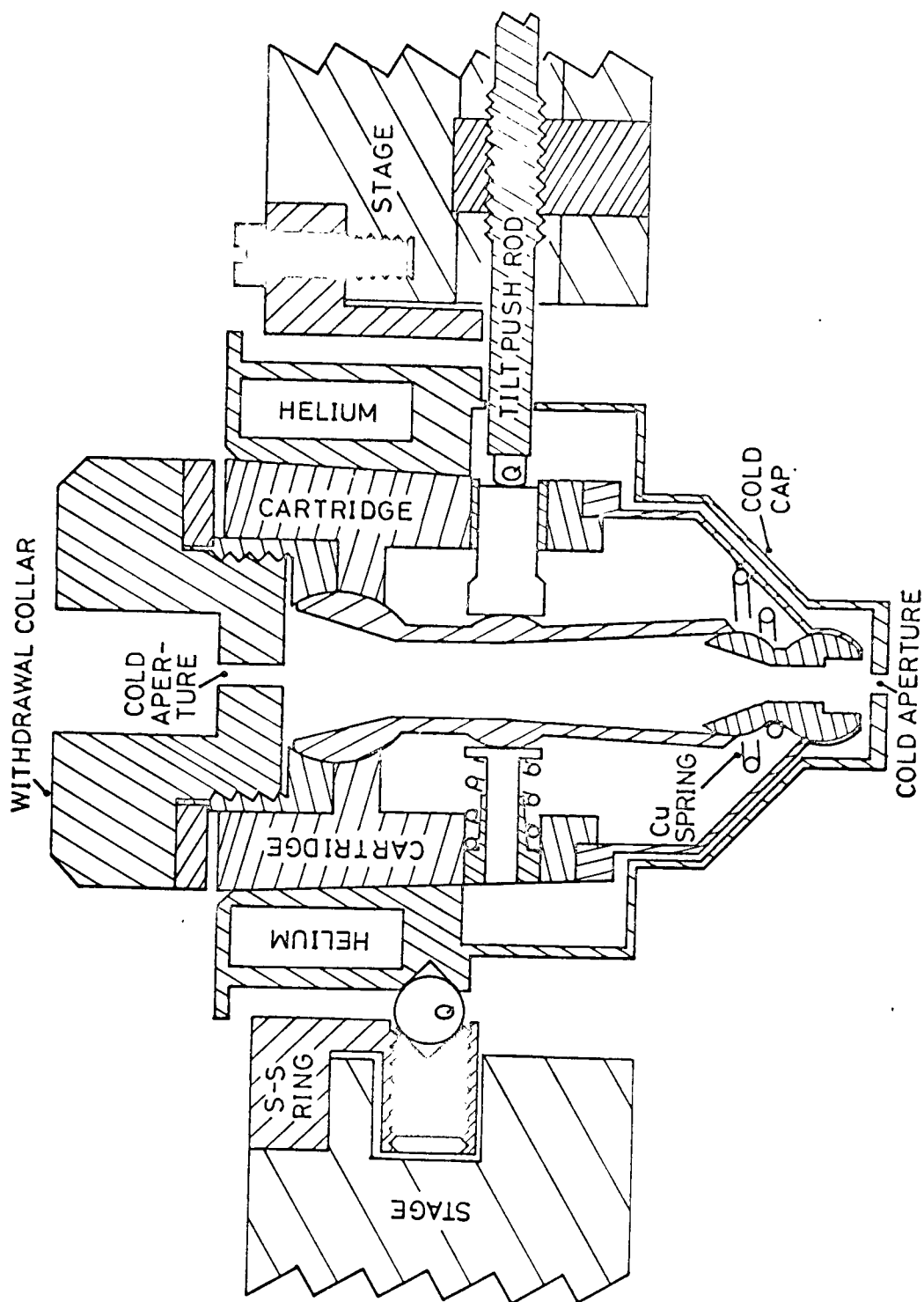


Fig. 4.21. Detail of the quartz ball suspension, stainless steel ring mounting and integral contamination shield. The dog-leg right hand tilt drive clears the vacuum loading lock when cold stage is assembled on the microscope column. Cryofluid is normally supplied via the two flexible bellows couplings.



Fig. 4.22. The complete cold stage assembly installed on the Siemens Elmiskop 1 microscope. Helium is supplied from the 17 l dewar at left through a transfer tube to the cold stage installed in a special steel chamber replacing the customary specimen chamber. The loading lock is installed at the right hand side of this chamber. A microvoltmeter (top of instrument rack) monitors stage temperature from a Au/Fe vs chromel thermocouple, the liquid nitrogen reference junction for which is mounted on the left hand side of the microscope cabinet. A helium gas cylinder provides pressurisation for the dewar, and also reverse warm gas flow for rapid stage warming. A picoammeter (bottom of instrument rack) measures irradiating current, while the milliammeter above indicates objective lens current. The portable tape recorder is used for recording data in the dark, while the timer monitors helium consumption.

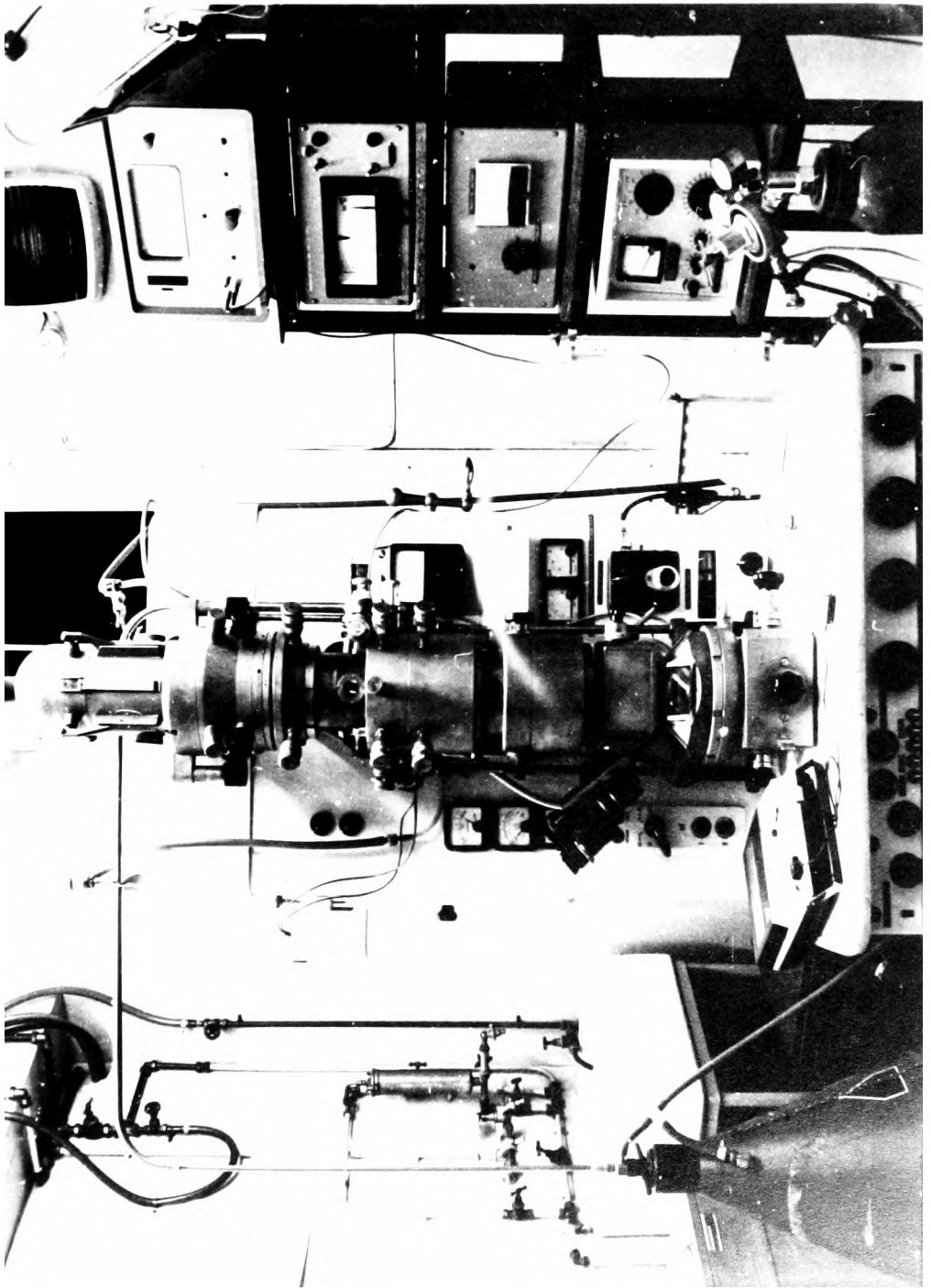


Fig. 4.23. Stress birefringence pattern from a crystal of NaCl quenched into liquid nitrogen from room temperature, indicating the danger of quenching stresses during fast specimen cooling in the cold stage.

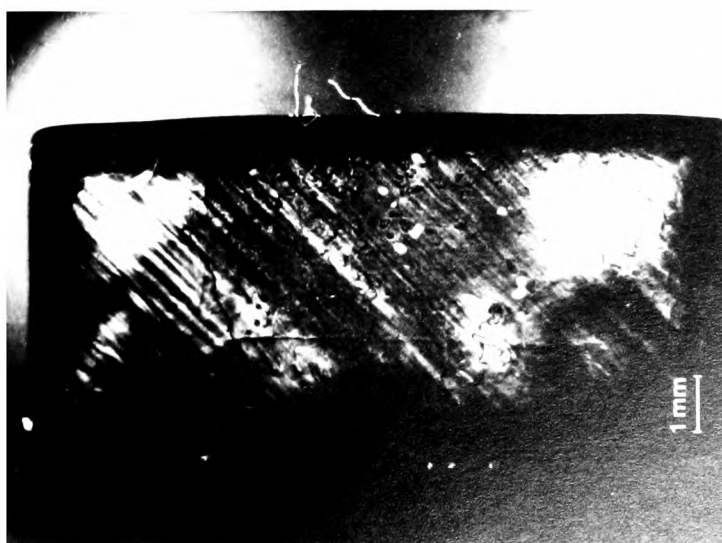
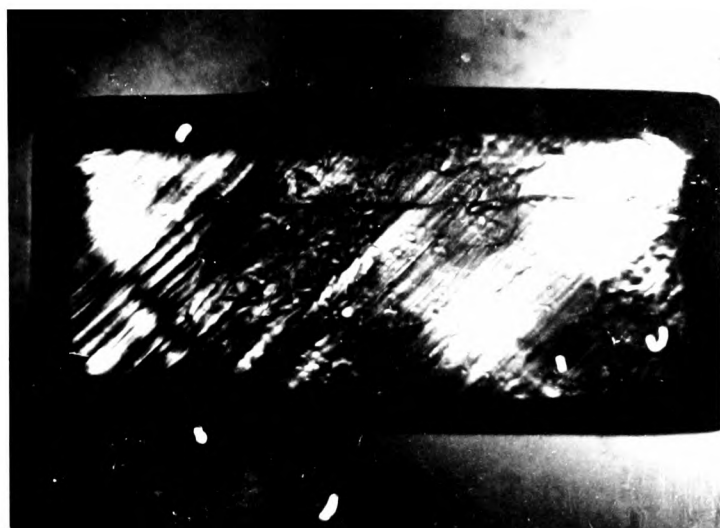


Fig. 4.24. Comparative thermal contractions of NaCl, Zn and Cu cooled to liquid helium temperatures and the thermal expansion coefficient of NaCl. Zn is the most convenient structural material with thermal contraction characteristics approaching those of NaCl.

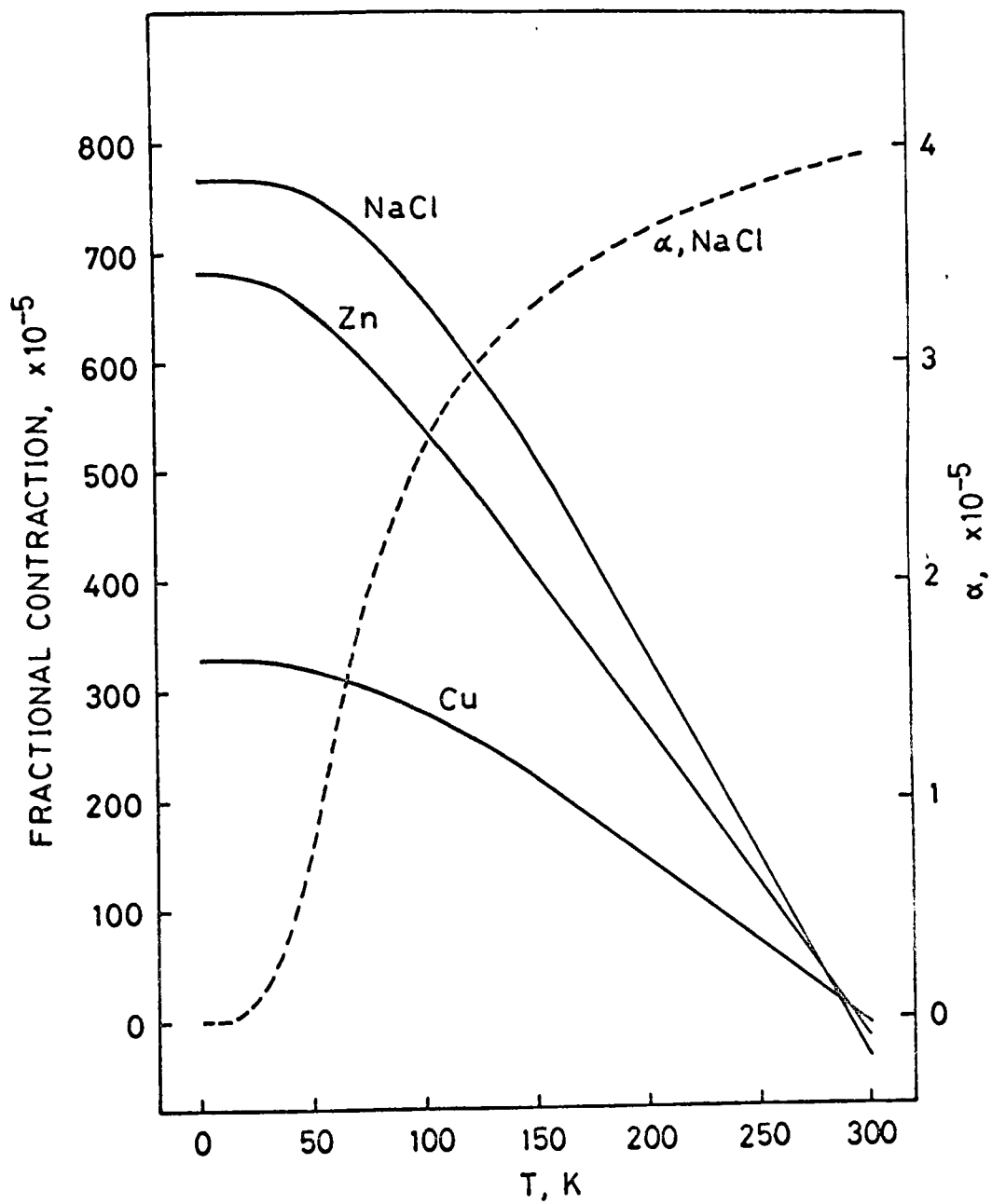
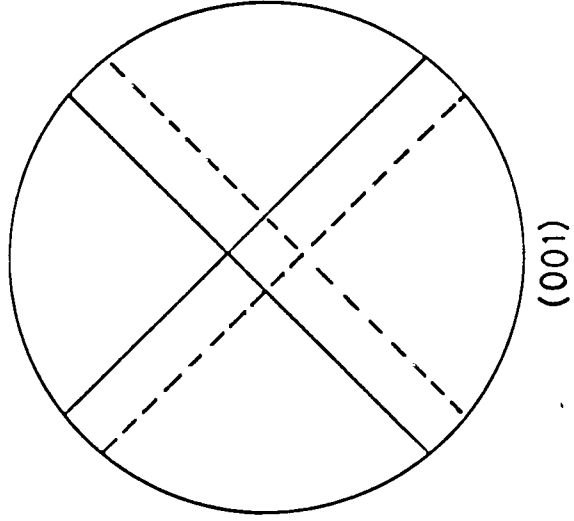


Fig. 4.25. Analysis of thermal contraction accommodation slip in (001) and (101) alkali halide foils. The slip trace patterns are to be compared with micrographs, fig. 4.26.

(a)



$\rightarrow \text{I} \text{---} b\sqrt{2}/2$



(b)



$\rightarrow \text{I} \text{---} b\sqrt{3}/2$

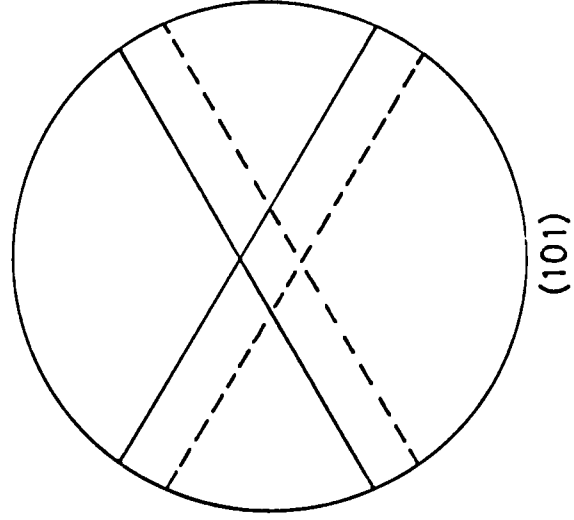
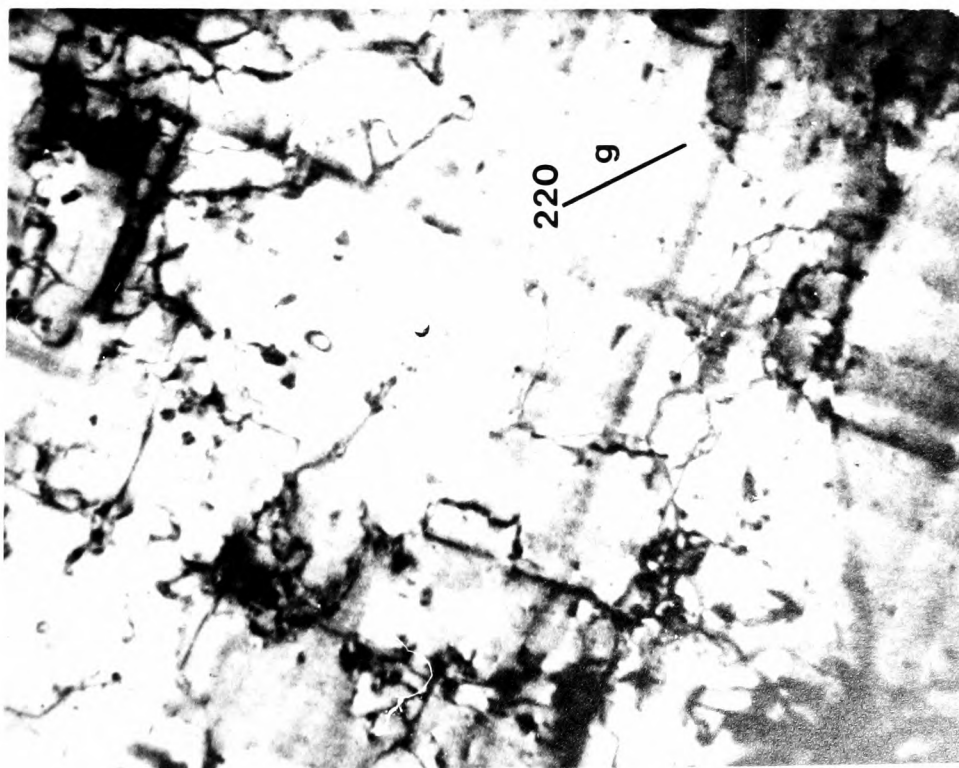
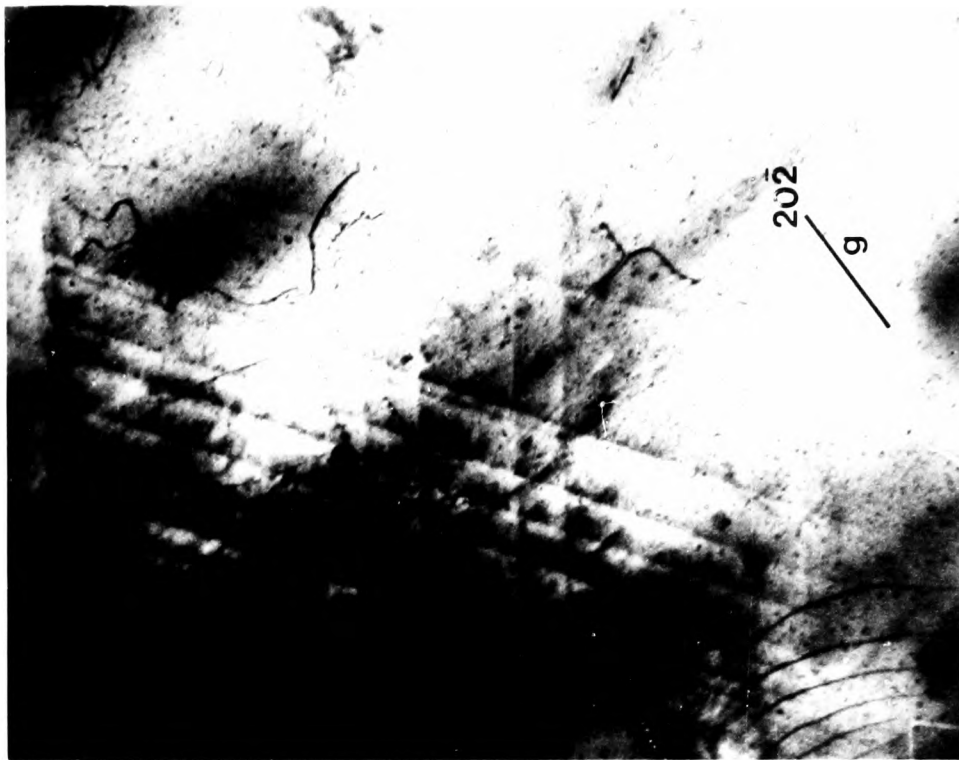


Fig. 4.26. Micrographs of slip traces in KCl foils induced by differential thermal mounting stresses during cooling to liquid helium temperature for examination.
(a) (001) foil, (b) (101) foil.



A



B

500 nm

§5. Electron Microscopy of Mechanical and Irradiation Defects

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Tables

Figures

5.1 Previous Electron Microscopy

Although the history of alkali halide electron microscopy now spans twenty years, few results of real substance have emerged until very recently, even though this period has seen the explosive growth of colour centre research and interest in irradiation damage studies. The reasons for lack of success are easily understood. First, suitable thin foil specimens are somewhat more difficult to prepare than for other commonly studied materials, and a great deal more care must be taken of them after preparation. In particular it has proved difficult to obtain thin foils which are likely to be representative of the state of bulk materials. These difficulties and suitable techniques to overcome them are thoroughly discussed in §3.3 and §3.4. Second, the immense scale of irradiation damage under the investigating electron beam has restricted study of defects in pure alkali halides by electron microscopy to the radiation damage itself, and then only for a few metastable defects surviving in the thinnest foil regions. Until the work of this author and also of Izumi (1969, whose work will be discussed later in this section), it was not recognised that illumination levels previously employed for microscopy were orders of magnitude too high to reflect even irradiation behaviour in any way characteristic of the more conventional irradiation defect studies, §2.4. At room temperature in most alkali halides, even using the lowest electron current density consistent with the limit of statistical resolution for useful magnifications, defect saturation (§2.7) takes place in about 0.4 sec; furthermore, at least one defect species aggregates so readily at room temperature that in this short time the foil under examination

is filled with observable defect clusters of sufficient size and density to obscure previously existing lattice defects and even to prevent detailed analysis of the clusters themselves.

The two solutions to the irradiation damage problem to emerge have been the accidental discovery of Yagi and Honjo (1964, 1967) that heavy divalent cation impurity doping retards observable damage, and the application in this study of liquid helium electron microscopy, outlined in §4. Both approaches slow down the secondary aggregation process, the first by saturating the crystal with defect traps (§2.8.3); the second by altering the kinetics of the approach to saturation (§2.7.2.2). There is some indication (§2.8.1) that certain impurity additions may reduce the basic defect production rate as well. There is certainly ample indication that reduced temperature depresses primary defect production in certain alkali halides through quenching of the non-radiative electron-hole recombination mechanism (§2.5.3). Unfortunately, the amount of impurity that must be added to a crystal to induce the impurity effect is such as to render the material totally unrepresentative of pure alkali halides, both as regards mechanical properties and, of course, irradiation behaviour. The only alternative to study pure crystal properties is then low temperature electron microscopy (§5.4) and careful choice of alkali halide (§5.5), and it is hoped this conclusion will become apparent from the following summary of previous electron microscopical investigations. It is, nevertheless, possible to obtain a large quantity of preliminary information by extremely careful, rapid, marginal observations at room temperature, much of this evidence being largely ignored or misconstrued by previous workers; these observations are detailed in

§5.3 and serve as ground work for the more elaborate low temperature experiments of §5.4 and §5.5. Additional applications of low temperature microscopy are found in §5.6.

The first application of electron microscopy to alkali halides was that of McLennan (1951) who prepared thin single crystal films of NaCl, KCl and LiCl from water solution by vacuum evaporation. Beam current densities on the specimen were very high ($0.1-0.3 \text{ A cm}^{-2}$) and 40-50 keV electrons were used (the energy deposition rate of 40-50 keV electrons is about twice that of 100 keV electrons). For comparison the minimum beam current densities utilised in the present study (see §5.2) were $1-20 \text{ mA cm}^{-2}$. McLennan observed that his crystals deteriorated under the beam, forming etched $\langle 100 \rangle$ sided squares under intense irradiation. He also made the interesting observation that NaCl crystals irradiated at $< 0.1 \text{ A cm}^{-2}$ became amber in colour, whereas those irradiated at $\geq 0.1 \text{ A cm}^{-2}$ became deep purple; the amber colour bleached in a few days while the deep purple colour remained permanently. A similar result obtained in KCl, where the appropriate colours were blue and magenta. From what is now known of colour centres (§2.2) the coloration at low irradiating intensities was due to F centres, that at higher irradiation rates due to alkali metal colloids (§2.6.5.2). Indeed, McLennan made three other observations confirming this interpretation. NaCl crystals, exhibiting blue coloration, produced bubbling when dissolved in water; those sealed in moist Cl_2 and heated to 473 K reduced in colour and a clear overlayer formed. Both indications suggest presence of colloidal Na. LiCl, NaCl and KCl foils under intense irradiation developed extra electron diffraction rings which could be assigned to

alkali metal, alkali metal oxide, hydroxide or carbonate. It was suggested that the oxides, hydroxides and carbonates came from residual microscope gases; an alternative explanation was adsorption or diffusion of O_2 , OH^- and CO_2 into the foil during atmospheric exposure prior to microscopy, or from solution. The coloration suggests that the colloids were produced throughout the foil, although alkali halide foils subjected to this scale of irradiation show serious surface deterioration (e.g. Elliott and Townsend 1971) due to halogen desorption. McLennan supposed that the halogen atom complementary to the F centres responsible for these colloids wandered off interstitially with thermal vibrations, and did not contribute to his observed damage.

The next attempt was the work of Hibi and Yada (1960, 1961, 1962, 1963). Though comprising six papers this work represents essentially one set of experiments in which thin KCl films were produced from water solution by vacuum evaporation and observed with 50 keV electrons at relatively high beam current densities (Hibi and Yada 1962 eventually quote a range 0.5 mA cm^{-2} - 100 mA cm^{-2}). Two sorts of defects were observed: under "weak" irradiation defects exhibiting "double loop" contrast images, interpreted as voids, appeared (these defects are discussed in §5.3.2 and given a more precise assignment; for the time being they will be referred to as "double loop" clusters, reflecting only their characteristic contrast to avoid a premature supposition of their nature); and under heavier irradiation "bright squares" with $\langle 100 \rangle$ edges parallel to the (001) foil plane were formed. At a stage intermediate to these extremes, streaking in the diffraction pattern along $\langle 100 \rangle$ was observed. Replication showed that the "bright squares"

occurred in the interior of the film and not at the surface. Hibi and Yada explained both defects as different stages in the coagulation of vacancies, without apparently considering that both ionic sublattices were involved in such an interpretation. The assignment of voids to the "double loop" images derived from a similar assignment by Möllenstedt (1953) and Rang (1953) to such images induced by ion bombardment in mica and graphite. Such defects have also been observed by Mihama (1963) in irradiated MoS_2 ; in the latter case interpretation of these defects as voids was found to be inconsistent with their behaviour.

Tubbs and Forty (1962) and Bassett, Forty and Tubbs (1962) conducted similar studies in KCl, KBr and KI prepared by evaporation from water solution, irradiating with 80 keV electrons. The current densities they quote ($\sim 5 \text{ mA cm}^{-2}$), like Hibi and Yada's, appear an underestimate considering the scale of damage sustained, but it should be pointed out that in neither case was it indicated that the actual irradiating current densities had been measured (see §3.7.3.2). These workers also observed bright patches after a few minutes irradiation, and made a further observation at an earlier stage of irradiation of a tangled mass of overlapping dislocation ring contrast. These rings, appearing to lie parallel to the (001) foil plane, were also observed by Hibi, Yada and Kawamata (1963) in foils prepared from bulk crystal by thinning with water and they were found to collapse to the "double loop" images with continued irradiation; such rings were not often found in films prepared by evaporation from solution. A third defect, a narrow loop elongated along $\langle 100 \rangle$ appeared in thinned crystals during the earliest stages of irradiation. With further irradiation these defects disappeared and "double loop" defects developed.

At the same time and independently Tanaka, Mannami and Izumi (1963) observed the two identical defects in KCl films prepared by polishing thin cleaved plates with a water-alcohol mixture, making their observations with 100 keV electrons. They interpreted the narrow loop images as end-on "double loop" defects (this interpretation would appear to be in error; see §5.3 and the later work of Izumi 1969 below), and they ascribed both structures to voids. In annealing the foil to 473-573 K the double loop structures appeared to collapse and form some new entanglement of dislocation rings.

Tanaka et al. (1964) extended the study to LiF films prepared by polishing cleaved plates with orthophosphoric acid at 403 K.

"Double loop" images were observed under 100 keV electron doses ~ 50 mCoulomb cm^{-2} ; these grew to a maximum dimension ~ 100 nm by a dose of 5 Coulomb cm^{-2} . These defects were interpreted once again as voids.

Kawamata and Hibi (1965) undertook the first detailed study of these "double loop" defects using (001) KCl foils prepared by nearly dissolving cleaved platelets in water. Both "double loop" images and their precursors, dislocation rings, were observed under 50 keV electron bombardment. A particularly large ($> 1 \mu\text{m}$ diameter) variety of the latter defect was sustained in the very thinnest foil regions. These were believed to form less easily in foils prepared from water solution by evaporation. In thicker regions the rings soon collapsed into "double loop" clusters. Kawamata and Hibi purported to show by a dark field technique that the dislocation ring defects had a displacement vector such that they disappeared with $g = 200$. Not only is this point in error (see §5.3.2.2), but in Kawamata and Hibi's micrographs these

rings always exhibit a line of zero contrast normal to $\underline{g}$, the diffraction vector (for all $\underline{g}$), a behaviour consistent only with a principal displacement vector normal to $\underline{g}$ for all $\underline{g}$, i.e. in this case a pure edge loop or a planar precipitate with principal displacement normal to the plane of the precipitate. This evidence went unnoticed. The "double loop" images exhibited a similar line of zero contrast always normal to $\underline{g}$. Both defects were again interpreted as stages in the growth of voids, formed by condensation of vacancies (species unspecified).

An alternative foil preparation technique was investigated by Yagi and Honjo (1964, 1966, 1967) who were particularly concerned with preparation of foils from extremely hygroscopic NaCl - 0.1% CaCl₂ intended for CaCl₂ precipitation studies. Cleaved platelets were thinned to <10 μm thickness in a water-alcohol mixture, mounted on a copper grid and exposed to sudden increase in irradiating current ("beam flashing" technique, §3.3.2), scaling off sections of the platelet to produce regions thin enough for transmission. The resulting areas were examined with 150 keV electrons; Yagi and Honjo, unlike their predecessors, actually measured the beam current densities employed with a Faraday cage. An observation limit in agreement with the calculations of §3.7.1.3 ($\sim 3 \text{ mA cm}^{-2}$ current density on the specimen) was derived. Pure NaCl foils damaged immediately with a high concentration of "speckle" defects, and mechanically introduced dislocations were never seen in pure NaCl foils. Most spectacularly, however, it was discovered that in NaCl heavily doped with CaCl₂ (~ 0.1 mole %) dislocations could be observed in the foil, i.e. apparent

radiation damage was reduced, and dislocations were seen to climb during irradiation. Since their foils had been prepared without exposure to water, they attributed the sort of damage reported by Hibi et al. in water-thinned crystals as due to an affected surface layer. This thesis is relatively untenable; the very high Ca^{2+} impurity level is undoubtedly responsible, probably primarily as an interstitial trap, §2.8.3. In fact, heavy damage was observed in some areas of the doped specimen, presumably due to inhomogeneous impurity distribution, or more favourably set diffracting conditions. The climb of dislocations was interpreted as condensation of vacancy pairs created during irradiation (that large concentrations of cation-anion vacancy pairs are formed by ionizing radiation in alkali halides seems a curiously persistent notion in alkali halide microscopy literature). The number of supposed vacancy pairs condensed per incident electron, derived from the radius and number of helical turns formed in screw dislocations, was calculated at between 10^{-6} and 10^{-5} , no difference being found between 100 keV and 150 keV electrons. This figure, of course, is only a measure of the efficiency of the dislocation sink, not necessarily of the primary defect production efficiency; since saturation is unquestionably achieved early on in the irradiation (even in heavily Ca^{2+} doped crystals, which might exhibit up to tenfold depression of defect production rate, §2.8.1), the condensation rate reflects the probability of a defect reaching a dislocation sink before annihilation, the overall total defect production rate being zero at saturation. The measurement is therefore somewhat meaningless as an indication of defect production or density. Yagi and Honjo (1967)

later concluded that the sign of this climb was positive, i.e. climb by vacancy condensation, from inspection of the projected form of an inclined helix and the behaviour of partial dislocations bounding a CaCl_2 platelet. There is some basis for such postulated climb, as a large number of cation vacancies are also present because of the Ca^{2+} concentration; they are, however, likely to be associated into complexes and unlikely to migrate quickly enough in large numbers to dislocation cores. In §5.6.4 we illustrate similar climb produced under conditions where no appreciable anion vacancy mobility obtained and cation involvement could not be detected; accordingly we advance there an alternative model for the climb observed by Yagi and Honjo.

By this time, Mannami, Akisue and Tanaka (1967) had continued their earlier work in LiF and considered defects produced by neutron irradiation. Foils were prepared as before in orthophosphoric acid. In an attempt to circumscribe the effects of in situ microscope irradiation they worked at low magnifications (10^4) and exposed fast Fuji HS photographic plates blindly (i.e. by focussing on adjacent areas, blanking the beam, then moving to a virgin foil area and exposing). By this procedure they found they could reduce electron damage for one picture in very thin areas to small clusters exhibiting black/white contrast with density $\sim 5 \times 10^{13} \text{ cm}^{-3}$; with further irradiation these clusters grew to loops $\sim 20 \text{ nm}$ diameter. "Double loop" images also formed under electron irradiation. The minimum electron dose at which they could produce pictures is quoted as $10^{14} \text{ electrons cm}^{-2}$. However, the calculations of §3.7.2.3 indicate that pictures of the statistical quality illustrated are unlikely to be produced with $< 10^7$

electrons cm^{-2} on the photographic emulsion, which at a magnification of 10^4 corresponds to at least 10^{15} electrons cm^{-2} emerging from the bottom of the specimen; a better estimate of total current incident on the specimen would be $\sim 10^{16}$ electrons cm^{-2} .

Clusters introduced by neutron irradiation $> 10^{15}$ nvt could apparently be briefly distinguished from in situ damage. Clusters due to neutron irradiation were of the same form (small loops elongated along $\langle 100 \rangle$) as those produced by in situ electron irradiation, and grew with continued observation under the electron beam. It was found that the density of these defects did not change with neutron dose over doses from 10^{13} to 10^{18} nvt. It is difficult to assess how much of the observed defect distribution was due to neutron irradiation, and how much to in situ electron irradiation; these results do suggest, however, that at least the number of initial nucleation sites introduced by neutron irradiation remains relatively constant regardless of dose, and that this number is larger than that obtaining in thin foil electron irradiations. Mannami et al. interpreted their clusters (because of a double arc contrast characteristic of them) as 20 nm in diameter and 5 nm thick. The sort of contrast they observed is, of course, typical of small dislocation loops (e.g. Bullough, Maher and Perrin 1970) where "thickness" is of atomic dimensions.

Izumi (1969) has mounted a more systematic approach during the course of the present study. His experiments were largely performed on (001) foils of KCl and NaCl prepared by the "beam flashing" technique developed by Yagi and Honjo (1964, 1967), and examined at irradiating currents 1-100 mA cm^{-2} incident on the specimen, similar to the present study. The defects observed were of two types; in KCl only, the

"double loop" sort as seen by Hibi et al. and Tanaka et al.; and in both KCl and NaCl, elongated loop clusters lying along $\langle 100 \rangle$. Clusters of the former sort were not analysed and were presumed to be voids. Three apparent orientations of the latter defect were observed, which Izumi attributed to rectangular platelet defects lying on $\{100\}$ and seen flat-wise, on edge and on end. He observed these defects for various other incident electron beam directions ($\langle 011 \rangle$, $\langle 111 \rangle$) by bending his foils. From the strain field of those defects apparently on end, he surmised that the platelets had a displacement vector normal to the plane of the platelet along $\langle 100 \rangle$. This deduction is shown in §5.3 and §5.5 to be incorrect (simply from the contrast behaviour apparent in Izumi's pictures), and the initial assignment of the "end-on" defect appears to be incorrect as well; a probable model accounting for the morphology of these defects is advanced in §5.7.

Izumi also conducted annealing experiments on these clusters which compare favourably with results obtained previously during the course of the present study. During annealing in the range 373-573 K the elongated defects in KCl and NaCl are seen to disappear. Although "double loop" clusters were observed in KCl at room temperature, they were not present in NaCl unless irradiated at elevated temperatures. By comparison with (and slight misinterpretation of) other experiments, Izumi concluded that the platelet defects were alkali metal colloids formed by coagulation of chlorine ion vacancies produced during irradiation. Since this work is similar to room temperature observations of the present study, Izumi's results and conclusions will be examined more critically in §5.3.

Brief electron microscope studies have been made by three other groups in several alkali halides. Smiser and McGee (1969) published a short note reporting marginal observation of the remains of dislocation tangles in NaCl by working at minimum beam current densities, low magnification and exposing plates blindly, as per Mannami et al. (1967). They used optical grade NaCl of unspecified purity (their limited observations may well have been made possible by the impurity content of their crystals), which they thinned with drops of water from an eye dropper. They were, however, unable to free their micrographs completely from the effects of severe radiation damage. Curiously, they mistakenly interpreted large (> 100 nm) clusters elongated in $\langle 100 \rangle$ as the product of quenching their crystals after anneal. Dworschak and Waidelich (1970) reported observation of irradiation defects in LiF, NaCl, KCl and KBr thinned by a jet polishing technique (Booker and Stickler 1962). The quality of their micrographs is relatively poor, although the characteristic damage features can be discerned. It has recently come to light (Ayai, private communication) that Ayai and co-workers (Ayai, Osawa and Hagihara 1965; Hagihara and Ayai 1966, 1967, 1968, 1969) have been conducting a series of experiments in KI. The quality of their preparations has been poor (KI is very hygroscopic), and their analysis dubious. These experiments will not be discussed further, as an elaborate analysis of irradiation defects in KI appears in §5.5.

Finally, we mention a series of experiments not directly related to irradiation defects but of interest to alkali halide microscopy. Yada and Hibi (1966, 1969) have succeeded in obtaining lattice fringes from a large number of alkali halide foils (LiF, NaF, KF, LiCl, NaCl, KCl, LiBr, NaBr, KBr) prepared from water solution by evaporation, using

axial illumination and a pointed cathode. Although beam current densities for such work are extraordinarily high ($>1 \text{ A cm}^{-2}$) compared with that tolerable in alkali halide defect studies, the areas examined for lattice fringes were necessarily very thin. Square bright patches of the sort reported by Ilibi and Yada (1962) and Tubbs and Forty (1962) for intense electron irradiation were present in the areas examined. It is probable that, in the very thin foil regions used, the diffusion of radiation induced defects to the surface prevents formation of defect aggregates (in all studies reviewed it has been shown that in thin foil regions relatively stable isolated defect clusters can be sustained, and in the very thinnest regions defect clusters are altogether absent). The steady-state defect density will immediately saturate probably at $<10^{20} \text{ cm}^{-3}$ and simply maintain a dynamic equilibrium with the surfaces sufficient to preserve the semblance of relatively perfect lattice. Nevertheless, it must be remembered that at the illumination levels ($> 1 \text{ A cm}^{-2}$) necessarily employed in lattice fringe studies, every anion is being displaced on average at least once every second. The cation sublattice remains (presumably) relatively unperturbed, and it may be this fact which enables the necessary phase differences for imaging fringes to be preserved.

5.2 Experimental Conditions

It is useful at this point to summarise how the findings of §2, §3 and §4 relate to specimen preparation procedures and specific conditions of microscope use. Alkali halide crystals intended for

study were cleaved or string sawn from bulk crystals. The resulting slices were mounted using the methods described in §3.4.3 and §4.11. Thin foils suitable for electron microscopy were prepared in dry inert atmosphere with the appropriate dried solvents and thereafter transported under dry inert atmosphere or vacuum. A thin layer 10-20 nm thick of Al was evaporated onto the lower foil surface to prevent charging behaviour in the electron beam. The central hole appearing in the dish-polished foil was generally accurately aligned in the centre of the foil so that this region did not have to be searched for in the microscope, i.e. in most cases the foil did not have to be irradiated, albeit at low beam current densities, prior to actual observation.

We indicated in §2.4 that the energy deposition rates obtaining in the electron microscope are orders of magnitude larger than those resulting from more usual radiation sources which permit a rather more leisurely approach to saturation (Table 2.3). Calculations in §3.6 indicate that the intensity transmitted through a specimen of sufficient thickness to be representative rarely amounts to more than a few per cent of incident intensity even at the maximum of the bright field rocking curve. On the other hand, acceptable recording statistics require a total electron dose $>10^7$ electrons cm^{-2} (2×10^{-12} Coulomb cm^{-2}) at the photographic emulsion (§3.7.2.3). Ilford type LN and XK emulsions (on glass plates) were used because they provide sufficient density at this exposure level. These two conditions correspond to a total electron dose incident on the specimen $\sim 10^{17}$ electrons cm^{-2} (10^{-2} Coulomb cm^{-2}) at a magnification of 15,000 or four times this at 30,000.

The former magnification provides an ultimate resolution ~ 10 nm, sufficient to observe general defect features such as small defect clusters > 10 nm in size. Much higher beam current densities are needed to adequately study irradiation damage occurring on any smaller scale. To ensure adequate mechanical stability (particularly for liquid helium microscopy), image recording was limited to 10-20 sec, which implies maintaining an incident beam current density at least in the region $1-4 \text{ mA cm}^{-2}$. Illumination, as supplied by standard tungsten hairpin filaments operated in the saturation region, may be reduced controllably to this level by using $50 \text{ }\mu\text{m}$ diameter condensor apertures.

It should be remarked that normal electron microscope illumination levels are typically 100-1000 times greater than the levels employed here. As observed above, even under these illumination conditions defect saturation in most alkali halides at room temperature occurs within the first half second of irradiation. At low temperatures saturation can occur at these levels within ~ 20 sec, which enables at least one micrograph to be recorded. That room temperature micrographs are possible at all arises from the particular distribution of room temperature saturation damage, viz. a low density of large clusters, whereas at low temperatures a high density of small clusters obtains and defect production spells the end of observation. Therefore, to avoid damage in adjacent areas the illumination was focussed with the first condensor lens adjusted for an ultimate spot size $5 \text{ }\mu\text{m}$ diameter. An adequately small value of divergence was maintained using the $50 \text{ }\mu\text{m}$ condensor aperture. The phosphor screen was viewed and focussed through

a 1.5X magnifying lens, and microscopy in total darkness was attempted only after a 15 min period of dark adaptation. The highest (100 kV) accelerating voltage attainable with the Siemens Elmiskop I microscope was used throughout the work to maximise penetration and minimise energy deposition rate, except for one set of experiments at low temperature when the Cambridge high voltage microscope was used at 600 kV.

The special specimen chamber mentioned in §3.4.2 and the liquid helium stage described in §4.10 were installed in the Siemens microscope column in place of the conventional specimen stage and chamber. The specimen was located 1 mm above the normal focal plane in the standard 6.5 mm bore objective lens. A 10 μ m diameter thin-film objective aperture was utilised because of the small scale of alkali halide diffraction patterns (d_{200} is typically twice that of metals) and to improve contrast at room temperature where diffuse scattering is strong. However, the camera length of 1.43 m (§4.9) was not deliberately increased (e.g. by changing projector lens pole pieces) because the area of the diffraction pattern embraced then became inconveniently small to recognise Kikuchi patterns, particularly at room temperature when these are masked by diffuse scattering. Experiments at liquid helium temperature were carried out at microscope vacuum typically 10^{-5} torr.

5.3 Room Temperature In Situ Irradiation

In this section we divide observations into two sorts of behaviour: "pre-saturation" behaviour which comprises defect kinetics

and morphology up to and including saturation irradiation dose and any defect state arising during this period and maintained essentially unaltered throughout further irradiation; and "post-saturation" behaviour, which includes sufficiently altered forms of defect aggregation resulting from continued irradiation, large increases in irradiation current, significant beam heating or subsequent foil anneal, etc. It will be shown in §5.4 that many of the characteristic features of pre-saturation behaviour are similar to those obtaining in bulk crystal irradiation (though with some differences), while many of the post-saturation features are largely specific to the foil irradiations and are not found in external irradiations at lower dose rates. In particular, it is to be noted that many of the results reported in early microscopical observations (e.g. Hibi and co-workers 1960-64; Tubbs and Forty 1962) were post-saturation features and bear little resemblance to defect distribution obtained in conventional external irradiations. In at least one case (large "dislocation" rings in KCl foils prepared by water thinning: Kawamata and Hibi 1965), a previously reported feature was sensitised by certain foil preparation techniques.

5.3.1 Pre-saturation behaviour

5.3.1.1 KCl

Fig. 5.1a illustrates room temperature irradiation behaviour typical of a thin region (~ 100 nm thick) of an (001) KCl foil at saturation. The behaviour illustrated was induced with an irradiating current density of 6 mA cm^{-2} . During the first second of irradiation,

narrow loop defects nucleate and elongate along $\langle 100 \rangle$ to an equilibrium size ~ 100 - 150 nm, thereafter growing only slowly with continued irradiation. The morphology of these defects suggests that three orientations are present. Defects A, characterised by a narrow loop image elongated in $|100|$ or $|010|$ and lying approximately parallel to the (001) foil plane; defects B as in A, but lying on edge, i.e. with the short loop axis normal to (001); and defects C, apparently growing with long axis normal to the (001) foil plane, and observed end-on. A similar distribution occurs in crystals externally irradiated in bulk, see §5.4.

These orientations are indicated schematically in fig. 5.2. However, in the thinnest foil regions, fig. 5.1c, only defects of orientation C are present. There are contrast features of defects C discussed later in this section which suggest that defects C are not simply an end-on equivalent orientation of defects A and B.

All defects exhibit strongly anisotropic strain fields. For example, there are two $\langle 100 \rangle$ axes for these defects in the (001) foil plane, and defects with either axis are imaged in $\underline{g} = \pm 220, \pm \bar{2}20$; in $\underline{g} = \pm 200$ contrast from A and B defects aligned along $|100|$ vanishes, as does contrast from those lying along $|010|$ using $\underline{g} = \pm 020$. Defects C exhibit the sort of contrast discussed by Ashby and Brown (1963b) for prismatic loops or planar precipitates lying normal to the foil plane; both orientations are imaged in $\underline{g} = \pm 220, \pm 2\bar{2}0$, but in $\underline{g} = \pm 200$ or ± 020 only those with trace normal to $\underline{g}$ exhibit the strong double lobe contrast; those with a trace parallel to $\underline{g}$ are imaged as thin streaks along their trace, fig. 5.1d.

From the behaviour of C-orientated defects, Izumi (1969) surmised that all planar defects observed are different equivalent

orientations of platelets lying on $\{100\}$ with associated displacement vector $\underline{R}$ normal to the platelet. However, this general assignment of $\underline{R}$ is inconsistent with the strong contrast exhibited by defects A, which on Izumi's scheme should have $\underline{R}$ normal to the $|001|$ foil and electron beam axis in fig. 5.1a and exhibit only residual contrast (e.g. Howie and Whelan 1962). Two contrast features indicate that such is not the case. First, images of defects A are in strong diffraction contrast and exhibit neither the weak contrast normally associated with residual contrast nor the line of zero contrast normal to $\underline{g}$ (see fig. 5.1a for $\underline{g} = 220$). An analysis of the strain field from defects C (§5.3.3) assuming $\underline{R}$ is along $\langle 100 \rangle$ indicates that the magnitude of the displacement is rather less than $a/\sqrt{2}$ in this case, the residual contrast parameter $m = 1/8 (\underline{g} \cdot \underline{R} \wedge \underline{u}) \sim 0.13$ for low order $\underline{g}$ (200, 220), which is rather too small to induce contrast on a scale with $\underline{g} \cdot \underline{R} \neq 0$, even in so strongly anisotropic a material as KCl ($A \sim 0.37$); see §5.5.2 for a proper residual contrast image ($m \sim 0.25$) in equally anisotropic KI ($A \sim 0.38$); also see Head, Loretto and Humble (1967); Humble (1967); France and Loretto (1968); and Loretto and France (1969). Second, those defects imaged strongly in $+\underline{g}$ are imaged weakly in $-\underline{g}$; a pair of defects, one imaged strongly and the other weakly in $\underline{g} = \pm 220$ and labelled A and A' can be seen in fig. 5.1a. This image asymmetry is discussed in §5.5.3 and §5.5.4 and indicates that $\underline{R}$ for each defect has a non-zero projection in the (001) plane which is oppositely directed for defects A and A'. We therefore surmise that for defects A, $\underline{R}$ lies in that (100) or (010) plane normal to the long axis, but is inclined to $|001|$.

Nevertheless, contrast behaviour (in figs. 5.1c and d) from defects C lying with traces parallel to $|100|$ appears to be incompatible

with such a displacement vector for defects in this orientation. Disappearance of the strong doublelobe contrast in $g = 200$ implies $\underline{R}$ lies in (010), though not necessarily normal to the axis which runs top-to-bottom (as assumed by Izumi); for example $\underline{R}$ along $|011|$ would equally satisfy observed behaviour. The apparent residual contrast exhibited in fig. 5.1d is consistent with this conclusion. For the defect segments lying in the (001) foil plane, $\underline{g} \cdot \underline{R} \wedge \underline{u}$ would be zero, whereas for the top-to-bottom segments $\underline{g} \cdot \underline{R} \wedge \underline{u}$ is non-zero; enhanced residual contrast at each end of the defect trace is in fact observed. The appearance of these defects in residual contrast is reminiscent of structure-factor contrast from thin precipitates when the matrix strain field is not imaged. The inference that $\underline{R}$ lies in (010) implies that the displacement from defects C relative to the loop geometry is different from that in defects A. It is also curious that only defects of the sort C are found in the thinnest foil regions.

There are good reasons, on models later advanced for these clusters (§5.7), why only the one sort of defect is formed in thin foil regions and might exhibit a specific displacement field. In this model it is assumed that these clusters nucleate as $\{100\}$ planar precipitations of halogen molecules aligned in $\langle 110 \rangle$ directions. In the thinnest foil regions or near to the surface of thicker foils, image forces are expected to strongly influence defect growth. Even in a region of sufficient thickness to sustain A and B type defects (fig. 5.1a), surface proximity is illustrated by the large number of defects of the sort D exhibiting contrast characteristic of surface relaxations; these latter defects are in all probability planar defects lying normal to the foil near or intersecting the foil surface(s).

In very thin foils on the molecular precipitation model, the alignment of halogen molecules along $|011|$ would be energetically more favourable, due to stress relaxation at the foil surfaces, than the expected alignment along $|110|$; it is shown further in §5.7.4 that in the presence of large image forces, a planar precipitation normal to the (001) foil is preferred to one in the foil plane and is self-stabilising. Essentially this argument implies that defects C as an equivalent orientation of defects A envisaged in fig. 5.2 do not exist in thin foils; the only stable defect in the thinnest regions is orientation B with $\underline{R}$ along $|011|$, and defects labelled C in fig. 5.1a are accordingly relabelled B' in fig. 5.1c. Thus fig. 5.2 (and a similar interpretation by Izumi) may not be correct for thin foils. A further detailed discussion of this point and further indications of the subtle role of surface effects in defect nucleation and growth appear in §5.7.4.

One further defect sort, labelled E in fig. 5.1a, remains to be discussed. This defect exhibits a double arc image with a line of zero contrast always normal to $\underline{g}$. The occurrence of such defects in the presence of the planar defects represents an incipient form of a defect cluster observed at a later stage in KCl irradiation and discussed in §5.3.2.

Fig. 5.1b illustrates in a general way the dose rate dependence of cluster morphology inherent to in situ irradiation. This micrograph depicts the state of the foil region in fig. 5.1a after increasing the irradiating current by a factor of two to 12 mA cm^{-2} . The growth of most clusters and confusion of their strain fields underscores the impossibility of analysis under more useful illumination conditions, and also indicates

that saturation cluster size is not unique in thin foil irradiations but a function of irradiation rate. This behaviour suggests that some sort of equilibrium is established during thin foil irradiation characterised by a static equilibrium cluster size for a given irradiation rate. At illumination levels much higher than that represented in fig. 5.1b the equilibrium is lost, and growth becomes dynamic at any irradiation rate, growth rate accelerating with the irradiation level. It should be pointed out that even at lower irradiation rates, individually recognisable defects are not sustained over any useful period of time except in the thinnest foil regions; in thicker regions continued growth, repeated intersections, high projected defect density and general confusion of the strain fields entirely preclude analysis. At higher irradiation rates dynamics of cluster nucleation, growth and collapse make further observation pointless and cannot, of course, be recorded statically. At beam current densities approaching those utilised in more conventional microscopy ($> 100 \text{ mA cm}^{-2}$) catastrophic degradation of the specimen surface is observed (good examples of this are the early studies of McLennan 1951 and Hibi and co-workers 1960-63), presumably due to surface halogen desorption (sputtering) via the replacement sequence as described in Elliott and Townsend (1971).

5.3.1.2 KBr

Fig. 5.3a, b illustrate saturation irradiation behaviour at room temperature in an (001) KBr foil at beam current densities $\sim 5\text{-}10 \text{ mA cm}^{-2}$. Again directed defect growth along $\langle 100 \rangle$ is noted, together with a new feature, the broadening out of initially narrow defects into square

planar loops. These defects grow to equilibrium size in nearly the same time as KCl though the room temperature production rate is down by a factor of 10 in KBr over that in KCl. That more difference is not noted between the two crystals probably arises from differences in effective recombination volume (due to vacancy mobility) obtaining at the lower irradiation rates used in production rate measurements (Hughes et al. 1967; Dawson and Pooley 1969), particularly as the production rate of KBr at 195 K is three times that of KCl at any temperature (KCl has about the same measured production rate at 195 K as at room temperature); these differences would be less in evidence at the higher irradiation rates employed during electron microscopy as explained in §2.7. Apparent differences in defect aggregation kinetics may as well not arise because the defect formation rate is so much higher than the defect aggregation rate, i.e. the actual rate of defect (in this case interstitial, see §5.5.3) diffusion is the rate limiting parameter; there is little indication from mobility temperatures (fig. 2.13) that these rates differ very much in KBr and KCl.

Continued irradiation or increased irradiation rates, fig. 5.3b, eventually induce all defects to broaden out into square planar loops. These loops appear to lie approximately on {100} (in fig. 5.3b some loops appear to lie approximately normal to the (001) foil plane as well as parallel to it, as in fig. 5.1a). The image width along one set of loop edges is consistent with this segment being pure edge, and the displacement vector of the loops is normal to this segment (this is discussed in considerably more detail for KI in §5.5). The narrower image width of the adjacent segments suggests either that these segments are not pure edge, and thus that the loop is not pure edge, implying that the loop

displacement vector is not $|001|$, or that these segments are inclined to (001). Since these loops are in all ways similar to those produced in KI and subsequently analysed extensively, little more will be said of KBr until §5.7.

5.3.1.3 KI

Fig 5.4a,b illustrate irradiation behaviour in an (001) foil of KI at room temperature under similar irradiating conditions. It is evident that planar loops are produced in KI as well as in KBr. The loops nucleate and elongate initially in $\langle 100 \rangle$, reaching an equilibrium size ~ 10 -15 nm in about 1/2 sec, after which they broaden out to a more circular form (defect production rate in KI is about one-fifth that of KCl at room temperature, but only about half at 195 K, which probably better reflects high irradiation rate behaviour). The loops also appear to broaden slightly more readily than in KBr. Again the same disparity in image width between adjacent sides of the loop is apparent; in KI the loops appear to prefer to retain a slightly longer wide image component, whereas the situation is reversed in KBr.

Continued irradiation results in general slow growth of all loops, many of these intersecting each other and forming irregular shapes. Fig 5.5a, b, c indicate two particular modes of interaction: in one case (a) loops of evidently the same character and displacement vector intersect and form a larger loop of the same sort; in (b) two loops of an evidently opposite sort (in this case the projections of their displacement vectors on the (001) foil plane are oppositely directed; this determination is made in §5.5.2) butt up against each other on the same or near neighbour habit planes but do not intersect; in

(c) an extremely irregularly shaped loop results from many repeated interactions of types (a) and (b). The fact that both loops interacting in (b) have displacement vectors in the same (100) plane (it can be shown that they both disappear in $g = 020$) indicates that there is a subdivision within any group of defects elongating along a particular $\langle 100 \rangle$ direction, i.e. all those appearing in a particular $\langle 200 \rangle_g$ vector. Differences in apparent loop contrast evident in fig. 5.4a (and also at A and A' in fig 5.1a for KCl) relate to this division and are explored further in §5.4.2. Interaction between loops elongating along orthogonal $\langle 100 \rangle$ directions can also occur with similar non-intersecting behaviour. As might be expected the broadening of KI defect aggregates into loops considerably simplifies the problems of analysis and provides additional experimental information.

5.3.1.4 NaBr

Fig. 5.6a,b illustrate irradiation behaviour in an (001) foil of NaBr at room temperature. In fig. 5.6a the defect clusters can be seen to be very small indeed, ~ 10 nm in length, but of a similar sort to those occurring in KCl, fig. 5.1a. Again the axis of growth lies along $\langle 100 \rangle$, and image contrast disappears with g parallel to this growth axis. The accumulation of these defect clusters occurs much more slowly in NaBr (the defect production rate at room temperature is two orders of magnitude lower than in KCl or KI; Hughes et al. 1967, Dawson and Pooley 1969, Calverd and Tubbs 1971; see §2.5.3 or fig. 2.12), saturation cluster size occurring only after many seconds. Fig. 5.6b indicates (in a (101) foil of deformed NaBr sectioned parallel to the slip plane) that images of defects such as dislocations existing in the

foil before irradiation are preserved at room temperature sufficiently well even after a 10 sec micrograph. This is a virtual impossibility in KCl, KBr or KI at room temperatures as the irradiation appears to destroy such defects; their strain field contrast is rapidly masked by large defect clusters in any event.

The disparity in both defect size and aggregation kinetics with alkali halides of the KCl sort are two separate but related effects. Low temperature observations of KCl and KI crystals externally irradiated at orders of magnitude smaller irradiation rates (§5.4.3) show that eventual defect size at room temperature is a function primarily of total defect production only. Thus the slow onset of observable damage in the form of small defect clusters can be attributed to the low defect production rates in NaBr; but the eventual (small) size of the clusters must arise from another cause, e.g. a low defect mobility. The latter is indicated for the case of interstitial diffusion in NaBr by the difficulty of maintaining a replacement collision sequence (§2.5.3) during the defect production process, probably because of ion size disparity. Thus, in a sense, the two observable features of room temperature damage production arise from the same cause, i.e. difficulty of propagating an interstitial, although they are really separable effects. The assumption here that the observable damage is interstitial in character is shown for the case of KI in §5.5.3 and indirectly for NaBr (by low temperature irradiation) in §5.4.3.

An interesting feature of fig. 5.5b is helical climb of screw dislocations in the NaBr foil under irradiation: this climb is only just discernable, but can be best appreciated by comparing the image of dislocations near edge orientation (E) which exhibit a wide contrast image

and, of course, linear climb normal to b which is not observable, with dislocations in screw (S) or mixed (M) orientation in which the helical cusps can be clearly seen, whose pitch increases with increasing edge character. In §5.6 we show that this sort of climb is considerably more marked in a material like KI (deformed, then externally irradiated), which is consistent with the increased interstitial mobility (and thus the increased interstitial trapping cross section of a dislocation) in this material compared with NaBr.

5.3.1.5 NaCl

It is most difficult to isolate individual defect aggregates in NaCl due to their peculiar shape. These defects are planar elongated loops as in KCl, but they are considerably distorted in the centre where they broaden out into loops. Izumi (1969) has succeeded in isolating individual defects in extremely thin "beam-flashed" foils, but these lie very close to both surfaces and may not be representative of defect morphology in bulk irradiations. Cluster behaviour in slightly thicker regions is discussed in §5.3.2.1 and illustrated in fig. 5.8a.

5.3.1.6 Dose rate dependence in thin foils

It might be imagined on the basis of saturation models (§ 2.7) that the final cluster size in KCl, KBr and KI, irradiated at room temperature, arises solely from eventual defect saturation in the foil. However, as briefly indicated in §5.3.1.1, additional factors also contribute during thin foil irradiation as demonstrated by observing the dose rate dependence of cluster size or cluster size as a function of foil thickness. These effects are most clearly illustrated in KI.

Fig. 5.7 illustrates two very thin region (~ 100 nm thick) of an (001) KI foil initially irradiated at room temperature to saturation (in $\sim \frac{1}{2}$ sec) with a beam current density of 6 mA cm^{-2} . The first three micrographs (a), (b) and (c) depict consecutive 10 sec intervals at this irradiation rate and show only small changes, both additive and subtractive, with time; in general, a gradual broadening of the defect clusters results. Doubling the irradiation current density to 12 mA cm^{-2} in (d) immediately results in a larger saturation cluster size.

There are presumably two effects at work here. First, the saturation defect concentration attainable in a crystal appears to be a function of dose rates at very high doses (Soul 1970; his dose rates were nearly comparable to those employed in microscopy). In fig. 5.7d growth of the clusters (and thus increase in the number of stable defects) by $\sim 50\%$ results from a dose rate higher by a factor of two. This is not inconsistent with the data of Soul, presuming that the majority of mobile irradiation defects aggregate into these clusters. On the other hand, there is also likely to be considerable defect diffusion to the foil surfaces in thin foils, and an equilibrium must be established between defect production, aggregation and escape to the surface. Increasing the production rate upsets this equilibrium and requires an increase in the number of internal defect sinks, which increase can be accommodated by a larger cluster size. In either case, of course, the rapid change in cluster size indicates that a defect species of immense mobility is involved in the clusters observed. This is certainly inconsistent with what is known about vacancy mobility (either F or F^+ species) at room temperature, and suggests that interstitials may be involved.

5.3.1.7 Significance of room temperature aggregation

It was indicated in §2.6.3 that the one measurable defect species existing at room temperature, the F centre, is unlikely to be aggregated to any considerable extent, and even those aggregations accruing at higher temperatures are rather small (Durand, Farge and Lambert 1969). As it was impossible to measure optical absorption spectra of these irradiated foils, nothing can be said of the vacancy distribution (e.g. from isolated F centres, F centre aggregates or colloid bands); this could be done in externally irradiated crystals and is detailed in §5.4. However, the number of sites involved in formation of these clusters (whether they are dislocation loops fed by condensation or planar precipitates) is $\sim 10^{19} \text{ cm}^{-3}$, which is the expected Frenkel defect density. It is unlikely that the isolated F centre concentration is appreciably lower than this by comparison with other high dose rate irradiations (e.g. Soul 1970).

It was indicated in §2.6.4 that the V bands apparently attributed to interstitial halogen species (e.g. Ishii 1966) are not well characterised at room temperature, primarily because no isolated interstitial species appears to exist at room temperature (from unsuccessful EPR searches). Together with other accumulated evidence for interstitial clustering (§2.6.4.2) this result suggests that the defect clusters observed at room temperatures might well be the long-sought interstitial aggregations. Izumi (1969) has assumed on the basis of rather questionable earlier evidence for colloids (Westervelt 1953; Yoshida and Ikeda 1959; see §2.6.5.2) that these defect clusters in KCl and NaCl are alkali metal colloids. This assumption is unlikely in view of either the large number of sites involved in these clusters

(~ a saturation F centre concentration) or the immense mobility of the point defect(s) responsible (cf. the relative immobility of anion vacancies at room temperature), and the results from other irradiation experiments indicating that the vast majority of anion vacancies remain in isolated form. Of course, this sort of information cannot be applied with certainty to in situ observations until it is established that in situ irradiation sufficiently resembles conventional irradiation in bulk. This is done in §5.4.3 and these clusters are then proved to be interstitial in character in §5.4.2 and §5.5.3.

Little can really be said about the comparative sizes of these defects in different alkali halides (except for the case of NaBr), as the equilibrium size is shown in §5.3.1.5 to be critically dose rate and foil thickness dependent. Much more can be learned from the observations of externally irradiated bulk crystals detailed in §5.4.3. Certainly, clusters in all alkali halides examined in situ exhibit a decided initial preference for $\langle 100 \rangle$ growth normal to the displacement vector, and a near $\{100\}$ habit plane. Loop clusters in KI are the most regular and easily analysed and were selected for further study in §5.4 and §5.5; use of KI is particularly advantageous because this crystal exhibits considerably reduced defect production at low temperature. Differences in cluster morphology among the alkali halides are useful in confirming a model for these clusters advanced in §5.7.

5.3.2 Post-saturation behaviour

5.3.2.1 Extrapolation of saturation behaviour

Continued irradiation at the low beam current densities utilised in §5.3.1 or increase in irradiating current caused in most alkali halides

a simple extrapolation of the sort of behaviour obtaining at saturation. For example, fig. 5.8a illustrates the confused strain field contrast in NaCl resulting either from irradiation of thicker foil regions or continued irradiation after saturation. Similar contrast appears in KCl, as indicated in fig. 5.1b. In NaCl (room temperature defect production rate similar to KCl) it is particularly difficult to isolate individual defect clusters in all but the very thinnest regions where the resulting clusters may be far from representative (e.g. see Izumi 1969). In KI, in which regular loops are formed at saturation, repeated intersections after prolonged irradiation result in the sort of large loops illustrated in fig. 5.8b. Although these irregular loops retain the contrast features of smaller regular loops, they are often seen to intersect the foil surface, leaving behind segments of apparent dislocation line. In NaBr large irradiation doses nucleate a few rather larger clusters with an apparent axis considerably displaced from $\langle 100 \rangle$, fig. 5.8c. Apart from these cluster morphology remains unchanged.

In all these crystals the damage is never static during room temperature irradiation but is in continual flux. Apart from the inconvenience for analysis, such behaviour implies that a continual regrouping of defect clusters is occurring through repeated interstitial-vacancy creation, diffusion and recombination. It is, of course, not surprising that in easily damaged crystals (KCl, KBr, KI, NaCl) existing defects, such as dislocations, do not long survive, when during the course of a single photographic exposure every anion has been displaced several times from its lattice site.

5.3.2.2 Nucleation of symmetrical clusters

Fig. 5.9a illustrates an (001) KCl foil irradiated at a beam current density $\sim 50 \text{ mA cm}^{-2}$ after many seconds irradiation. During this time the planar clusters discussed in §5.3.1 form quickly, intersect, then largely disappear to be replaced by a new defect exhibiting the strain field contrast illustrated. This defect was the only one observed in the early studies of KCl (Hibi and co-workers 1960-63; Tubbs and Forty 1962) in which much higher illumination levels were employed. The "double loop" image characteristic of this defect has a pair of contrast lobes symmetrical about a line of zero contrast normal to g . The strain field about the defect is therefore approximately spherically symmetrical and arises from radial displacements of the lattice. Contrast from defects inducing such displacements has been observed by Müllenstedt (1953) and Rang (1953) for the case of defects induced by ion bombardment which were thought to be voids, and both observed and computed by Ashby and Brown (1963a) for the case of symmetrical coherency strains surrounding a spherical inclusion.

The growth of these defects in KCl foils during in situ electron microscopical irradiation has been observed by Hibi and Yada (1962), Tubbs and Forty (1962) and Kawamata and Hibi (1965). Hibi et al. have called them voids (entirely without justification) and Izumi (1969) termed them "lens-shaped defects" (again without justification), both by inferences from the earlier assumptions of Rang and Müllenstedt. Ashby and Brown have shown, of course, that the geometrical shape of a small defect is of little consequence to its contrast if the displacement field at large distances is approximately radial, and of course the strain may

be either positive or negative, i.e. either adilatation or relaxation of the lattice, the lattice being in compression or tension. Therefore we shall abandon both previous notations and instead call these defects simply "spherical clusters" where it is understood that "spherical" applies to their radial displacement field and not to their detailed shape and that "cluster" applies to an unspecified aggregation of either vacancy or interstitial character. For example, an alkali colloid or high pressure halogen gas bubble might introduce a strain centre of the former sort (see §5.3.3) and a void or low pressure halogen gas bubble one of the latter.

Kawamata and Hibi (1965) have established that these clusters nucleate from large circular dislocation rings occurring in thin foil regions and lying in the (001) foil plane. (It should be remarked that platelet clusters of the sort described in §5.3.1 were not frequently observed by Kawamata and Hibi because the beam current densities they employed were considerably larger than used in the present study.) A much smaller loop of a sort thought to be the precursor of these defects was indicated at E in fig. 5.1a. Large dislocation rings in irradiated KCl were also observed in this study, fig. 5.9b. Kawamata and Hibi somehow established to their satisfaction that the displacement vector $\underline{R}$ for these loops lay inclined to the $|001|$ foil normal (their purported evidence does not demonstrate this, and evidence found in this study and their micrographs contradicts such an assignment). Unrecognised by them, but obvious from their micrographs, are the comparatively weak contrast exhibited by these ring structures, the line of zero contrast always normal to $\underline{g}$ and image doubling characteristic of a pure edge prismatic dislocation loop or coherent planar precipitate, for which $\underline{g} \cdot \underline{R} = 0$

everywhere (in this case $\underline{R}$ is normal to the (001) foil and loop plane), contrast arising from secondary displacements wherever $\underline{g} \cdot \underline{R} \wedge \underline{u} \neq 0$ ($\underline{u}$ the local dislocation direction). There is therefore little doubt that the primary displacements are indeed either normal to the loop plane or symmetrical in the foil plane, and (from its behaviour with continued irradiation) that this defect is a planar precursor to a later three dimensional defect. However, we shall continue to denote these defects as "rings" to distinguish them from the planar loops described in §5.3.1 which they are not.

A likely explanation is the planar precipitation of some interstitial or vacancy defect species on (001). One possibility is an initial planar precipitation of the interstitial halogen species in some form, eventually aggregating into a three-dimensional halogen gas bubble. It will be established in §5.5.3 and §5.7 that the planar loops described in §5.3.3 reflect at least some major fate of the interstitial halogen species at and below room temperature and induce a displacement vector $\underline{R}$ along $\langle 110 \rangle$; therefore, if the prismatic rings on (001) with $\underline{R}$ along $|001|$ arise from halogen molecular precipitation, they must represent a rearrangement in the stage of halogen aggregation. Other aggregates can be envisaged involving halogen gas: for example, gas-filled voids deriving either from the aggregation of cation and anion vacancies and halogen interstitials, or from the aggregation of cation vacancies alone. These latter models require large cation vacancy concentrations; and, while it is unlikely (from the discussions of §2.5) that the cation sublattice

is involved in the basic irradiation damage process, a mechanism for generating cation vacancies via the stabilization of halogen interstitials is indicated in §5.7.5 and a possible aggregation model is discussed in §5.7.6.

A second possibility is a planar precipitation of anion-cation vacancy pairs collapsing to a pure edge dislocation of vacancy character. It is, however, difficult on this model to imagine a subsequent mechanism for conversion to a three-dimensional void. Again, both anion and cation vacancies are required, there being little evidence for the latter. Also, the activation energy for cation vacancy (or cation-anion vacancy pair) motion (~ 1 eV; Barr and Lidiard 1970) is rather high for large aggregate formation at room temperature.

A third possibility is a planar precipitation of F centres to form plates of alkali metal. In this mechanism the F centre (probably migrating initially as a radiation-induced F^+ centre, then aggregating and retrapping an electron) donates its electron to the alkali ion, forming a much larger alkali atom which is initially constrained (for energetic reasons) to reside in its original f.c.c. position in the KCl lattice. Collapse into spherical clusters may result simply from subsequent three dimensional growth to minimise accommodation strain and may even be accompanied by reorganisation into the normally occurring b.c.c. alkali metal arrangement. It should be noted here that in either structure, the volume occupied by the alkali "colloid"

may be larger or smaller than that occupied by the region of KCl lattice embracing an equivalent number of alkali ions depending upon the alkali halide/alkali combination; therefore the lattice strain may be positive (dilatation) or negative (relaxation), i.e. the lattice can be either in compression or tension from the colloid particle (cf. a void for which the lattice relaxes). It should be possible to deduce the sense of lattice strain by analysis of the so-called anomalous images exhibited by those inclusions lying very near to either foil surface (Ashby and Brown 1963a) and also the magnitude of lattice strain induced and the size of the included particle. These determinations are discussed in §5.3.3.2.

5.3.2.3 Annealing behaviour

Before conducting heating experiments one should first ascertain what foil temperatures are induced by the irradiating electron beam itself. In §4.2 we derived an expression for the foil temperature rise as a function of thermal conductivity and beam current density for dish-polished alkali halide specimens. At room temperature the thermal conductivity of KCl is $70 \text{ mw cm}^{-1} \text{ K}^{-1}$ (McCarthy and Ballard 1960), and setting $j = 10^{17} \text{ electrons cm}^{-2} \text{ sec}^{-1}$ (20 mA cm^{-2}) we arrive at temperature rise of only a few K. Therefore we conclude that the observations of §5.3.1 and

§5.3.2 were representative of room temperature behaviour.

In order to investigate higher temperature behaviour, brief annealing experiments were conducted (in 1967) during in situ irradiation of KCl and NaCl foils in a grid-heating specimen cartridge (Whelan 1958). Unfortunately, the temperature of the heating grid was known only approximately to $\sim 50^{\circ}\text{C}$ and it was difficult to relate behaviour in two different crystals. However, general trends were established, which still correlate with more quantitative annealing experiments subsequently conducted by Izumi (1969). In KCl the elongated loop defects sustained under low irradiation rates disappeared first upon heating above 373 K, followed by nucleation of spherical clusters similar to those produced by higher levels of irradiation at room temperature. All damage appeared to anneal out above 673 K and further heating resulted in sublimation of the crystal. In NaCl spherical clusters were never produced at room temperature, even at high irradiation levels, but readily formed above 473 K, fig. 5.9c, and annealed out above 623 K. These were of size and distribution similar to those produced in KCl. Izumi's results were that the elongated loop clusters in NaCl were more stable than those in KCl, the former disappearing at 573 K and the latter at 423 K. Both results are listed in Table 5.1; they appear to correlate with at least the general trend of temperature dependence of F^{+} mobilities in the two materials, fig. 2.13.

The annealing sequence reported above does correlate with

other indications of a change in defect behaviour. Westervelt (1953) observed a decrease in hardness induced by irradiation in x-rayed and electron irradiated KCl upon annealing at 423 K; in NaCl both Westervelt and Aerts, Amelinckx and Dekeyser (1959) observed a decrease at 473 K. Hardness in the two crystals completely annealed out at 573 K and 623 K respectively. These annealing temperatures also correspond in a general way to thermal evolution of colloid absorption bands (2.6.5.2); for example Jain and Sootha (1965) found $F \rightarrow$ colloid in additively coloured KCl at 553 K; Yoshida and Ikeda (1959) found a shift (although interpreted incorrectly) from the X band to the colloid band at 663 K in previously irradiated NaCl. Izumi (1969) has presumed that the planar loops were colloids, and has interpreted Yoshida and Ikeda's shift of the absorption band as due to break up of colloids; both assumptions are incorrect. It will be noticed that the initial temperatures are somewhat lower during thin foil irradiation than for annealing of previously irradiated bulk crystals; this undoubtedly reflects not only surface effects but also dynamic irradiation conditions as well. For example, Yoshida and Ikeda have observed that irradiation at temperatures above 573 K in NaCl induced colloidal scattering in the crystal (cf. 663 K for anneal without further irradiation), while Durand, Farge and Lambert (1969) observed presumed colloid formation (surmised from low angle x-ray scattering) in LiF during electron irradiation at temperatures as low as 473 K.

A similar effect has been reported by Guinier and Lambert (1966) in neutron-irradiated LiF. This additional evidence is also listed in Table 5.1 for comparison.

Guinier and Lambert find evidence from diffuse x-ray scattering for thin platelet defects (which they attribute to alkali metal) which are unstable under prolonged anneal above 573 K and are replaced by microcavities giving rise to small angle x-ray scattering during anneal at or above 673 K. Irradiation at 423 K induces microcavity formation directly without platelet formation (Lambert and Guinier 1957, 1958; Lambert et al. 1959). The platelets were established to be 0.3-1.0 nm thick and ~ 100 nm in extent (Lambert, Mazieres and Guinier 1961), and they are almost certainly not Li colloid as surmised by Lambert et al., but instead the interstitial planar loops detected by electron microscopy; Spalt and co-workers (Spalt 1969; Trinkhaus et al. 1970; Spalt and Peisl 1971) have in fact interpreted their diffuse x-ray scattering measurements of electron irradiated LiF in terms of interstitial halogen aggregates. The microcavities were presumed void, and their density was estimated at $\sim 2 \times 10^{16} \text{ cm}^{-3}$, decreasing for anneal above 573 K. At this temperature the fraction of the lattice which is void was estimated at $\sim 2 \times 10^{-4}$. The annealing results suggest that microcavities are coalescing above 573 K; similar behaviour occurs at lower temperatures under dynamic irradiation.

The disappearance of the planar loop clusters, which are shown in §5.4 and §5.5.3 to involve interstitial halogen, is significant. These may disappear from two causes: annihilation by mobile vacancies or loss of interstitial cluster stability (on models discussed in §5.7). Since in KCl these clusters are stable for low irradiation dose rates at room temperature and unstable at room temperature for higher irradiation dose rates with the arrival of large spherical clusters, this suggests that it is annihilation by mobile anion vacancies (probably radiation-induced F^+ centres), which are also aggregating into large clusters, that effects their loss. For NaCl the case is less clear, because considerable thermal activation (~ 1 eV) is present at the temperature at which these clusters do disappear (~ 500 K). Thus it is probable that additional thermal activation is required. This suggests actual dissociation of interstitial clusters. Indeed, Lambert and co-workers (Lambert et al. 1959; Guinier and Lambert 1966) have discovered evolution of fluorine gas together with some form of spherical cavity upon annealing neutron-irradiated LiF, while Knutson, Hooper and Bray (1965) have detected NMR spectra from bulk molecular $^{19}F_2$ in a fluid or gaseous state, which they interpret as F_2 molecules trapped in microcavities. These results confirm that the planar interstitial clusters have in fact dissociated, releasing halogen gas which diffuses out of the crystal or to the microcavities detected by Lambert et al. The actual composition of these cavities remains a mystery, but it must necessarily involve aggregated cation vacancies with molecular

halogen trapped in them.

Thus we have two likely explanations for the spherical clusters: microcavities, possibly halogen gas filled, but certainly requiring appreciable numbers of cation vacancies; and large alkali metal colloids requiring anion vacancy aggregation. In order to ascertain which explanation best accounts for the spherical clusters observed, more direct evidence was sought in electron microscopical measurements described in §5.3.3. A discussion of the evidence follows in §5.3.3.4. Detailed experiments revealing more precisely the nature of the planar interstitial loop clusters are outlined in §5.5.

5.3.3 Analysis of room temperature clusters in KCl

5.3.3.1 Planar loop clusters

Bright-field images of the planar loop defects lying normal to the foil in fig. 5.1c may be analysed using the method developed by Ashby and Brown (1963b) for edge-on pure edge dislocation loops or planar precipitates with displacement vector $\underline{R}$ normal to the defect plane and in the plane of the foil. The extent of the contrast lobes normal to the defect plane, for example the 20% image width for diffracting conditions near $s = 0$ (s the deviation from the Bragg condition), can be compared for different loop radii r (plotted as r/ξ_g) to obtain a value for the parameter $\log_{10} \left\{ \frac{r^2}{\xi_g^2} g R \cos \theta \right\}$, where ξ_g is the two beam extinction distance (assuming two beam diffraction conditions adequately obtain) and θ is the angle between $\underline{g}$ and $\underline{R}$. From

this parameter the magnitude of $\underline{R}$ may be derived.

In the present case it is expected (from the discussions of §5.3.1.1 and also §5.7.4) that $\underline{R}$ does not lie normal to the defect plane, but inclined out of the foil by 45° with a projection in the foil plane normal to the loop plane. It is not known what effect this inclination of the displacement vector has. Moreover, the defects are not circular either (the ratio of length to width may be very large). In the former case, Ashby and Brown have indicated that loop tilts (for $\underline{R}$ normal to the loop plane) of up to 30° have very small effect on the image width. No data are available to confirm applicability in the latter case. Measurements were made on a number of loops in KCl imaged under bright field $s = 0$ conditions for $g = 220$ ($\theta = 45^\circ$ if θ is defined between g and the projection of $\underline{R}$) from the data of this study and those of Izumi (1969). Both sets of data agreed closely. ξ_{220} for KCl at room temperature was computed as outlined in §3.6.2 using Doyle-Turner (1968) ionized-atom electron scattering factors, and temperature factors from International Tables for X-Ray Crystallography (1962) ($\xi_{220} = 87.2$ nm). The "radius" of the loop was assumed to be the trace of the defect in the foil plane. Both data sets yielded an average value of $R = 0.24$ nm, Table 5.2. This displacement corresponds to 0.55 times the perfect $a/2 \langle 110 \rangle$ lattice shear, i.e. $R = 0.55 a_0/\sqrt{2}$. This value is in good agreement with the displacement expected for a $|\text{Cl}_2^0|$ chlorine molecule squeezed between neighbouring chlorine ions along $\langle 110 \rangle$, Table 5.6, on one model advanced in §5.7, and provides possible support for this

interpretation in the discussion of §5.3.1.1 concerning morphology of those defects lying normal to the foil in very thin foils.

5.3.3.2 Spherical clusters

Bright-field images of the spherical clusters in KCl, fig. 5.9a, can be analysed according to the method derived by Ashby and Brown (1963a) for contrast from symmetrical coherency strains to determine both the inclusion size and also the magnitude of the strength of the elastic strain ϵ (this parameter will be rigorously defined in §5.3.3.4). The image profiles observed agree well with the profiles computed by Ashby and Brown for a material with absorption parameters similar to alkali halides ($\epsilon_g'/\epsilon_g \sim 20$). A plot similar to that used in §5.3.3.1 is utilised; in this case image width as a fraction of ϵ_g is plotted against the parameter $\log_{10} (\epsilon g r_o^3 / \epsilon_g^2)$ at 20% and 50% contrast levels. The radius of the inclusion, r_o , can be derived from behaviour of the image profile along the line of zero contrast. The projected perimeter of the inclusion is taken to be where the outer contrast lobe departs abruptly from an approximately straight line (this criterion is evident from Ashby and Brown's computed profile map). This is not an easy assessment to make, and the radii derived must be treated as only approximate: unfortunately the value of ϵ varies as r_o^{-3} and so is very sensitive to radius determination.

Measurements were taken from spherical clusters observed in this study, in that of Izumi (1969) and in that of Kawamata and Hibi

(1965) for $g = 200$ in approximately $s = 0$ conditions. Ashby and Brown have shown that the image width does not vary greatly with deviation parameter provided $w = \xi_g s \lesssim 1$, which is within the useful region for best transmission; furthermore, for the magnitude of image widths measured here, the parameter $\log_{10} (\epsilon g r_o^3 / \xi_g^2)$ is less sensitive to small changes in image width than for the much smaller defects considered by Ashby and Brown where the $s = 0$ condition is critical. A value of ξ_{200} at room temperature for KCl was computed as in §5.3.3.1 ($\xi_{200} = 64.7$ nm). Results for the different cluster sets were consistent (for any given criterion for determining r) and are listed in Table 5.3. It should be noted that these determinations span a factor of three in cluster size.

Of particular interest is the estimated size of the inclusions, up to ~ 20 nm diameter. As indicated in §5.3.3.4 this is a large cluster and involves $\sim 10^7$ condensed defects per clusters. The size is considerably larger than the ostensible colloidal clusters produced during irradiation of LiF at ~ 500 K by Durand, Farge and Lambert (1969), and it correlates more closely with the pits observed by replication in additively coloured crystals treated to produce colloids (§2.6.5.2). The observed density of clusters ($\sim 4 \times 10^{13} \text{ cm}^{-3}$) implies that they occupy a substantial fraction ($\sim 2\%$) of the lattice.

It is possible in theory to determine the sign of the observed strain by dark field analysis of the "anomalous" (unusually wide and asymmetric) images exhibited by inclusions lying within $\xi_g/4$ of the surface. In such cases, at the Bragg condition ($s = 0$) in dark field,

the anomalous image exhibits an intensity maximum on the side of positive g and an intensity minimum on the side of negative g for negative strain ϵ (lattice relaxing into the inclusion) and conversely for positive strain (lattice displaced outwards from the inclusion). Suitable anomalous images were not often found, perhaps because these inclusions are not formed close to the surface, for example because the surface regions become depleted of vacancies, or because the inclusion diameter is considerably larger than $\xi_g/4$ (in fact $2r_o \sim \xi_g$). However, those that did appear (fig. 5.10a) were analysed and in dark field $s_g = 0$ conditions showed an intensity maximum on the side of negative s (fig. 5.10b).

Izumi (1969) has one dark field micrograph of KCl (reproduced as fig. 5.10d) which by chance (he was not analysing his defects for this effect) includes some small spherical clusters, of the sort labelled E in fig. 5.1a, lying near enough to the surface to exhibit anomalous contrast (fig. 5.10c). The intensity maximum for these defects lies on the side of indicated positive g , opposite to that indicated in fig. 5.10b. However, it is perfectly possible that Izumi has neglected to allow for the inversion of the diffraction patterns with respect to the micrograph (e.g. Groves and Kelly 1962), whereas this was definitely included for the micrographs in fig. 5.10a, b. We therefore prefer to believe the latter assignment, which confirms a positive strain, i.e. the lattice in compression by the

inclusion. This determination incidentally rules out the empty void explanation (which Izumi assumed).

5.3.3.3 Energy loss measurement

A method exists, comparable to optical measurements in thick crystals, for analysis of electronic and ionic defects produced in thin foils during electron irradiation, viz. energy loss or so-called "velocity" analysis of high energy electrons transmitted through a thin foil specimen. This technique was briefly outlined in §2.4.1 in the context of energy loss modes and is discussed here because of its particular relevance to alkali colloid production. With this technique, electrons emerging from a particular foil region are spread in energy, for example by an electrostatic or electromagnetic lens to provide a spectrum of discrete energies lost.

In addition to the normal exciton and plasma loss spectra, two electron energy loss studies (Pradal and Gout 1964; Creuzberg 1966a) have revealed additional loss peaks below the first exciton level (i.e. in the "optical" range, $\sim 0-6$ eV). Pradal and Gout (1964) found losses at 3.7, 5.7, 7 and 8 eV for 20 keV electrons in NaF foils prepared by thermal evaporation, evaporation in air from water solution or powdering. Creuzberg (1966a) found loss peaks in a variety of thermally evaporated alkali halide foils (summarised in Table 5.4) which slowly developed under well-characterised 50 keV electron irradiation ($\sim 10^{-5}$ A cm $^{-2}$)

with increasing dose. These peaks were interpreted as due respectively to surface and bulk plasma losses characteristic of colloidal alkali particles ~ 10 nm in size suspended in the alkali halide dielectric medium. Subsequently Fujimoto and Komaki (1968) formulated a semi-classical theory describing the effect, going to specific lengths to derive a relation between surface plasmon energy loss and particle size, which was then applied to Creuzberg's data. Notwithstanding, it is difficult to appreciate how alkali colloid formation could occur, given the small irradiation doses employed, at least for the one example of NaI which produced recognisable loss peaks at 2.1 and 5.7 eV after 10 min 50 keV electron irradiation at $6 \times 10^{-6} \text{ A cm}^{-2}$. It is known (§2.5) that the NaI F centre production rate at room temperature is very low ($5.5 \times 10^{-8} \text{ F eV}^{-1}$), and assuming an energy loss rate (fig. 2.6) of $1.1 \times 10^7 \text{ eV cm}^{-1}$ for 50 keV electrons we obtain at most an F centre production of $1.2 \times 10^{16} \text{ F cm}^{-3}$ which is three orders of magnitude below saturation. In all other alkali halides the F centre density was nearer saturation.

An alternative explanation for at least one of the energy loss peaks (the low energy one) is that it represents an excitation in the F band (analogous to F band optical absorption) arising from the presence of F centres in the irradiated crystal. F band positions have been indicated in Table 5.4, and the close correlation with the data both of Pradal and Gout and of Creuzberg is particularly evident. There is no direct experimental evidence to confirm that F band excitation can give rise to inelastic scattering of high energy electrons, although the similarity of electron energy loss spectra (Creuzberg 1966b) and those obtained optically (Milgram and Givens 1962) suggest a consistent

correlation, and there is recent evidence (Alexandropoulos 1970, 1971) of inelastic x-ray scattering correlating with F band excitations in LiF and NaCl. The higher energy peak does not appear to correlate with a known colour centre band, but does agree well with the bulk plasmon loss in the respective alkali metal and is characteristic primarily of the alkali species only. Creuzberg has estimated the colloid size as ~ 10 nm from the width of diffraction rings attributable to alkali metal in electron diffraction patterns. Colloid clusters this size, however, have not been detected in room temperature electron microscopy of foils of those alkali halides Creuzberg studied.

On the other hand it does appear likely that in materials such as KCl (which was not measured by Creuzberg or Pradal and Gout) the large spherical clusters produced under intense irradiation should be of sufficient size and density to produce characteristic energy loss spectra. Therefore, this material and another, NaCl, with similar room temperature damage properties but in which large spherical clusters are absent at room temperature, were examined for electron energy losses in the single crystal thin film state in the electron microscope. The system used in the present study utilises a Mllenstedt cylindrical electrostatic lens, designed as a compromise between high dispersive power and high resolution, which is placed beneath the camera chamber of a Siemens Elmiskop I electron microscope. This system is based on the design of Metherell and Whelan (1966) and has been described in detail by Cundy (1967). The cylindrical analyzer electrodes were maintained at the same potential as the tip of the microscope filament; for calibration, accurately known voltages were applied to these electrodes to simulate a decrease in electron energy. A dispersive capability of 70 eV

was attainable with a resolution ~ 0.2 eV for the electrodes employed. The special specimen chamber and loading lock facilities described in §3.4, as well as the liquid helium stage, were installed in this microscope, though the latter was not used extensively in the experiments described here. 100 keV electrons were utilised in all measurements.

Fig. 2.5a, b illustrate graphically the energy loss profiles in KCl and NaCl derived by microdensitometric traces across the velocity analyzer spectra as recorded on photographic plates. Those peaks designated numerically correspond to those found by Creuzberg (1966b) relating to alkali halide exciton and plasmon excitations. The one exception, in KCl, is a very weak peak at 3.4 eV which approximately correlated with the bulk K plasmon loss. A corresponding peak was not detected in NaCl at room temperature. These results are consistent with the microscopical observations in KCl and NaCl but are not especially revealing. Certainly, a really strong colloid peak was not detected which might be expected from spherical alkali inclusions of the order of the film thickness in diameter and occupying fully 2% of the lattice. Nevertheless, it should be pointed out that the microscope analyzer system is considerably less sensitive than Creuzberg's energy analyzer, though of course Creuzberg's instrument has no provision for simultaneous microscopy.

5.3.3.4 Models for spherical clusters

We first consider if the evidence enables a colloid model to be proposed for the nucleation of dislocation rings and spherical clusters during the later stages of thin foil irradiation. On this model anion vacancies initially created as F centres are rendered mobile by excitation to F^+ or by thermal activation. These vacancies first condense as planar aggregates on {001} forming a planar alkali metal precipitate with face-centred cubic structure. It is possible that strain relaxation at foil surfaces in (001) foils makes this habit plane attractive. In the thinnest foil regions, the impossibility of additional growth normal to the initial habit plane, due to vacancy depletion at the foil surfaces, causes the defect to extend in the (001) plane, forming a large loop. The resulting planar sheet of f.c.c. alkali metal would exhibit two displacements, one radial in the sheet plane, the other normal to the sheet plane; both displacements would yield images characteristic of $\underline{g} \cdot \underline{R} \wedge \underline{u}$ residual contrast. The normal $\langle 100 \rangle$ spacing of alternate {100} layers in KCl is 0.267 nm, while the diameter of the potassium atom is 0.462 nm; incorporation of a sheet of potassium atoms in the plane between them results in a displacement normal to a sheet of $0.3 \langle 100 \rangle$. Electron diffraction patterns ostensibly from thin sheets of Li metal in a f.c.c. structure or from Li_2O in heavily irradiated LiF have been detected during electron microscopy (Carroll and Birnbaum 1965; Russell, Martin and Bowen 1970); however, the sheets observed appeared to be normal to the foil and rather thicker than only a few

atom layers. Furthermore diffraction patterns from K or Na metal have not been observed in the present work, although streaking of the diffraction pattern along $\langle 100 \rangle$ does not occur during heavy electron irradiation. However, this streaking is at a later stage of irradiation than when spherical clusters first nucleate, and may correspond as well to degradation of the foil, possibly through halogen desorption (see also Hibi and Yada 1962).

In thicker foil regions the defect can grow three-dimensionally to minimise the accommodation strain, forming at first lenticular, then spherical, inclusions of alkali metal. Spherical Li agglomerates ~ 36 nm diameter have been ostensibly detected by EPR in neutron-irradiated LiF (Kaplan and Bray 1963). The defects then continue to grow until they achieve dimensions approaching the foil thickness. The normal alkali metal structure at room temperature is body-centred cubic. The face-centred cubic form may at first obtain because initial condensation of halogen vacancies will leave the alkali cation lattice in f.c.c. form; however, at some stage in the growth a transformation may take place from an f.c.c. to a b.c.c. structure. The molten alkali phase may be important also because alkali metal melting points are only just above room temperature (K, 335 K; Na, 370 K; Li, 459 K), and at higher foil temperatures a molten phase may exist. The conditions present during thin foil irradiation (e.g. loss of interstitials) may render this sequence rather atypical of bulk crystal behaviour.

If these spherical clusters are the controversial alkali colloids (see §2.6.5.2) usually formed under conditions of higher temperature, one must ask why they form so readily at room temperature in thin KCl foils. It has been shown that, in fact, raising the temperature of irradiation does induce spherical cluster nucleation in an alkali halide (NaCl) which does not occur at room temperature. However, these temperatures are still considerably below those required by Durand, Farge and Lambert (1969) to induce small, presumably colloidal, particles of the order of 1 nm in diameter in LiF. One explanation may be altered saturation kinetics in thin foil irradiations. It is seen from fig. 5.9a that spherical clusters of the sort described in §5.3.1 are present (these are shown to be interstitial in §5.5.3). On the athermal recombination model (§2.7) for saturation kinetics, all that is required is a sink for interstitials, and the foil surfaces serve this purpose nicely; however, this model described only the approach to saturation (first $\frac{1}{2}$ sec of irradiation!) and does not imply an absolute defect saturation level. For absolute saturation some additional back reaction must be supplied, e.g. F aggregate formation, annihilation of mobile F centres at interstitial clusters, etc. The only likely mechanism for absolute defect saturation in the absence of interstitial clusters is Farge's (1969) model of mobile interstitials annihilating vacancies on the way to interstitial sinks (in this case the foil surfaces).

For an interstitial mean free path length ℓ and an

interstitial vacancy interaction volume v , the probability of an interstitial annihilating with a vacancy is given by

$$\pi \left\{ \frac{3v}{4} \right\}^{2/3} \ell F^i, \quad (5.1)$$

where F^i is the isolated F centre concentration. This probability will be unity at absolute defect saturation, i.e. at saturation

$$F_{\text{sat}}^i = \left(\pi \left\{ \frac{3v}{4} \right\}^{2/3} \ell \right)^{-1}. \quad (5.2)$$

For a saturation F centre concentration of $10^{19} \text{ F cm}^{-3}$ and the recombination volume calculated by Hughes and Pooley (1971) the interstitial mean free path is $\sim 3 \text{ nm}$, considerably less than the foil thickness involved. Therefore, it is unlikely that appreciably higher F centre concentrations will be sustained more than about 3 nm from the foil surface. However, (5.2) neglects F centre aggregation which considerably reduces the recombination volume per F centre, v . In other words, the total recombination volume available for interstitial annihilation may decrease from its bulk crystal value and more than $10^{19} \text{ F cm}^{-3}$ may be accommodated in the crystal in aggregated form.

For example, suppose that the clusters in fig. 5.9a are spherical colloidal alkali inclusions. The analysis of §5.3.3.2 indicates that these inclusions are likely to be $\sim 100 \text{ nm}$ across. This cluster size represents condensation of $\sim 8 \times 10^6$ F centres per cluster. The cluster density in fig. 5.9a is estimated at $\sim 4 \times 10^{13} \text{ cm}^{-3}$, so a total of $\sim 3 \times 10^{20} \text{ F centres cm}^{-3}$ have condensed.

The total prohibited volume associated with these clusters is $\sim$ the total cluster volume, since the athermal recombination interaction radius is so much smaller than the cluster size. This volume corresponds to a volume fraction only about 2% of the total crystal volume, whereas it is supposed on the athermal model that near saturation the prohibited volume nearly fills the crystal.

It was indicated in §2.6.5.1 that vacancy aggregation would not proceed past aggregates of a few unless the aggregation volume w was substantially increased from its athermal value. The probable mechanism for achieving an increase in w is through thermal diffusion of the aggregating species. At room temperature, at high irradiation rates, this process is almost certainly radiation activated, as the mobility of the F centre itself is virtually zero. A mechanism for this involving F^+ production was indicated in §2.6.5.1.

The total capture surface area represented by the spherical clusters of the size and distribution appearing in fig. 5.9a is $\sim 1.2 \times 10^5 \text{ cm}^2 \text{ cm}^{-3}$; for a 300 nm thick foil the surface sink area is $\sim 3 \times 10^4 \text{ cm}^2 \text{ cm}^{-3}$. In other words a mobile vacancy/interstitial is slightly more likely to join/annihilate in a cluster than to escape to the surface. Since these probabilities are about equal for both species, and because the interstitial is considerably more mobile than even an F^+ centre, it is expected that the factor limiting both cluster growth kinetics and eventual cluster size will be the steady state distribution of isolated or small aggregate F centres which will control the athermal rate of interstitial-vacancy recombination.

This distribution will depend on both F^+ mobility and $F \rightarrow F^+$ conversion rate. A saturation cluster size should thus be dose rate dependent, which is observed, viz. considerable growth and profusion occurs only for beam current densities in excess of 50 mA cm^{-2} . An absolute cluster size limit appears to be $\sim 200 \text{ nm}$ which is of the order of the foil thickness.

We may calculate the expected strain ϵ arising from alkali inclusions in alkali halide lattices by considering the elastic field of an inhomogeneous inclusion. Suppose we have a spherical inclusion I^* with Lamé constants λ^* and μ^* surrounded by an isotropic matrix M with Lamé constants λ and μ . If we denote by v' the volume fraction by which the matrix must be increased to accommodate the inclusion with the latter in a stress free state, i.e.

$$v^* = (v_{I^*} - v_M)/v_M;$$

We can define a fractional volume change v for an inclusion I having the same elastic properties as the matrix, such that when both inclusions are imbedded in the matrix, identical elastic strain fields will be sustained. The volume changes v , v^* are specific cases of generalised transformation strains for inclusions of arbitrary shape; when an inclusion has spherical symmetry, all accommodation strains are purely dilatational.

Eshelby (1957, 1961) has shown that the condition for identical elastic fields arising from I and I^* is

$$\lambda(\alpha-1) \nu + \frac{2\mu}{3} (\alpha-1) \nu = \lambda^*(\alpha\nu-\nu^*) + \frac{2\mu^*}{3} (\alpha\nu-\nu^*), \quad (5.3)$$

where $\alpha = (1+\nu)/3(1-\nu)$ and ν is Poisson's ratio in the matrix. Rearranging (5.3) and expressing the Lamé constants in terms of bulk moduli, we have

$$\nu = \frac{B^*\nu^*}{\alpha B^* + (1-\alpha) B} \quad (5.4)$$

Alternatively, after some manipulation, we can also obtain

$$\nu = \frac{B^*\nu^*}{\alpha B^* + 2\alpha Y/3(1+\nu)} \quad (5.5)$$

where Y is Young's Modulus for the matrix.

Eshelby has shown that for a spherical inclusion of radius r_o the radial displacements are given by

$$\begin{aligned} \underline{u}(r) &= -\alpha\nu r_o^3/3r^2 & \text{for } r > r_o \\ \underline{u}(r) &= -\alpha\nu r/3 & \text{for } r < r_o \end{aligned} \quad (5.6)$$

Inside the inclusion we have a constant strain field

$$\epsilon = \frac{d\underline{u}(r)}{dr} = -\alpha\nu/3 \quad \text{for } r < r_o, \quad (5.7)$$

which is the strain parameter which one obtains from the Ashby-Brown (1963a) strain field analysis (§5.3.3.2). From (5.5) and (5.7) we have

$$\epsilon = \frac{B^*\nu^*}{3B^* + 2Y/(1+\nu)} \quad (5.8)$$

Alternatively, if only compressibility data are available, we can use

$$\epsilon = \frac{B^*\nu^*}{3B^* + 3B(1-\alpha)/\alpha} \quad (5.9)$$

The fractional volume change v^* can be obtained most easily for the case of the alkali colloid from the lattice misfit δ^* .

$$v^* = 3\delta^* = 3 \left\{ \frac{a_o^I - a_o^M}{a_o^M} \right\}$$

where a_o^I and a_o^M are the lattice parameters of the inclusion and matrix materials, provided the two have the same crystal structure (in this case f.c.c.). In the case of b.c.c. or molten inclusions, an equivalent f.c.c. unit cell size can be derived. It should be noted that a somewhat different expression for δ^* (in this case an average misfit) appears in Hirsch et al. (1965), and is incorrect for use as one-third the transformation strain v^* in (5.3).

Table 5.3 indicates the magnitude of the expected strain for potassium colloids in KCl, sodium colloids in NaCl and lithium colloids in LiF, existing in f.c.c., b.c.c. and molten states. Compressibility data were available only for alkali metals in the b.c.c. structure, and these values were utilised for all three colloid forms. The calculated strain from potassium inclusions may be compared in Table 5.3 with the strain determined by the strain field analysis of spherical clusters in KCl, §5.3.3.2. It must be emphasised that the latter values, though internally consistent, can be only approximate given the uncertainty in r_o , the inclusion radius. Nevertheless, it can be seen that there is a large difference between the measured strain and the expected colloid strain, and it seems unlikely that inaccuracy on quite this scale could be sustained in the strain field analysis. The small value of expected strain for potassium colloids in KCl arises because of the extreme compressibility $K^*(=1/B^*)$ of the alkali metals ($K_K^* = 36 \times 10^{-12}$ dynes cm^{-2}) compared with alkali halides or in the terms of (5.8), the smallness of the alkali

metal bulk modulus ($B_K^* = 0.29 \times 10^{11}$ dynes cm^{-2} compared with the stiffness of alkali halides ($Y_{\text{KCl}} = 3.8 \times 10^{11}$ dynes cm^{-2}). Therefore, the alkali colloid model does not appear to satisfy the observed strain data.

It will also be noted that the sign of the expected colloid strain ($\epsilon > 0$ for the surrounding lattice in compression, $\epsilon < 0$ for the lattice in tension), although consistent with the measurements in KCl is in fact opposite for K colloids in KCl and Na colloids in NaCl. This should permit unambiguous elimination of the colloid model if dark field measurements on anomalous images of spherical clusters in NaCl show them to be interstitial as in KCl.

If the colloid model is incorrect, as it appears from Table 5.3, we are left with the void or microcavity model necessarily involving cation vacancy condensation (the grossly three-dimensional precipitation of halogen molecules alone, in the absence of vacancy diffusion, is considered energetically most improbable). The sense of strain in KCl insists that such a cavity must be filled under high pressure, which suggests halogen gas or liquid. A one-to-one correspondence between halogen molecules and cation vacancies may provide the required strain, and discussion of a model for spherical clusters based on a halogen molecule + anion-cation divacancy defect unit is postponed to §5.7.6, following discussion of the normal form of room temperature halogen interstitial stabilisation.

5.4 Low Temperature Observations

It was indicated in §2.6 and §2.7 that three particular advantages should accrue from maintaining very low temperatures during electron microscopical irradiation. (i) All defect mobility will be considerably reduced, implying that aggregation should proceed only by a spontaneous

(athermal) rather than by a diffusive mechanism and will therefore remain small in scale (though not necessarily low in density).

(ii) Kinetics of saturation will be appreciably retarded due to alteration of the athermal recombination conditions normally obtaining at room temperature and will afford more observation time from reduced defect production efficiency until eventual statistical clustering alters recombination conditions towards those obtaining at room temperature. (iii) In some alkali halides (e.g. NaCl, KI, NaBr) appreciable reduction (as much as three orders of magnitude) in production efficiency occurs at low temperature since non-radiative exciton decay is a thermally activated process. Accordingly, specimens were prepared as detailed in §3.2, paying heed to the special cautions cited in §4.11 for low temperature microscopy, and examined below the threshold for bulk interstitial mobility (i.e. at ~ 10 K) in the liquid helium stage described in §4.10.2. Marginal beam currents were again utilised ($1-10 \text{ mA cm}^{-2}$).

5.4.1 The diffraction pattern

An additional advantage deriving from low temperature observation is evident in the diffraction patterns obtained from alkali halide foils. Fig. 5.11a and b compare selected area diffraction patterns obtained from identical adjacent areas of an (001) KI foil after ~ 5 sec irradiation at 300 K and 10 K respectively. It is immediately apparent that considerable diffuse scattering accompanies irradiation at room temperature and is notably absent at low temperature. This effect is not due solely to reduction in phonon scattering by cooling, for two

reasons. First, the differences in the phonon contribution to inelastic scattering, $V_o^i(\text{ph})$ (as computed by Radi 1970), are not large enough in comparison with the core electron excitations, $V_o^i(\text{el})$ (as computed by Radi and corrected in this study, §3.6). Even if we assume that Radi's value of $V_o^i(\text{el})$ is as much as four times too high (e.g. as ascertained from many-beam thickness fringe profiles compared with experiment §3.6), we find the contributions

<u>T</u>	<u>$V_o^i(\text{el})$</u>	<u>$V_o^i(\text{ph})$</u>	<u>$V_o^i(\text{total})$</u>
20K	0.45	0.24	0.69
300K	0.45	0.60	1.05
			} 0.36

or a difference in $V_o^i(\text{ph})$ only just comparable with the core electron contribution and only about 1/2 the total V_o^i . The difference appears unlikely to contribute the magnitude of effect illustrated in fig. 5.11a and b. Second, if observed from the instant of initial irradiation, the diffuse scattering at room temperature is seen to increase spectacularly over the first second or two of irradiation, whereas at low temperature no change is seen over many tens of seconds irradiation. It appears likely, then that the radiation damage process somehow contributes to this diffuse component. Calculations, based on the treatment of inelastic scattering from point defects (Hall, Hirsch and Booker 1966), indicate that there should be little effect from simply the presence of $\sim 10^{19}$ isolated point defects in the lattice. It must therefore be the mobility of point defects at room temperature, together with the fast production kinetics, that introduce additional scattering.

The practical consequence is that accurate diffraction conditions are virtually impossible to set at room temperature because the dense diffuse scattering obscures the Kikuchi line/band contrast from which orientation information is normally derived. At low temperatures,

pronounced Kikuchi lines/bands are clearly observed and render accurate tilting routine. The advantage of such detailed structure in the diffraction pattern may be appreciated from the 131 diffraction conditions set in fig. 5.32; such critical adjustment for weak operating reflections (see rocking curve for 311 systematic row, fig. 3.18) would prove impossible at room temperature.

Additional information can also be derived from the diffraction pattern. In fig. 5.11b parallel diffuse streaks are observed perpendicular to $g = 200$, both through the reciprocal lattice points and midway between them. These streaks may be thermal in origin, i.e. arise from acoustical or optical lattice vibration modes (Honjo et al. 1964; Kashiwase and Kainuma 1966; Harada, Tanaka and Honjo 1966; Harada and Honjo 1967), or they may be the result of scattering from precipitates or the lattice distortions they generate (e.g. Guinier 1959). Because blanket diffuse scattering develops during higher temperature irradiations, it was not possible to investigate whether this streaking was enhanced at higher temperatures.

Diffraction information may also be utilised to provide a sensitive indication of foil temperature if suitable gases are available for condensation as described in §4.5.3. Fig. 5.11c illustrates a diffraction pattern from polycrystalline neon (sublimation point ~ 9 K) condensed onto a thin region of a (001) KI foil in the beam, indicating that temperatures below 10 K can be attained in alkali halide foils during examination. To introduce sufficient gas for condensation in the vicinity of the protected specimen foil, a special gas delivery tube had to be passed through the anticontamination shield contiguous with the helium stage illustrated in fig. 4.21. This information on foil temperature is

important in considering defect aggregation under low temperature irradiating conditions, as it is crucial to know with certainty whether foil temperatures below measured defect mobility thresholds are actually achieved during irradiation. The Au/Fe vs chromel thermocouple attached to the specimen stage read 5 K under the conditions obtaining for fig. 5.11c for KI and upon subsequent warming of the stage indicated ~ 10 K as the neon sublimed from the specimen. This suggests that foil temperatures as low as 5 K may be obtained, although condensation of hydrogen (sublimation point ~ 5 K) was not attempted. An upper limit to foil temperature could be established with certainty for every specimen examined when, at the end of each experiment, the stage slowly warmed. Since the anticontamination shield is considerably less massive than the specimen holder and exposed to greater heat inputs, this shield warms more quickly than the specimen foil, and nitrogen sublimed from the shield then condenses on the colder foil, completely obscuring transmission. As the indicated stage temperature rises above the 30 K sublimation point of nitrogen, this condensed layer then sublimes from the foil, indicating that foil temperatures < 30 K have been previously attained.

5.4.2 Onset of low temperature damage

Four alkali halides were examined: KCl, with equally efficient defect production at room temperature and low temperature; NaCl, with efficient room temperature production and somewhat reduced low temperature efficiency; KI, with efficient room temperature production and considerably reduced low temperature efficiency; and NaBr, with reduced room temperature production and even smaller low temperature efficiency.

These relative production efficiencies may be compared in fig. 2.12. By this selection it was hoped it would be possible to differentiate between defect mobility effects and defect production effects.

Fig. 5.12 illustrates two consecutive 10 sec micrographs of an (001) KCl foil thinned from a cleaved section and examined at 10 K under a beam current density $5 \times 10^{-3} \text{ A cm}^{-2}$. Two features are immediately apparent. First, defects initially present in the foil (in this case, cleavage dislocations of the sort described in §3.2.1) are seen to survive at least 20 s irradiation and can be recorded without confusion from in situ irradiation defects. Second, low temperature damage does eventually accumulate (in ~ 20 s in KCl) in the form of small clusters of sufficient size ($\lesssim 5 \text{ nm}$) and density ($\gtrsim 10^{16} \text{ cm}^{-3}$) to obscure further observation. The eventual cluster size is significant, since it implies that at low temperature appreciable defect clustering (> 50 defects per cluster) occurs at saturation defect concentration; this result is not entirely unexpected, considering the high defect concentration levels ($> 10^{19} \text{ cm}^{-3}$) attained in alkali halides at saturation irradiation, and simply serves to underscore the ease of defect production in these crystals. Nevertheless, it is worth remarking that other workers have not really considered the possibility of appreciable defect aggregation (beyond the di-interstitial level; Itoh and Saidoh 1969) at liquid helium temperature, even in saturation experiments (Pooley 1966c; Hughes and Pooley 1971). The retardation of observable clustering over that occurring at room temperature must be due principally to reduction of defect mobility, since KCl damages rather equally efficiently at both temperatures. The kinetics of clustering are precisely those expected from the discussion of low temperature

saturation kinetics, §2.7, viz. a period of cluster-free observation corresponding to reduced defect production efficiency on the athermal recombination model (i.e. saturation effects reduce the actual production efficiency more quickly than at room temperature) followed by a short period of very rapid cluster growth corresponding to the sudden increase in production efficiency as clustering alters recombination conditions to resemble more nearly those obtaining at room temperature. We have not specifically implied that the clustering defects are interstitial (this will be shown below), but this assignment is certainly suggested on the athermal recombination model. If it were assumed that the effect of low temperature were simply to retard defect mobility and not to alter the defect production rate saturation kinetics, then statistical clustering (if it occurred) should occur in the same time as room temperature saturation, viz. ~ 1 sec; since clustering does indeed occur, but only after 20 sec, we conclude that saturation kinetics have altered. This result lends strong support to the athermal recombination models of Pooley and Hughes. The advantage gained (a factor of 20 in the observation time) is, significantly, precisely the offset of the low temperature saturation curve, fig. 2.15, from that at room temperature for defect levels $> 5 \times 10^{18} \text{ cm}^{-3}$.

Fig. 5.13 illustrates at higher magnification the low temperature clusters produced in four alkali halides (KCl, NaCl, KI, NaBr) by in situ irradiation to saturation below 10 K. Black spot and black/white contrast typical of small loop defect clusters are clearly seen in all instances. The contrast size is $\sim 20\text{--}40 \text{ nm}$ ($\sim 5g/3$), which according to the image simulations of Bullough, Maher and Perrin (1970) suggest a cluster size

~ 5 - 10 nm diameter. Such a size implies a rather large number of defects per cluster (~ 150 - 1000) for low temperature irradiating conditions. Cluster density is $>10^{16} \text{ cm}^{-3}$ which suggests that a large fraction of the $\sim 10^{19}$ defects produced during saturation irradiation at low temperature are involved in the aggregations (those defects aggregating will be shown subsequently to be interstitials). Aggregation on this scale comes about in one of two possible ways: creation of a thermal spike at the initial creation site, or a relatively long focussed replacement collision sequence. As indicated previously, such a collision sequence might be relatively more efficient at low temperature due to smaller thermal ion motions. A replacement collision sequence 10 - 20 lattice sites in length effects appreciable interstitial mobility and samples a rather large amount of lattice even at only nearest neighbour or next-nearest neighbour interactions.

The onset of low temperature defect clustering does not occur equally quickly in all alkali halides and in fact does scale crudely with expected defect production rate. However, if one orders the alkali halides according to their initial low temperature F centre production efficiency $(\partial F/\partial E)_0$ and compares the actual time advantage gained in observation at low temperature over that in KCl with their decrease in low temperature production rate relative to KCl (Table 5.5) one finds rather less influence of basic production rate than would be expected. From the saturation analysis in §2.7 we expect that the time $t(N)$ to reach any defect level N should go as

$$\begin{aligned} t(N) &= \frac{\exp vN}{vRE} \text{ for room temperature kinetics;} &) (5.10) \\ t(N) &= \frac{\exp 4vN}{4vRE} \text{ for low temperature kinetics,} &) (5.10) \end{aligned}$$

where R is the initial defect production rate $(\partial N/\partial E)_0$, E is the energy deposition rate and v is the athermal recombination volume. For conditions of constant irradiation rate, we expect a straightforward R^{-1} dependence for $T(N)$.

There are two possible explanations for the apparent insensitivity to R indicated in Table 5.5. The first is that a defect creation rate different from R , as measured by Hughes et al. (1967), somehow obtains during thin foil irradiations. One way this could come about is if the F centre production efficiencies measured by Hughes et al. did not reflect total defect production at low temperatures. For example, it is well known that the ratio F^+/F at low temperatures is dose rate dependent (Ritz 1966), and it is probable that during intense irradiation in the microscope a large F^+ population forms. However, this should not affect the total initial production which is always $F:H$ ($F^+:I^-$ is a subsequent conversion process, and the sum of F^+ and F must always equal the number of F centres produced if no F^+ centres were formed). Only if Hughes et al. neglected to include a large F^+ absorption in their data could their measured production efficiencies be misrepresentative of total defect production, and they have ascertained that no appreciable F^+ absorption was present in their experiments. Another way the basic production rate could alter is by some form of luminescence quenching, increasing the non-radiative exciton decay component where the latter is normally suppressed at low temperatures. For example, it is known that the presence of a strong electric field can quench recombination

luminescence (a field alters the energy diagram depicted in fig. 2.9), and it has been shown in the treatment of charge acquisition, §3.5, that strong electric fields do exist within alkali halide foils irradiated at low temperatures.

The second, alternative explanation is that the low temperature saturation kinetics are appreciably different in the different alkali halides, despite similarities in room temperature defect production. NaBr provides one key piece of information. It has been shown in §5.3 that NaBr damages extremely slowly at room temperature, and its damage clusters are very small (~ 10 nm); it was also indicated in §2.5.3 that a probable cause was ion size disparity such that the replacement collision sequence (essentially interstitial propagation) proceeds with considerably more difficulty. It is altogether probable, therefore, that since the room temperature interstitial aggregation volume is apparently smaller than in other alkali halides (leading to a higher density of smaller clusters), the low temperature interstitial aggregation volume u and the correlated athermal interstitial-vacancy recombination volume v are also considerably smaller. In fact, Pooley (1971 private communication) noticed a dependence of v on ion size in his saturation measurements. It can be seen from (5.10) that available time depends exponentially on v ; a factor of 2 reduction in v can offset an order of magnitude decrease in R . Since $v \propto r_i^3$, a factor of 2 in v reflects only a very small change in the interaction radius r_i . This effect also explains why saturation at room temperature in NaBr occurs rather more quickly than might be expected from its low room temperature production rate. The (athermal) interaction radius also has an appreciable effect on the stable defect production

efficiency; for example, NaBr exhibits a higher F centre production efficiency at 4K than at 77 K, probably because the interstitial is so resistant to athermal interactions (such as recombination), leading to a higher stable Frenkel pair production rate. Although the production efficiency of NaBr at 4 K is actually higher than that of KI and the expected recombination volume is smaller, the likewise smaller interstitial aggregation volume may prolong the time before actual clustering begins. Thus, there are rather subtle interconnected relationships between interstitial aggregation volumes, athermal recombination volumes, defect production efficiencies and saturation kinetics, so that the behaviour depicted in Table 5.5 is not entirely unreasonable.

5.4.3 Temperature dependence of cluster formation

It was more or less tacitly assumed that the defect clustering eventually obscuring low temperature observations is interstitial in character. This is not entirely obvious, except that optical measurements, even at room temperature, indicate few vacancy aggregates (even M is <0.1 F), and below 200 K vacancy aggregation is limited to nearest neighbour interactions (e.g. Horn and Peisl 1966; see §2.6.5.1). A more direct confirmation is obtainable from observations of the temperature dependence of cluster kinetics. Fig. 5.14 illustrates an (001) KI foil at 30 sec intervals during electron microscopical irradiation at 13 mA cm^{-2} at 10 K. The large loop clusters were formed during prior irradiation of the bulk crystal with 400 keV electrons. The small loop clusters are those nucleating and growing during low temperature in situ irradiation. Low temperature cluster nucleation actually begins somewhat

earlier and in somewhat different distribution in previously irradiated crystals than in virgin foils; this is discussed in §5.4.4. However, the important feature is that small cluster growth proceeds slowly over the 90 sec illustrated. Irradiation at 5 K yields an identical sequence and, conversely, raising the irradiation temperature to 30 K has little effect on clustering kinetics, indicating that any interstitial ion mobility (if it exists in this temperature region as in KBr) has little effect on aggregation. At 35 K, fig. 5.15, however, cluster formation accelerates noticeably, achieving an observable cluster density considerably in excess of that produced by irradiation at 10 K for the same 30 sec intervals. By 65 K, fig. 5.16, cluster aggregation is rapid indeed, with most observable features obliterated after the first 30 sec of irradiation.

The temperature range over which clustering kinetics suddenly increase corresponds closely to the temperature at which the interstitial halogen species (H or I^-) becomes mobile (see §2.6.1 and fig. 2.13). Similar behaviour is noted in other alkali halides, rendering microscopy at liquid nitrogen temperature very much out of the question, except for NaBr with a singularly low production efficiency ($2 \times 10^{-8} \text{ eV}^{-1}$) at 77 K and very restricted interstitial mobility. It is unlikely that the sort of defect mobility required to account for observed clustering kinetics at these low temperatures can arise in the vacancy species, since even F^+ centres are mobile only above 200 K. Therefore, we conclude that interstitial halogen defects are responsible for observable low temperature clusters which is clearly in accord with the saturation kinetics analysis. As might be expected, at high temperatures where there is significant defect mobility, a low density of large clusters is formed, whereas at

lower temperatures a high density of small clusters results. A monotonic progression of defect size with irradiation temperature from 4 K to 300 K is further support for the interstitial character of observable aggregations throughout the temperature range.

A further experiment confirms the observed temperature dependence. An (001) KI foil previously irradiated at room temperature was briefly irradiated (< 30 sec as in fig. 5.14a) at 10 K with no formation of observable low temperature clustering, fig. 5.17a. Next the foil was annealed without further irradiation to near room temperature and then recooled to 10 K for further observation, fig. 5.17 b. The result is nucleation and growth of new clusters similar to those formed by continued irradiation at low temperature and accompanying growth of clusters previously formed at room temperature. Anneal to liquid nitrogen temperature has a similar but somewhat reduced effect. This behaviour indicates significant mobility of the defect species responsible, even in the absence of radiation (a possible role for radiation in inducing F* mobility was indicated in §2.6.3.4). Such mobility cannot be attributed to a vacancy species.

The effect on existing clusters formed previously at room temperature is a significant result also; in fact, a consistent feature of all low temperature irradiations, whether accompanied by subsequent anneal or not, is the accompanying minor growth of clusters formed at other temperatures. Such behaviour indicates that at least one species of defect produced at low temperature is substantially the same as that aggregating at higher temperature or room temperature. It also indicates that the large loops formed at room temperature are effective defect sinks, which is in accord with speculation about the fate of the

interstitial at room temperature (Pooley 1966c; Farge 1969; Hughes and Pooley 1971). Since, almost certainly, the interstitial halogen species is the only defect mobile at low or intermediate temperatures (see fig. 2.15), this result is strong circumstantial evidence for the interstitial character of all loop aggregates formed between 5 K and room temperature.

The number of defects involved in growth of existing loop clusters following anneal is also significant. Estimates from micrographs such as fig. 5.17b indicate that $> 5 \times 10^{18}$ defects cm^{-3} are involved, which is about the saturation defect density expected on the basis of low temperature saturation measurements, fig. 2.15; shorter irradiations ($\sim$ a few seconds) do not result in such measurable growth. This result suggests that, as discussed in §2.7, low temperature microscopy slows the saturation kinetics, i.e. a saturation defect level ($\sim 10^{19} \text{ cm}^{-3}$) is not reached at low temperature until many times more irradiation than at room temperature. Measurements of loop growth in fig. 5.17b also suggest that that number of defects equivalent to the number of Frenkel defects created at low temperatures cluster at intermediate temperatures. It is most unlikely that all vacancy defects created at low temperatures cluster at intermediate temperatures, since $\sim 10^{19} \text{ cm}^{-3}$ isolated vacancies in the form of F centres are measurable even at room temperature after external low temperature saturation experiments.

The further growth of existing clusters is also curious for another reason. The large loops in fig. 5.17a were grown under saturation irradiation conditions at room temperature. That further Frenkel pairs can be introduced into the lattice at low temperature and that the room temperature loops can be made to grow by about 50% upon annealing the

products of low temperature irradiation indicate that it is (i) somehow possible to fit more vacancies into the lattice at low temperature without affecting recombination behaviour, and (ii) that this increased concentration of vacancy distribution is stable up to room temperature despite a large number of mobile interstitials.

5.4.4 Externally irradiated crystals

Fig. 5.14a indicates that aggregated defect products of external irradiation can be briefly examined at low temperature without confusion from the investigating electron beam. This facility provides a number of distinct advantages over in situ irradiation. For example it is shown in §5.3.1.6 that in situ foil irradiations are non-representative and depend on the equilibrium set up between defect production rate and defect diffusion to foil surfaces. Rather large surface forces exist in thin foils (e.g. image forces and electrostatic forces) which can alter defect behaviour and aggregate morphology from that occurring in bulk material. The energy deposition rates for the electron microscope are orders of magnitude larger than those customarily employed in colour centre studies, and defect production at saturation level is nearly instantaneous; there is accordingly no opportunity to study pre-saturation behaviour, except possibly at low temperatures, or the effects of dose rate on defect aggregation. Furthermore, important properties such as defect concentration cannot be measured, so little connection can be established between a given aggregate distribution and the density of defects produced.

For these reasons (and others evident in §5.6) advantage was taken of the increased time available at low temperature before observable

defect clustering to characterise the aggregation products of external irradiations. Bulk crystals were irradiated in a variety of external radiation sources: 0.8 MeV ^{60}Co γ (Harwell spent fuel element γ pond), 4 MeV electrons (Wantage electron accelerator) and 400 keV electrons (Harwell van de Graff generator). Crystals for γ irradiation could be large ($\sim$ cms), whereas those for 400 keV electrons were cleaved to 1 mm thick plates, which was in fact a convenient starting size for foil preparation and absorption measurements. F centre density determinations were made on crystals before electron microscopical examination and could be compared with estimates of the number of defect sites involved in observable aggregates. The γ dose rate was $\sim 2 \times 10^{17}$ eV cm $^{-3}$ sec $^{-1}$, whereas the 400 keV electron dose rate could easily be varied from 10^{17} - 10^{20} eV cm $^{-3}$ sec $^{-1}$. Previously coloured crystals are, in fact, rather more convenient for thinning to foils than perfectly transparent ones, as the depth of colour serves as a useful indication of remaining thickness at any stage in thinning.

Fig. 5.18a illustrates in a low temperature micrograph an (001) foil prepared from a KCl crystal irradiated in bulk at room temperature with 4 MeV electrons to a total dose of 1.2×10^{23} eV cm $^{-3}$ (1000 MRad) which corresponds to an F centre concentration close to saturation ($\sim 10^{19}$ cm $^{-3}$; see fig. 2.14). Clusters formed are predominately those of platelet type lying along $\langle 100 \rangle$ and are of similar size and distribution to those found in in situ irradiated foils. We have compared the distributions found in external irradiation with in situ irradiation products in fig. 5.18b, from which a direct comparison can be made. Cluster size (~ 100 nm long, < 20 nm wide) and morphology are certainly identical. However, fig. 5.18a represents a foil region perhaps two to three times

thicker than the thin regions required for observation of isolated clusters during in situ irradiation experiments. The density of clusters (estimated at 10^{15} cm^{-3}) then appears to be about a factor of 5 smaller for this irradiation level than for microscope levels. This is found to be a feature of most external irradiations, implying that a slightly higher defect concentration is attainable at the high dose rate of the electron microscope ($> 10^{23} \text{ eV cm}^{-3} \text{ sec}^{-1}$) as noted by Soul (1970) for the high energy deposition rates inherent in low energy electron irradiations ($\leq 5 \times 10^{23} \text{ eV cm}^{-3} \text{ sec}^{-1}$). Other defect structures are occasionally found in externally irradiated KCl, for example the large loop inset in fig. 5.18a. Significantly, no "spherical" clusters were produced, suggesting that these defect aggregates are either a thin foil anomaly or a product of the exceptionally high irradiation rates or immense doses obtaining in thin foil irradiations.

A feature which is clearly evident from fig. 5.18a is the degradation in image quality for examination of externally irradiated crystals; the loss of resolution arises from two interrelated effects. The primary cause is that onset of low temperature damage, of the sort illustrated in fig. 5.12, occurs a good deal sooner in previously irradiated crystals; in fact, this damage is apparent within the 10 sec interval required for image recording. Therefore, to preclude confusion with in situ irradiation products, the illumination was reduced by a factor of ~ 2 with an attendant loss in recording statistics; the statistical image grain, as discussed in §3.7.2, is clearly seen in fig. 5.18a, and simply underscores the marginal illumination conditions under which electron microscopy of alkali halides must proceed. KCl is,

of course, the very worst alkali halide so far as low temperature damage efficiency is concerned, and the beam current limitations imposed prevent adequate microscopy above magnifications $\sim 20,000$; a considerable improvement may be expected in other alkali halides, particularly those such as KI with a low temperature reduction of defect product efficiency. This behaviour implies that, besides the observable aggregated products of irradiation, there may also be a sizeable distribution of isolated defects or sub-observable aggregates; since room temperature optical absorption measurements indicate no single interstitial defects (H or I^-), the inference is that rather smaller aggregations than those observed are also present in significant number. This could be an important result, particularly for radiation hardening studies (see §5.6). Alternatively, the presence of large (interstitial) room temperature clusters early on in the low temperature irradiation may appreciably alter saturation kinetics and result in a higher effective production rate, leading to more rapid low temperature clustering; this effect is strongly suspected in the present case. Because of the poor resolution afforded in KCl examination, it was not possible to ascertain if very small observable aggregates < 5 nm were also present. Certainly, there is no continuous distribution of aggregate size, and if small clusters are present, only apparently two rather uniform sizes, one certainly ~ 5 nm, the other (depending on dose) ~ 100 nm.

Rather better resolution for KCl is afforded in crystals irradiated externally to less than saturation. Fig. 5.19 illustrates a low temperature micrograph of an (001) KCl specimen externally irradiated in bulk at room temperature to about 1/20 saturation with

400 keV electrons, total dose $\sim 10^{21}$ eV cm⁻³. Small clusters ~ 20 nm in size are revealed exhibiting black-white contrast in those regions of the foil near the Bragg conditions ($s=0$). The direction of the black/white streaking under $g = 220$ diffracting conditions is generally along either $\langle 100 \rangle$ axis, much as larger clusters are seen to have principal strain field axes whose projection on the (001) foil plane is $\langle 100 \rangle$. Foil thickness is estimated, from nearby dislocations running top-to-bottom in the foil (slip planes assumed to be $\{110\}$), at 400 nm. The density of these clusters is then calculated at 3×10^{14} cm⁻³, similar to the density of larger clusters formed with continued irradiation, indicating that clusters tend to nucleate early on in the irradiation and grow in size rather than in number with further irradiation. The large strain fields associated with small defects under strongly dynamical conditions make an estimate of defect size difficult; assuming the defects are planar, 20 nm long and about the same width as larger clusters, leads to an estimate of 1000 defects per cluster or 3×10^{17} defects cm⁻³, remarkably close to the total defect pair concentration of $\sim 5 \times 10^{17}$ cm⁻³ as indicated by F centre concentration. Since it is known that $\sim 5 \times 10^{17}$ F centres cm⁻³ are in isolated form, and the foil is far from saturation, the implication is again strong that halogen interstitials are involved in the clusters. Incidentally, at this sort of defect level little trouble is experienced with in situ low temperature damage over the first 20 sec of irradiation in KCl at 10 K; this result suggests that if very small aggregates are responsible for acceleration of observable in situ damage in KCl irradiated externally to saturation, they are either smaller or absent or in lower density in foils irradiated to considerably less than

saturation; if their size is reduced in proportion to the larger clusters and they were unobservable at saturation, their size would be $\sim$ atomic dimensions, which would explain absence of the effect. An alternative explanation is that the smaller (but not denser) observable clusters produced earlier in the irradiation are poorer interstitial sinks than larger clusters produced with more irradiation, and lead to more recombination.

A better estimate of the number of defects involved in the large loops as well as of the density of submicroscopical aggregates comes from the observations of externally irradiated KI. Considerably more observation time is possible, even in pre-irradiated KI, than in KCl, enabling increased resolution. However, it is still difficult to ascertain if the very small defect aggregates suggested above are initially observable; if they exist they are certainly < 5 nm initially, and would appear to constitute effective nucleation centres for the growth of low temperature clusters, as evidenced by the lower density of larger low temperature clusters formed in previously irradiated crystals, fig. 5.14c, as compared with previously unirradiated foils, fig. 5.13. Like room temperature defects, low temperature clusters tend to grow in size rather than in number under continued irradiation, testifying to the appreciable athermal mobility of interstitials at even the lowest temperatures; their density is constant at $\sim 2 \times 10^{14} \text{ cm}^{-3}$. In comparison the density of large loops formed at room temperature is an order of magnitude smaller, $\sim 2 \times 10^{13} \text{ cm}^{-3}$.

Fig. 5.20 illustrates the distribution of large loops formed

in KI externally irradiated with 0.8 MeV γ irradiation to a dose of 1.2×10^{23} eV cm⁻³ (1000 MRad) at a dose rate of $\sim 2 \times 10^{17}$ eV cm⁻³ sec⁻¹. The corresponding F centre concentration was measured at 1.9×10^{18} F cm⁻³ by optical absorption. These loops are nearly circular and exhibit no apparent preferred growth direction. It will be shown in §5.5 that these loops do not lie exactly in the (001) foil plane illustrated, but are tilted out of this plane some 35°, and also that the indicated contrast diameter can be either inside or outside the actual loop core depending on the diffracting conditions, a well-known fact from other loop studies (e.g. Groves and Kelly 1961; Maher and Eyre 1971). Bearing those two cautions in mind, an approximately true average loop area can be described (assuming the loops are planar which is also shown in §5.5), and from that and the measured loop density an estimate of the total number of defects derived. For the latter calculation a foil thickness of 400 nm was assumed, based on stereomicroscopy measurements in adjacent areas, and a defect distribution of four defects per unit cell projected area (the reason for the last assumption is discussed in §5.7 when models using this distribution are considered). The measured cluster density is 2×10^{13} cm⁻³, and the total number of defects involved in the clusters is 2×10^{18} cm⁻³, remarkably close to the total number of defects measured from the isolated F centre concentration. Each cluster then contains $\sim 10^5$ clustered defects. The exact correspondence of defects produced with defects clustered, together with the isolated F centre concentration and very low F aggregate concentration ($M < 0.1$ F), confirms that the clusters cannot possibly be vacancy in origin, but must arise from clustering

of the correlated interstitial halogen defect produced during irradiation.

5.4.3 Monovalent impurities

It was indicated in §2.8.2 that monovalent cation impurities, whose size was smaller than that of the alkali cation they replace substitutionally, serve as effective interstitial traps at low temperature to form H_A centres, and stabilise interstitials to temperatures considerably above their normal mobility thresholds. The chance incorporation of 200 ppm Na^+ impurity in one of the Harshaw KI crystals obtained for this study led to discovery of this effect during observation of KI foils at low temperature. The normal sequence of defect aggregation during in situ irradiation of previously irradiated crystals below the bulk interstitial mobility threshold is that indicated in fig. 5.14. Fig. 5.21 illustrates a similar sequence in KI:200 ppm Na^+ previously irradiated in situ at room temperature, only in this case the first three micrographs of the sequence are separated by 5 min intervals rather than the 30 sec intervals of fig. 5.14. The formation of normal large loops during in situ room temperature irradiation indicates that the Na^+ impurity has no effect on room temperature defect aggregation. However, at 20 K, even after 10 min of irradiation at 20 mA cm^{-2} , no detectable new clusters have nucleated; moreover, growth of existing large clusters is confined to rather minor additions. This remarkable phenomenon provides vastly increased observation time for analysis of existing lattice defects, such as prior irradiation products or mechanical defects, and is extensively utilised in §5.5 for complete characterisation of room temperature aggregate loops.

The inhibition offered by this level of Na^+ impurity is consistent with stabilisation of interstitial atoms ejected during the replacement collision sequence; that thermal diffusion of interstitials to trapping centres is not predominately involved is demonstrated in fig. 5.2ld where the irradiation temperature is raised to 35 K. Almost immediately nucleation of new clusters and growth of existing clusters begins. Nevertheless, noticeable cluster retardation continues up to liquid nitrogen temperatures, after which there is little further effect. Both sorts of behaviour are consistent with the notion that the Na^+ impurity can stabilise more than one interstitial; since the saturation defect concentration is in excess of 1000 ppm, each Na^+ ion presumably stabilises at least 5 interstitials. The last of these are probably less strongly bound than the interstitial at the H_A core, and as soon as interstitials are given a small thermal mobility, fewer are trapped as such sites. The evidence of annealing behaviour of V_1 absorption (and the correlated F band) is that the H_A centre does appear to remain stable up to ~ 130 -150 K (Giuliani 1970; Saidoh and Itoh 1970), whereas the observable effect of 200 ppm Na^+ impurity on cluster aggregation diminishes rapidly much above 50 K. Nevertheless, the impurity cation is expected to constitute at least a small obstacle to interstitial aggregation so long as it can continue to stabilise one or a few interstitials.

Monovalent doping is thus very useful in separating the products of prior and low temperature in situ irradiation and in releasing interstitials above a particular threshold temperature for studies of subsequent aggregation. The observations that the Na^+ impurity has an effect on that

defect which becomes mobile ~ 35 K and that these defects (which are almost certainly interstitials stabilised as H_A centres) then contribute to the growth of existing room temperature aggregate clusters provides yet another piece of evidence for the interstitial character of irradiation aggregates in alkali halides formed in the temperature range 5-300 K.

5.5 Analysis of Loop Clusters in KI

As indicated in §5.4 considerable circumstantial and phenomenological evidence exists that, in alkali halides irradiated at temperatures between 5 K and 300 K, the loop clusters observed in the electron microscope rely for their formation on the mobility and aggregation of anion interstitials. The general immobility of vacancy defects, even at room temperature, renders unlikely the formation of large vacancy aggregates; this is confirmed by the measurements of isolated F centre concentration and the very small concentration of small F aggregate centres. On the other hand, clusters formed at room temperature contain approximately the same number of point defects as there are isolated F centres produced over a range of F centre concentrations from 10^{17} cm^{-3} to saturation. Cluster nucleation is possible even at 5 K, and cluster growth becomes appreciable in the temperature range 35-65 K, which corresponds very well to the temperature range in which H centres become mobile. Furthermore, both clusters nucleated at room temperature and those formed previously at room temperature can be made to grow by continued irradiation at low temperatures or by anneal of low temperature irradiation products. The differences in clustering kinetics between room temperature and low temperature correspond well to the model of saturation relying on rapid interstitial diffusion

to sinks at room temperature and retardation of interstitial mobility followed by eventual spontaneous clustering at low temperature. The necessary aggregation volume for low temperature clustering is far in excess of that measured for F aggregate formation below 200 K, but it agrees well with estimates of H₂ aggregation volumes at 4 K (Itoh and Saidoh 1969). The inhibition of low temperature clustering by Na⁺ impurities is also clearly in line with interstitial anion involvement.

We now describe specific microscopical contrast experiments which unambiguously reveal the morphology, strain field and interstitial character of these clusters. For these experiments loops were produced in KI by irradiation in situ or by external irradiation at room temperature and were examined at 10 K. Use was made of the large tilting capacity of the low temperature cold stage to perform both tilting experiments and tilt/contrast experiments revealing the planar nature of the loops, their habit plane, lattice displacement vector and character. To provide more time for the initial analyses, foils intended for in situ irradiation (a few seconds at 10 mA cm⁻²) were prepared from KI:200 ppm Na⁺. Subsequent experiments were conducted with pure KI externally irradiated (1000 MRad) when certain general characteristics of the loops were ascertained sufficiently well to shorten analysis. Only minor differences in habit plane were detected for the two sets of loops. That these loops are essentially planar, rather than grossly three-dimensional, will become evident from various stereographic and tilting experiments to be discussed in this section; for the present discussion their planar configuration will be assumed.

5.5.1 Habit plane

We shall sometimes speak of a habit plane for these loops rather than the customary reference to direction of the loop normal, for reasons which will become evident in §5.7. Stereomicrographs of an (001) foil irradiated in situ at room temperature and examined at 10 K, fig. 5.22, indicate that the habit plane of most loops created in thin (001) foils is near (001). In fig. 5.22 the micrographs are tilted with respect to each other by about 16° ($\pm 8^\circ$ about $|220|$ either side of the $|001|$ pole). It was also ascertained that the loops were rather uniformly distributed throughout the foil thickness which was measured at ~ 300 nm. Many irregularly shaped loops A were revealed to consist of two sections at different heights with a stepped region between them. Often two loops B at nearly the same height and exhibiting an opposite strain (this is discussed in §5.5.2) are found to butt up against one another; this is a real effect rather than a contrast effect resulting from the overlapping images of two loops at different heights and is significant for the models of loop construction discussed in §5.7. Loops lying normal to the foil plane, which were few in number since the loop diameter is of the order of the foil thickness, were found to deviate as much as 30° from an (010) or (100) habit plane normal to the foil. Stereomicrographs of a (101) foil irradiated in situ and tilted $\pm 8^\circ$ from the $|101|$ pole about $|\bar{2}02|$ confirmed habit planes generally between $\{001\}$ and $\{110\}$ although deviations from either plane were more difficult to assess.

Loops in (001) foils prepared from crystals externally irradiated in bulk (γ , e^-) exhibited measurable deviations from an (001) habit plane. These loops are more conducive to assessment of habit plane

because they are relatively large and approximately circular. There are in principle several ways to determine the orientation of a loop normal and thus the habit plane. In the discussion following, we consider the orientation of a loop normal $\underline{n}$ with respect to the direction of the electron beam $\underline{z}$ expressed as a direction in the foil.

The first method involves tilting the foil axis until a loop projects end-on, then noting the position of its trace. This loop orientation already occurs in several micrographs previously illustrated with $\underline{z} \approx |001|$. For example, the traces of nearly edge-on bulk produced loops have been marked in fig. 5.14 and fig. 5.20a. These traces indicate habit plane deviations $\sim 35^\circ$ from $\{100\}$ about the $|001|$ foil normal. Some caution must be exercised in interpreting edge-on loops; it was indicated previously that, depending on diffracting conditions, a loop image can lie either inside or outside the loop core (this point is discussed further in §5.5.3); inside contrast can result in an apparent edge-on image for loops inclined less than normally to the foil. It is important, therefore, to image in both $\pm \underline{g}$ to confirm the true edge-on condition. Also, this technique is limited to loops initially steeply inclined, as it is usually difficult to tilt a foil more than $\pm 20^\circ$.

A second method entails measuring projected loop dimensions for two or more precisely known foil orientations. Foil orientations (i.e. $\underline{z}$) can be accurately determined from Kikuchi line positions in the diffraction pattern. In one variant, major and minor projected loop axes are measured for several foil orientations and compared with calculated projections for a range of expected loop orientations. This

technique is only applicable to perfectly circular loops which project as ellipses. A more general variant is to measure the maximum projected width along a direction in the projection plane normal to an axis of tilt for each of two tilt axes in the foil plane. Measurements at several foil tilts enable the inclinations of two vectors in the loop with respect to the foil plane to be determined. These two vectors define the loop plane and hence the loop normal. This procedure is applicable to non-circular loops provided they have two orthogonal axes of symmetry, but depends more critically on small differences in projected width than the first variant. Both methods require that the image position coincides with the loop core which seldom obtains. It is possible to ascertain an approximate core position by averaging projected widths for $\pm g$. However, since total tilt capability seldom exceeds 40° both variants remain sensitive to image position and variation in image width.

As an example, we apply these procedures to loops in an (001) foil of KI externally irradiated in bulk (γ , 1000 MRad), fig. 5.23. We have indicated in fig. 5.27 a loop situated in an (001) foil, and shall henceforth make reference to the indices established there. Tilting about $|100|$ failed to produce differences in projected loop length measured along $|010|$ for equal angles of tilt either side of $z = |001|$ (averaging loops in $g = \pm 200$). Hence, there is no inclination of the loop with respect to the (001) foil plane about the $|100|$ axis. Tilt about the orthogonal $|010|$ axis is not directly possible because loop contrast vanishes (as a consequence of the $g \cdot R = 0$ criterion for invisibility, see §5.5.2) under the $g = 020$ diffraction conditions necessarily

maintained for this tilt axis. This suggests that the loop normal lies in the same (010) plane as the displacement vector. Imaging in $g = \pm 220$ and tilting about $|110|$ leads to an increase in projected width for one sense of foil tilt and decrease for the other; we illustrate this latter tilt in fig. 5.23. Since there is no loop rotation about $|100|$, the major loop axis is a true diameter (assuming a circular loop), hence we may compare the projected width with the loop diameter, averaging both dimensions over $\pm g$ images, to obtain the loop rotation about $|010|$. For $\underline{z} \approx |001|$, the computed loop inclination amounts to $\sim 48^\circ$ from (001) about $|010|$; for $\underline{z} \approx |115|$, the width/length ratio indicates rotation of the loop about an axis in the foil which is the projected major loop axis. This axis differs by $\sim 6^\circ$ from $|010|$, hence loop rotation about $|010|$ may be computed and amounts to $\sim 51^\circ$, similar to that calculated for $\underline{z} \approx |001|$. Measurements of maximum width projected normal to the invariant $|110|$ direction are made with less accuracy; an error of 10% in projected width introduces an uncertainty of 20° . These measurements yield a loop inclination of $\sim 45^\circ$ from (001) about $|010|$.

A considerably more reliable third method suggested by Maher and Eyre (1971) makes use of the trace of the projected major loop axis which is independent of image position and width. Provided the loop is circular, the trace of the loop normal then lies orthogonal to the major axis trace in the projection plane. If the loop is imaged in two or more foil orientations $\underline{z}_i$, a stereographic plot of each family of possible loop normals $\underline{n}_i$ defines a unique $\underline{n}$ for the loop. In fig. 5.23 we have indicated the trace of the major axis in

each case; the projection of the loop normal is orthogonal to this trace. In the stereographic projection of fig. 5.24a we have plotted the two families of loop normals consistent with the major axis traces in fig. 5.23; these determine a loop normal $\underline{n}$ lying in (010) $\sim 55^\circ$ from $|001|$, i.e. a loop inclined 55° to (001) or 35° to (100). We note that this method directly indicates the absence of loop rotation about $|100|$ for loops inclined about an $|010|$ axis; it is also more consistent than image width measurements. Most loops measured by this method were inclined by $\sim 35^\circ$ from some $\{100\}$ plane (in agreement with the edge-on projection method, e.g. fig. 5.14) and thus differ markedly from their counterparts in insitu irradiated foils. It was later revealed (§5.5.2) that the lattice displacement vectors $\underline{R}$ associated with these loops are near those $\langle 110 \rangle$ directions lying inclined to the (001) foil plane and nearest the loop normals. Hence these loops tend towards pure edge loops, the loop normals lying within $\sim 15^\circ$ of $\underline{R}$. Closer adherence to an (001) habit plane in the case of in situ thin (001) foil irradiation undoubtedly reflects the role of surface constraints (image forces, defect diffusion to surfaces, etc.) in altering loop growth.

5.5.2 Displacement vector

The anisotropic displacement of a crystal lattice on either side of a planar defect may be characterised by a displacement vector $\underline{R}$, not in general an integral lattice translation. A special case is a perfect dislocation loop whose Burgers vector $\underline{b}$ is an integral lattice vector and can be characterised by the closure failure of a Burgers circuit.

A sufficient condition for the identification of the direction of the lattice displacement is the imaging of a defect in at least three non-coplanar reciprocal lattice vectors $\underline{g}$ for two of which strong contrast from the defect vanishes, a necessary condition for invisibility being $\underline{g} \cdot \underline{R} = 0$. That the strain field from the large loops formed by room temperature irradiation of alkali halides is highly anisotropic has been noted in such visibility experiments by Izumi and in the observations of §5.3. Since the nearest appropriate low index reciprocal lattice vectors are 18.4° apart in the NaCl system (see fig. 4.19), an unambiguous analysis requires tilting the defect through an angle $> 18.4^\circ$ or using two or more foil sections of orientations differing by at least this amount, provided that one is convinced that defects in either section are generally the same. Both approaches are utilised in this study: while the former is strictly rigorous and is applied in §5.3, the latter is more illustrative for the present discussion.

5.5.2.1 Direction of the displacement vector $\underline{R}$

Fig. 5.25 depicts loops produced by in situ irradiation at room temperature lying near the foil plane in an (001) KI foil; these appear imaged at a foil temperature of 10 K in eight coplanar low index diffraction conditions $\underline{g}$ belonging to the (001) reciprocal lattice plane. The distinctive change in loop size and contrast with reversal of $\underline{g}$ (fig. 5.25a, b) relates to the sense of local lattice rotation inside and outside the loop and is utilised in §5.3.

It is seen that all defects (there are four types labeled A, B, C, D) are imaged in $\underline{g} = 220$ conditions, but half of the defects (A, B)

disappear in $g = 220$ and the other half (C,D) in $g = 020$. Furthermore, within any one group there are two sets (A,B or C,D) of defects which exhibit opposite contrast behaviour in $\pm g$ (in externally irradiated crystals these two sets also exhibit opposite tilt with respect to the $|001|$ foil normal. The selective disappearances imply that the first group of defects (A,B) induces a lattice displacement lying somewhere in the (100) plane, the second group (C,D) somewhere in the orthogonal (010) plane. Izumi (1969), in fact, observed the disappearance of the elongated loops in KCl when g is normal to the long loop axis, but without justification assumed that the loop displacement vectors were of $\langle 100 \rangle$ type lying in or normal to the foil; that this interpretation is incorrect can be demonstrated by the analysis in fig. 5.26 of similar loops formed in a (101) KI foil.

In this case, again, all defects present in the series of diffraction conditions are imaged in $g = \pm 202$. One group of loops (E), ascertained from stereo measurements to lie steeply inclined to the foil, disappeared in $g = \pm 020$; however, another group of loops (F,G) also lying inclined to the foil, is imaged in both $g = \pm 202$ and $g = \pm 020$, which is inconsistent if the displacement vectors were of $\langle 100 \rangle$ type. In fact, the latter group of loops could be made to disappear (in two alternative sets F and G) using $g = \pm \bar{2}22$ and $g = \pm 2\bar{2}2$ respectively, indicating that the displacements associated with them lie in respectively $(\bar{1}\bar{1}1)$ and $(\bar{1}11)$ planes (which do not contain $\langle 100 \rangle$). Assuming that the different loop groups are simply equivalent defects in different crystallographic orientations, the only displacement vector that can lie in both $\{010\}$ and $\{111\}$ planes is $\langle 101 \rangle$; this is illustrated in the stereographic projection in fig. 5.24b.

A similar analysis of a number of single specific loops has been performed during characterisation of the loop sign in §5.5.3. In this case in addition to 020 reflections, 131 type reflections were also utilised by tilting an (001) foil 18.4° to an (013) pole; this analysis is also indicated stereographically in fig. 5.24b and rigorously confirms the $\langle 110 \rangle$ nature of the displacement vector. This direction of $\underline{R}$ is illustrated for the loop configuration in fig. 5.27.

It will be seen from fig. 5.26 that rather weak loop contrast can result by simple reversal of $\underline{g}$; this effect is critically dependent on the value of s , (i.e. of the deviation parameter $w = \xi_{\underline{g}} s_{\underline{g}}$) and the crystal anisotropy. There is a danger that this weak contrast can be mistaken for residual $\underline{g} \cdot \underline{R} \wedge \underline{u}$ contrast which does arise in the case of loops F,G for $\underline{g} = \pm 2\bar{2}2$. Therefore, defects were always imaged in pairs to differentiate between the two sorts of weak contrast. Residual contrast effects can be appreciable assuming the strength of $\underline{R}$ is near $a/2\langle 110 \rangle$ (the strength is discussed below); the parameter $m = 1/8(\underline{g} \cdot \underline{R} \wedge \underline{u})$ can be as large as 0.75, hence give rise to more than 50% contrast (Howie and Whelan 1962). For example, for the case of loops F appearing in residual contrast in fig. 5.26h, if we assume the loops to be pure edge with $\underline{R} = a/2 |110|$, the condition for maximum visibility in residual $\underline{g} \cdot \underline{b} \wedge \underline{u}$ contrast is $\underline{u} = |\bar{1}\bar{1}2|$, i.e. those loop segments whose projections lie normal to $\underline{g} = 2\bar{2}\bar{2}$, in which case $m = 0.75$. The condition for residual contrast to vanish is $\underline{u} = |\bar{1}\bar{1}\bar{1}|$, i.e. those loop segments lying along $\underline{g} = 2\bar{2}\bar{2}$. No residual contrast is seen for those defects disappearing in $\underline{g} = 020$; in this case $\underline{R}$ is in the foil plane along $|\bar{1}01|$ or $|10\bar{1}|$ and $\underline{g} \cdot \underline{R} \wedge \underline{u}$ is everywhere zero. Residual contrast can arise from those

loops in fig. 5.25 disappearing in $\underline{g} = \pm 200$ and $\underline{g} \pm 020$ where $\underline{R}$ does not lie in the foil plane, since for the mixed component, assuming it lies inclined by $<35^\circ$ from the foil plane, has $m \approx 0.12$ and is just barely visible at e.g. B in fig. 5.25e, f.

One sort of defect, at H in fig. 5.26, remains in weak residual contrast for all reflecting conditions; its behaviour is consistent with a loop whose Burgers vector is along $|101|$ normal to the foil. The double image contrast has been discussed by Howie and Whelan (1962). In this case m varies continuously around the loop for a given $\underline{g}$ and is always zero at positions perpendicular to $\underline{g}$. The resultant line of no contrast moves around with $\underline{g}$, as can be seen in each of the four $\underline{g}$ directions illustrated. Residual contrast from loops $\vec{\zeta}_{\underline{g}}$ in size has been considered by Bullough, Maher and Perrin (1970) for an isotropic material using computer simulations which reproduce the contrast features exhibited by loops H in fig. 5.26.

5.5.2.2 Strength of the displacement vector

The magnitude of the displacement vector $\underline{R}$ is especially important in deciding which defect is responsible for the observed lattice strain. Several contrast features suggest that the magnitude of $\underline{R}$ is near that of a perfect $a/2 \langle 110 \rangle$ lattice shear: these are the width of the bounding lattice dislocation image, the presence of multiple images in some diffraction conditions, and the absence of lattice fault contrast inside the loop.

The image width of the lattice dislocation bounding a loop provides information about the extent of the strain field and thus of the lattice

displacement field $\underline{R}$ ' at its origin. On the two beam theory (Howie and Whelan 1961; Howie and Basinski 1968) we may define a function β_g' such that

$$\beta_g' = \frac{d}{dz} (\underline{g} \cdot \underline{R})$$

specifies the defect present in the foil. This parameter then appears in the differential equations for the complex transmitted and diffracted wave amplitudes ϕ_o and ϕ_g (in the column approximation)

$$\begin{aligned} \frac{d\phi_o}{dz} &= \frac{-\pi}{\xi_o} \phi_o + \pi \left\{ \frac{i}{\xi_g} - \frac{1}{\xi_g} \right\} \phi_g \\ \frac{d\phi_g}{dz} &= \pi \left\{ \frac{i}{\xi_g} - \frac{1}{\xi_g} \right\} \phi_o + \left\{ \frac{-\pi}{\xi_o} + 2\pi i \left(\frac{w_g}{\xi_g} + \beta_g' \right) \right\} \phi_g \end{aligned} \quad (5.11)$$

as the sum $(s_g + \beta_g')$, i.e. acting as a local lattice rotation, altering the transmitted and diffracted intensities from those normally obtaining at a given $w_g = s_g \xi_g$ condition. $\underline{R}$ ' is, of course, governed by the strength and direction of the primary displacement at the defect core, $\underline{R}$.

It is clear from (5.11) that the form of a defect image will depend on a large number of variables, viz. g, w_g, ξ_g, ξ_g' , the orientation of the defect and its displacement field (which determine β_g'), and the lattice anisotropy. The function β_g' can be obtained by evaluating the elastic displacement field associated with the defect and (5.11) used to calculate the expected intensity in any column at some distance from the defect core, i.e. the image "width" which will depend on the initial displacement $\underline{R}$. For a simple isolated edge dislocation in a thick foil Howie and Whelan (1962) have shown that the image width for $\underline{g} \cdot \underline{R} = 1$ is $\sim 0.4 \xi_g$ at half intensity (depending on the angle $\underline{R}$ makes the foil normal, the inclination of the dislocation line, w_g , choice of ξ_g/ξ_g' , etc.).

If a dislocation loop with displacement vector $\underline{R}$ is large ($> \xi_g$) contrast from the individual pure edge segments should approximate to that of an isolated dislocation line. For example the image width of pure edge loop segments in fig. 5.20 (loop diameter $\sim 2.66 \xi_g$) with $g = 220$ was measured densitometrically (fig. 5.28) at $0.43 \xi_g \cdot \xi_{220}(20K)$ for KI was calculated from Doyle-Turner (1968) ionized atom electron scattering factors including a Debye-Waller correction, as outlined in §3.6 ($\xi_{220}(20 K) = 70 \text{ nm}$). The agreement between measured and computed width profiles (both $\sim 0.4 \xi_g$) suggests that $g \cdot \underline{R} \sim 1$ and that R is near $a/\sqrt{2}$. If R were appreciably less (for example $a/10\sqrt{2}$) the displacements introduced by the imperfection would be insufficient to locally rotate the lattice into a strongly diffracting condition (for $w_g \neq 0$) very far from the dislocation core, and the image width would be correspondingly narrower. Since image widths for $g \cdot \underline{R} = 1$ are typically $\sim 30 \text{ nm}$ ($0.4 \xi_g$), it is doubtful whether displacements $a/10\sqrt{2}$ would be detectable; this result is important in considering alternative models for loop structure, §5.7.

It is of course dangerous to apply width criteria too closely to a small dislocation loop since strain field interactions with other parts of the loop can significantly alter image contrast. If the loop is $\sim \xi_g$ the displacement field is considerably more complex internally and the strain field falls off more quickly externally than for an isolated dislocation. In alkali halides this applies to loop diameters $\sim 100 \text{ nm}$, i.e. generally below the loop size primarily under consideration. β_g' for a pure edge loop has been evaluated by Bullough, Maher and Perrin (1970) in the isotropic approximation and has been used to calculate image profiles for a limited range of loop sizes, orientations and

diffracting conditions. In particular it is found that large differences in image width occur for the cases of contrast inside or outside the loop core (with $\pm g$) and with choice of ξ_g/ξ_g' , w_g , depth and inclination of the loop. For example, for the vacancy loops considered by Bullough et al., computed inside contrast width at the widest point is $\sim 0.2 \xi_g$ while outside contrast width is $\sim 0.4 \xi_g$ for $w_g \sim 1$; this situation is reversed for the present case. There is also some disparity between computed and experimentally observed widths. The position of maximum measured width relates to that loop segment parallel to the axis of loop tilt (not necessarily the pure edge segment for a non-edge loop) and also to the direction of $\underline{g}$. "Shearing" of the image is also usually apparent in the direction of $\underline{g}$. Because of the complexity of these contrast parameters it is difficult to derive an unambiguous indication of the magnitude of $\underline{R}$ from image width criteria. We can expect to obtain only an order-of-magnitude estimate for R from such measurements on small loops. The contrast is, however, always sufficient to indicate whether a substantial lattice displacement is sustained.

If $\underline{g} \cdot \underline{R} = n$, n an integer > 1 , multiple contrast effects are normally present (Howie and Whelan 1962). Reference to fig. 5.26 indicates that for $\underline{g} = \pm 202$, ± 020 straightforward single image peaks are obtained; however, with $\underline{g} = \pm \bar{2}\bar{2}2$, $\pm \bar{2}22$ pronounced image doubling occurs (e.g. at F in fig. 5.26e, f) whose form depends on w_g . This behaviour is consistent with $\underline{g} \cdot \underline{R} \approx 1$ in the former case and $\underline{g} \cdot \underline{R} \approx 2$ in the latter, i.e. $\underline{R} \approx a/2 \langle 110 \rangle$. Under $\underline{g} \cdot \underline{R} = 2$ conditions a line of contrast often appears in the centre of the loop for inclined loops (for example at E, fig. 5.26f, h with $\underline{g} = 222$). The form of such contrast when $\underline{g} \cdot \underline{R} = 2$ has been produced

by Bullough, Maher and Perrin (1970) for both experimental and computer-simulated images in circular loops; a similar contrast form presumably obtains for the elongated loops in fig. 5.26. Relative caution must be exercised in this assignment, since in alkali halides strict first order diffracting conditions cannot be obtained for 222 excitations due to the presence of the weak 111, 333, etc., reflections. Computed many-beam rocking curves (§3.6) for the 111 systematic row indicate, however, that acceptable two-beam conditions can be obtained for 222, at least in KI.

Finally, if $\underline{R}$ fails by some amount $\underline{R}_f$ to equal an integral lattice vector, a lattice fault obtains across the loop plane from which appreciable fault contrast should be evident, provided $\underline{R}$ is not normal to $\underline{g}$ and $\underline{g} \cdot \underline{R}_f > 0.1$ (Humphreys, Howie and Booker 1967; Booker and Hazzledine 1967). Fault contrast in the interior of the loop will take the form of variations in intensity with depth in the foil, generating fringes with depth periodicity $\sim \xi_g / \sqrt{1 + w_g^2}$ for loops inclined to the foil plane or to differing contrast levels for loops situated at differing depths in the foil. In the present experiments neither effect has been observed for any loop orientation, either from stereographic foil observations or in foils sectioned and tilted to provide maximum projected area in a loop inclined to the foil.

Stereographic observations (of the sort discussed in §5.5.1, fig. 5.22) in (001) foils are sufficient to detect differences in interior loop contrast at different depths, even for loops lying near (001), since $\underline{R}$ lies inclined to the $|001|$ axis ($\underline{g} \cdot \underline{R}$ is non-zero for all but one $\underline{g}$ in the (001) reciprocal lattice plane). Foils of sufficient thickness, ~ 300 nm ($\sim 4 \xi_g$) were examined and no depth dependence of the loop interior

contrast was evident; in fact, reversing $\underline{g}$ (or altering w_g) has a very much larger effect on loop contrast levels than any detectable difference between loops, suggesting that the lattice dislocation strain field contrast is considerably stronger than any contrast arising from a lattice fault. Booker and Hazzledine (1967) have shown, for example, that a fault for which $\underline{g} \cdot \underline{R}_f = 0.1$ can exhibit contrast variations (depending on depth) up to about 30% in a material (Si) with similar absorption parameters ($\xi_g'/\xi_g \sim 30$) observed in the deviated position ($w_g > 0$); the dislocation strain field contrast in the interior of the loop is only of this order. It therefore appears unlikely that a fault of greater magnitude is introduced, as this should certainly be detectable.

It was indicated in §5.5.1 that the loop plane in externally irradiated foils is inclined $\sim 35^\circ$ to (001); therefore observations of these loops in (001) foils provide a reasonable opportunity for observation of fault fringe contrast. The diameter of these loops is $\sim 2.5 \xi_g$ (see fig. 5.28), providing a depth difference $\sim 2 \xi_g$ between the opposite pure edge sides. In practice this projected depth should be sufficient to provide more than one dark and one light fringe lying parallel to the edge components (since this is the loop tilt axis). These fringes, in a fault for which $\underline{g} \cdot \underline{R}_f \sim 0.1$, should exhibit a contrast difference $> 30\%$. Intensity variations of this sort clearly are not observed in fig. 5.20, nor are they observed for the steeply inclined loops in a (101) foil, fig. 5.26. As an additional check, a KI crystal was sectioned parallel to (013) and thinned to a foil; loops were created at room temperature by in situ irradiation and subsequently observed at 10 K. In such a foil, assuming an (001) habit plane for in situ irradiation of (001) foils, all loops should be inclined to the foil by $\sim 20^\circ$. The foil was then tilted back $\sim 20^\circ$ to provide the maximum projected

area for loops inclined to the foil; again, no fault contrast was discerned. These observations suggest that the lattice is unfaulted or nearly unfaulted ($\underline{R}_f \sim 0.1\underline{R}$), and therefore that $\underline{R}$ is near $a/2 \langle 101 \rangle$.

In summary, then, width criteria indicate the $\underline{R}$ is large, image behaviour that $\underline{R}$ is nearer one than two $\langle 110 \rangle$ lattice translations, and absence of fault contrast that $\underline{R}$ does not differ appreciably from a lattice vector. From these we conclude that $\underline{R}$ is near an $a/2 \langle 110 \rangle$ displacement. The implications of this result will be discussed in §5.7. However, it should be noted here that defect clusters in some alkali halides (notably KCl, also to some extent NaBr and NaCl) do not extend into planar loops but remain narrow dipoles; a similar conclusion (i.e. unfaulted loops) cannot be made for the defects in these alkali halides. There may be, in fact, morphological implications if a sufficiently large fault is introduced.

5.5.3 Character

Information about the loop normal $\underline{n}$, displacement vector $\underline{R}$, incident electron direction $\underline{z}$ and sense of local lattice rotations near a loop can be used to determine its vacancy or interstitial character (Groves and Kelly 1961, 1962; Mazey, Barnes and Howie 1962; Mazey and Barnes 1968; Maher and Eyre 1971). In order to establish a consistent criterion we formally define the displacement vector $\underline{R}$ via the FS/RH perfect crystal convention (Bilby, Bullough and Smith 1955) by assigning as a positive sense around the loop a clockwise circuit when viewed from the underside of the foil. This is the view represented by positive prints printed emulsion side to emulsion side from the original negative, a procedure

which minimises printing aberrations. An alternative assignment used for positives printed as viewed from the top of the foil is presumably more convenient as it obviates an inversion required of the viewer; however, it was felt that, given the marginal conditions under which micrographs of alkali halides are produced, all the image quality available should be utilised, and micrographs were printed emulsion to emulsion.

On the kinematical theory (Hirsch, Howie and Whelan 1960) it is assumed that the sense of displacement of a defect image relative to the defect core is determined by the local curvature of reflecting planes nearly parallel to the electron beam (Laue case); if the crystal is deviated by some amount s_g from the Bragg condition, the image then lies to that side of the defect core where the local lattice rotations tend to minimise deviations from the Bragg angle. This property in principle enables differentiation between vacancy and interstitial loops, since their sense of lattice rotations will be opposite for identical geometric conditions (n , z , g , direction of R the same). Alternatively, the precise sense of R can be considered opposite on the FS/RH perfect crystal convention. The usual criterion for image position is; then, inside the loop core when $(\underline{g}, \underline{R}) s_g > 0$ and outside when $(\underline{g}, \underline{R}) s_g < 0$ for R defined as above. Inside and outside positions are usually determined by reversing g , maintaining s_g in the same sense (usually $s_g > 0$ for best bright-field transmission, §3.6).

Of course, loops are seldom imaged in kinematical conditions (except, perhaps, in deliberate kinematical weak beam conditions: Cockayne, Ray and Whelan 1969; Cockayne 1970); and in the strong two-beam

dynamical conditions (necessary for acceptable electron statistics during observation/irradiation of alkali halides) the position of the image depends critically on both the deviation parameter w_g ($w_g = \xi_g s_g$) and depth in the foil (Howie and Whelan 1962; Bullough and Newman 1964). Additionally, in small loops strain-field interactions from other parts of the loop can significantly alter image contrast (Bullough, Maher and Perrin 1970). Also, strain fields in strongly anisotropic materials such as the alkali halides (for KI, $\Lambda = 0.38$) are considerably more complex and can give rise to contrast effects anomalous to ideal isotropic expectations (Head, Loretto and Humble 1967; Humble 1967). Visibility criteria may even impair analysis if $\underline{R}$ is not an integral lattice vector (Loretto, Clarebrough and Humble 1966; Tunstall 1969).

Therefore it is not altogether clear that the simple criterion assumed initially is applicable. However, calculations and experiments by Maher and Eyre (1971) have shown that, at least for two-beam conditions and unfaulted loops in a relatively isotropic material (Mo), the simple kinematical $(\underline{g} \cdot \underline{R}) s_g$ criterion applies and is depth independent for loops of diameter $\sim \xi_g$, provided w_g is maintained sufficiently large, $w_g > w_g^*$ (in their case $w_g^* \geq 0.6$). Their value of w_g^* is somewhere near the deviation for maximum bright-field transmitted intensity, which in alkali halides is often > 1.0 (§3.6). In the present experiments w_g was maintained at or slightly greater than the deviation for maximum transmission; this deviation produced consistent image shifts with $\pm \underline{g}$, as well as strong ancillary effects such as related image strengths and contrast in the centre of the loop, which were also useful in confirming lattice curvature. Maher and Eyre also showed that $\underline{g} \cdot \underline{R} = \pm 2$ images

required a lower value of w_g^* than $\underline{g} \cdot \underline{R} = \pm 1$ images, and that greater image shifts were obtained with increasing ξ_g .

So far as anisotropy is concerned, the inversion of a bright field image top for bottom with respect to the foil surfaces and side for side with respect to the defect core position, for a reversal of $\underline{g}$, is a centrosymmetric crystal property and therefore independent of anisotropy. Humble (1967) has shown that there is little difference (except width) between isotropic and anisotropic images provided $\underline{g} \cdot \underline{R} \neq 0$. Where non-integral displacement vectors obtain, Tunstall (1969) has shown that the $\underline{g} \cdot \underline{R} = \pm 4/3$ images analyzed by Mazey and Barnes (1968) obey $(\underline{g} \cdot \underline{R}) s_g$ criteria properly. However, the $\underline{g} \cdot \underline{R} = \pm 1/3, \pm 2/3$ images in faulted loops are unsuitable because of poor visibility of partials in the $\pm 1/3$ case and invisibility of the partials in the $\pm 2/3$ case (Silcock and Tunstall 1964); the latter property, however, was suggested as an alternative criterion for determining the precise sense of $\underline{R}$. In the present experiments strong fault effects were not observed, and obscuration of the bounding loop dislocation by fault contrast (e.g. Loretto, Clarebrough and Humble 1966) did not occur, sufficiently strong images being present in both $\pm \underline{g}$. Therefore, the kinematical approach was deemed applicable.

There exist, however, certain combinations of $\underline{n}$, $\underline{z}$ and $\underline{R}$ for which the $(\underline{g} \cdot \underline{R}) s_g$ criterion can give an incorrect result (Maher and Eyre 1971). The region of normal behaviour is bounded by the conditions $\underline{n} \cdot \underline{R} = 0$ and $\underline{n} \cdot \underline{z} = 0$; the region of reverse behaviour lies outside these limits. Ambiguity arises because two sets of loops with appreciable projected area (exhibiting opposite $(\underline{g} \cdot \underline{R}) s_g$ behaviour or the same behaviour for opposite kinds of loops) can have the same $\underline{R}$ and the same sense of tilt. Since

this region of reverse contrast is controlled by the angle between $\underline{z}$ and $\underline{R}$, careful choice of $\underline{z}$ will ensure that a particular defect analysis lies safely within the confines of normal behaviour.

It is known from the habit plane analysis (§5.5.1) that loops lie within $\sim 35^\circ$ of $\{100\}$, e.g. loop normals are $\sim 10^\circ$ off $\langle 110 \rangle$ in bulk-irradiated material and closer to $\langle 100 \rangle$ in in situ irradiated foils. Fig. 5.29a illustrates the regions of normal and reverse contrast for $\underline{R}$ lying along $|101|$ in an (001) foil, i.e. $\underline{z} = |001|$. For in situ irradiated foils it is clear that loops will lie approximately flat-on ($\underline{n} \cdot \underline{z} = 1$) with normals in the safe region, or else on-edge ($\underline{n} \cdot \underline{z} = 0$) where analysis cannot be carried out anyway. For loops produced by bulk irradiation, it is important to establish which $\langle 110 \rangle$ axis the loop normals lie nearest, i.e. whether the loops are nearly pure edge ($\underline{n} \cdot \underline{R} \sim 1.0$) or nearly pure shear ($\underline{n} \cdot \underline{R} \sim 0$). It can easily be established, by looking at edge-on loops such as in those imaged strongly in figs. 5.14 or 5.20, that the loop normal is nearest that $\langle 110 \rangle$ axis along which $\underline{R}$ lies, since if these edge-on loops were nearly pure shear they should appear only in residual contrast. Simultaneous $\underline{R}$ and habit plane analyses such as those depicted in fig. 5.24 confirm this relationship between $\underline{n}$ and $\underline{R}$. Hence all loops which lie other than edge-on are expected to exhibit normal contrast for $\underline{z} = |001|$, and analysis should be correct under these conditions. The same is not true of $\underline{z} = |101|$, fig. 5.29b if, in the case of in situ irradiations, $\{100\}$ loop habit planes obtain in this section since then half the loops with $\underline{R}$ in the foil plane could exhibit appreciable projected area and have loop normals falling into the region of reverse contrast.

Fig. 5.30 illustrates the four possible configurations, two of vacancy and two of interstitial character, for a loop whose normal lies within the safe region defined above, for example a loop lying close to an $|001|$ foil plane (for $\underline{z} = |001|$ and $\underline{R} = |101|$ the safe region is defined for $\underline{n} \cdot \underline{R} > 0.26$, i.e. $<75^\circ$ between $\underline{n}$ and $\underline{R}$ for loops inclined $<60^\circ$ to the foil, i.e. $\underline{n} \cdot \underline{z} > 0.50$). The local lattice curvature for reflecting planes nearly parallel to the electron beam (Laue case) is depicted for each configuration, as well as the absolute sense of the displacement vector using the convention defined above. It is evident from fig. 5.30 that neither the form of lattice curvature nor the general direction of the displacement vector is alone sufficient to distinguish between vacancy and interstitial configurations (i.e. absolute direction of $\underline{R}$); both properties must be determined for the same loop. The general direction of the displacement vector may be ascertained using experiments of the sort outlined in §5.5.2 but performed on a specific loop. Alternatively, it can be assumed that $\underline{R}$ is always of $\langle 101 \rangle$ type and that, in the case of externally irradiated foils, the loops are nearly pure edge, so that $\underline{R}$ can be identified from $\underline{n}$; then using an (001) foil and $\underline{g} = \pm 200$ ensures that $\underline{R}$ is that $\langle 101 \rangle$ normal to $\underline{g}$ and closest to $\underline{n}$. This determination distinguishes between, for example, cases a and b. The lattice curvature is obtained from the $(\underline{g} \cdot \underline{R})/s_g$ contrast criterion denoted above; the resultant behaviour is sufficient to distinguish between, for example, cases a and c.

Fig. 5.31 outlines an analysis scheme to distinguish between an interstitial and a vacancy loop lying near the foil plane in an (001) foil. We first set $\underline{z} = |001|$ and utilise $\underline{g} = \pm 020$ to show that the

loop disappears as in fig. 5.25g, h. Then using $g_1 = 200$ and $g_2 = \bar{2}00$ we distinguish the sense of R (specifically, the projection of absolute R along g_1 or g_2). Next we tilt the foil by 18° to $z = |013|$ and utilize $g_3 = 13\bar{1}$ and $g = \bar{1}3\bar{1}$ to confirm the $\langle 101 \rangle$ type displacement vector and distinguish between $R = |10\bar{1}|$ (interstitial) and $R = |101|$ (vacancy) by a $g \cdot R = 0$ criterion. In this case $m = \frac{1}{8}(g \cdot R \cdot u)$ varies from $m \sim 0.13$ for the mixed section to $m \sim 0.19$ for the edge section of the loop; assuming the loop lies exactly on (001) this should be sufficient to produce appreciable residual contrast, but hopefully distinguishable from strong $g \cdot R$ contrast. As indicated in §3.6, 131 type reflections are weak reflections, but because of the much larger extinction distance of 262, relatively good two-beam conditions can be nevertheless established in KI and sufficient excitation of 131 to be useful is obtained (fig. 3.18); this is not likely to be the case for KCl, where the cation and anion scattering factors are so similar.

Fig. 5.32 illustrates such an analysis for two sets of loops produced by in situ irradiation of an (001) KI foil. Micrographs appear with their respective indexed diffraction patterns properly oriented with respect to directions in the foil. The sets of micrographs imaged in $g = 200$ and $\bar{2}00$ near the $|001|$ pole with $s_g > 0$ ($w_g \sim 1$) establishes the lattice curvature for each set of loops, e.g. $(g \cdot R) s_g > 0$ for the top most set of loops in $g = 200$. Both sets of images disappear for $g = 020$ and $0\bar{2}0$, indicating that the projection of their displacement vectors onto the foil plane lies along $|100|$ (as might be expected given that their slight elongation occurs normal to R). In the set of micrographs using $g = 13\bar{1}$ and $\bar{1}3\bar{1}$ the foil is tilted by

18° to $\underline{z} = |013|$ (down the 200 Kikuchi band). The sense of this tilt was established by carefully relating the motion of the Kikuchi lines to an actual foil tilt, taking into consideration the various lens inversions and the inversion of the diffraction pattern with respect to the micrograph (Groves and Kelly 1962). An independent determination was made by direct measurement, performing the same tilts on a carbon film, then focussing at extreme edges of the film to determine whether the focal plane was raised or lowered relative to that at the opposite side of the film by the tilt (an increase in objective lens excitation lowers the focal plane, §4.9). The specimen translation axes were then related to the image, and from the known relation between the tilt axes and the translation axes on the microscope, the tilt axes and precise sense of tilt could be established for the micrograph image. This procedure served as a comforting assurance that the tilt was properly interpreted. It is clear from the 131 diffraction patterns that relatively good two-beam conditions were established. It is also clear that strong contrast from each set of loops alternately vanishes with either $\underline{g} = 13\bar{1}$ or $\underline{g} = \bar{1}3\bar{1}$; residual contrast remains, but is relatively distinguishable as predicted. It should be noted that the 131 reflections illustrated are such as to produce strong $(\underline{g} \cdot \underline{R}) s_{\underline{g}} > 0$ contrast in both sets of loops; as indicated previously in $-\underline{g}$ the $(-\underline{g} \cdot \underline{R}) s_{\underline{g}} < 0$ contrast is weak and too easily confused with $\underline{g} \cdot \underline{R} = 0 / \underline{g} \cdot \underline{R} \Delta u \neq 0$ residual contrast. This disappearance of one set of loops in each reflection, together with the sense of lattice rotation established previously, indicates that the loop displacement vectors are respectively $|\bar{1}0\bar{1}|$ and $|10\bar{1}|$,

both consistent with loops of interstitial character. A similar analysis was performed for loops produced by external irradiation in bulk with the same result.

5.6 Electron Microscopy of Deformation Defects

The role of deformation in the generation, sensitisation or stabilisation of colour centre defects has been of considerable interest in colour centre studies ever since Przibram's (1927) observation that plastic deformation led to increased colorability of alkali halides by irradiation. Seitz (1950) proposed that the movement of dislocations results in an increase in vacancy concentration, and the Seitz (1954) mechanism for defect production in alkali halides invoked the de-excitation of mobile excitons at dislocation jogs, evaporating alternate anion and cation vacancies. Ever since F centre production has been shown to be an intrinsic process (§2.5) it has still been recognised that prior deformation has a marked effect on subsequent early stage colourability (e.g. Przibram 1956). It has recently been shown that subsequent plastic deformation of previously irradiated crystals also effects marked changes in the optical absorption spectra of irradiation defects. Prior irradiation is additionally shown to result in a marked increase in flow stress.

In this section we consider interaction between dislocations themselves and between dislocations and colour centre defects.

In §5.6.1 we consider the basic processes of plastic deformation in the sodium chloride structure and illustrate several features of

dislocation behaviour observed by direct transmission electron microscopy. In §5.6.2 we review the effects of plastic deformation on colour centre behaviour, which fall generally into two groups: plastic deformation followed by irradiation, and irradiation followed by plastic deformation. In §5.6.3 we discuss observed dislocation-irradiation defect interactions and indicate their relevance to interpretation of defect aggregate clusters.

5.6.1 Plastic deformation of alkali halide crystals

5.6.1.1 Compression tests

Crystals intended for study were deformed in uniaxial compression rather than tension because of their propensity to sustain catastrophic cleavage cracks when pulled in tension. Stokes, Johnston and Li (1960) have shown that this behaviour arises from the presence of surface microcracks which nucleate larger cleavage cracks under tension; these microcracks originate in a recrystallised surface layer resulting from exposure to atmospheric moisture, and they are difficult to avoid, particularly in the more hygroscopic alkali halides. No similar difficulty was experienced in compression.

Crystal blanks intended for compression testing were cleaved from Harshaw-supplied slabs of NaCl, KCl, NaBr and KI to dimensions 4.5 x 6.5 x 13 mm with a light hammer and razor blade. This procedure yielded consistently clean cleavage faces and least incidental deformation (Shlichta 1966). Cleaved blanks were polished on a soft flat polishing cloth saturated with water (KCl, NaCl) or methanol (KI, NaBr) to remove cleavage rivers and cleavage damage. The blanks were washed in propyl

alcohol and diethyl ether, dried quickly in a draught of hot air to prevent condensation of atmospheric moisture, annealed for 12 hr within 50 K of their melting points under dry argon and furnace cooled approximately 100 K hr^{-1} to room temperature. In some cases the annealed blanks were repolished in a static bath of $\text{H}_2\text{O}:\text{HCl}$ (NaCl , KCl) or methanol (KI , NaBr) to remove annealing effects. Blanks were then washed in propyl alcohol and diethyl ether and thereafter carefully handled only with foam-cushioned tongs. Shlichta (1966) has demonstrated the necessity of careful handling, as the surface dislocations introduced by even incidental handling can alter subsequent deformation behaviour appreciably. NaCl and KCl blanks were stored in vacuum, KI and NaBr blanks in vacuum or under dried silicone oil. Blanks were deformed in $[001]$ axial compression at a strain rate of $\sim 5 \times 10^{-5} \text{ sec}^{-1}$ on a small table model Instron (TM/M/L) in a special zero-friction compression jig (fig. 5.33) between PTFE-lubricated hardened steel anvils. Tests on some KI and NaBr crystals were performed under silicone oil when ambient humidity proved objectionable. All tests were conducted at room temperature, nominally 300 K. No cracks were introduced into specimens during deformation.

Deformed crystals were examined and photographed on each face under polarised light to indicate the operative slip system(s). Glide bands exhibit birefringence if there is an excess of edge dislocations of one sign associated with them; in this case there is a residual stress distribution changing from compression to tension on crossing the slip plane. Kear and Pratt (1959) have shown that the sign of this excess can be determined by the stress birefringence patterns. In the

symmetrical $|001|$ orientation the four equivalent $\{110\}\langle\bar{1}\bar{1}0\rangle$ primary slip systems in the NaCl structure (fig. 1.3) are equally stressed, and there is no resolved shear stress on the $\{100\}$ cross slip planes. Significant slip on all four systems rarely occurs, however, and slip normally initiates on two orthogonal $\{110\}$ systems, usually those with the shortest slip distance in the crystal. Unless a large number of accidental surface sources has been introduced through careless handling, one of the orthogonal systems soon becomes inactive, and glide bands of this inactive system act as barriers to further slip on the primary system, forming what have been called "kink" or "deformation" bands (Mendelson 1962). Once slip is established on either orthogonal set, slip is strongly inhibited on the oblique systems. These features can be seen from the stress birefringence patterns associated with each $\{100\}$ crystal face for a KCl crystal deformed 6%, fig. 5.34.

All four alkali halides tested (NaCl, KCl, KI, NaBr) exhibited similar three-stage work hardening behaviour in shear stress-shear strain curves fig. 5.35, (derived from load-elongation data assuming single slip on a $\{110\}\langle\bar{1}\bar{1}0\rangle$ system). Such results have been found by Davidge and Pratt (1964) for NaCl, Hesse (1965, 1967) for NaCl and Alden (1964) for KCl, KBr and NaF. The yield stress, generally in the range $20\text{--}50 \text{ g mm}^{-2}$, is determined chiefly by the divalent impurity content (which was low in these crystals, Table 1.5); this is because divalent cation impurity-cation vacancy complexes segregate at dislocation cores and provide an effective pinning mechanism (Bassani and Thomson 1956; Newey 1963; Brown and Pratt 1963; Pratt, Harrison and

and Newey 1964; Chang and Graham 1964; Frank 1968). The work hardening rate in Stage I, which persists up to ~5% shear strain, is ~G/1000. This rate, and the extent of Stage I are temperature and strain rate dependent. Therefore, the tendency in most colour centre studies to quote only strain, without indicating strain rate or stage of deformation, introduces considerably ambiguity in the evidence presented, particularly as regards what dislocation interactions are likely to be occurring (this point will be discussed below). The rate of Stage II hardening is appreciably larger, ~G/500, and is relatively temperature and strain rate independent. Stage III is characterised by a slowly decreasing work hardening coefficient.

5.6.1.2 Work hardening

The stress-dislocation density relation in NaCl oriented in $|001|$ compression has been established by Hesse (1967) in Stage I and extended to Stages II and III by Matucha, Franzbecker and Wilkens (1969) and is of the form

$$\tau = 0.37 Gb \sqrt{\rho}, \quad (5.12)$$

where b is the strength of the Burgers vector and ρ is the ^{screw} dislocation density in cm cm^{-3} . Matucha (1968) has studied the slip line distribution by microscopical replication. This has provided some indication of the density and activity of dislocations but not the details of dislocation distribution or, particularly, of dislocation debris. For the latter, transmission electron microscopy is required. Some indication of what dislocation interactions exist comes from decoration techniques (Amelinckx 1958) and studies of latent hardening behaviour (Alden 1963,

1964; Kear, Silverstone and Pratt 1966). For $\langle 1\bar{1}0 \rangle \{110\}$ slip, the possible interactions have been investigated by Amelinckx (1958) and Kear, Taylor and Pratt (1959). These are either dislocation intersections or dislocation reactions between dislocations on orthogonal or oblique slip systems, of one of the following sorts.

Intersections

(a) Oblique intersections of either edge-edge, edge-screw or screw-screw components lead to the formation of single charged jogs of width $b/2$ on each intersecting dislocation, which if forced to move do so non-conservatively, trailing behind alternating positive and negative ion vacancies or interstitials.

(b) Orthogonal intersections lead to formation of double neutral jogs of width b , which in moving trail behind alternate double rows of positive or negative ion vacancies or interstitials.

Reactions

(c) The orthogonal reaction

$$\frac{a}{2} |\bar{1}01| + \frac{a}{2} |101| \rightarrow a|001| \quad (5.13)$$

leads to no net decrease in elastic energy but has been observed by Amelinckx (1958) by decoration in annealed crystals.

(d) The oblique reaction

$$\frac{a}{2} |\bar{1}01| + \frac{a}{2} |0\bar{1}\bar{1}| \rightarrow \frac{a}{2} |\bar{1}\bar{1}0| \quad (5.14)$$

proceeds favourably with reduction in elastic energy and leads to a sessile pure edge dislocation lying on $(1\bar{1}2)$ along $|\bar{1}11|$. For several of these reaction product dislocations on near-neighbouring planes, the resulting configuration will have a minimum energy when these dis-

locations are lined up one above the other in (110).

(e) The oblique reaction

$$\frac{a}{2} |10\bar{1}| + \frac{a}{2} |0\bar{1}\bar{1}| \rightarrow \frac{a}{2} |1\bar{1}\bar{2}| \quad (5.15)$$

leads to a net increase in elastic energy and should result in repulsion away from $|\bar{1}11|$, producing cusped dislocation lines.

(f) The annihilation reaction

$$\frac{a}{2} |\bar{1}01| + \frac{a}{2} |101| \rightarrow 0 \quad (5.16)$$

results from interaction of dislocations of opposite sign on the same slip plane, or on neighbouring slip planes (for example, dipoles) if either dislocation is supplied with point defects sufficient to induce climb.

It is instructive to consider the sign of the point defect produced at dislocation intersections, i.e. whether the jogs formed are vacancy or interstitial producing jogs. Rules for predicting this have been derived by Hornstra (1962) as follows. Suppose we have two dislocations with Burgers vectors $\underline{b}_1$ and $\underline{b}_2$ and positive directions $\underline{u}_1$ and $\underline{u}_2$ respectively. We assume dislocation (2) to be stationary and let dislocation (1) approach (2) in the direction $\underline{r}$. If $\underline{r}'$ represents the distance and direction of continued motion of (1) with respect to the lattice after intersection (usually $\underline{r}$ and $\underline{r}'$ have the same direction), the number of point defects produced in its wake is

$$N = \frac{\{\underline{u}_1 \cdot (\underline{r} \times \underline{u}_2)\} \{\underline{b}_1 \cdot (\underline{r}' \times \underline{b}_2)\}}{\Omega |\underline{u}_1 \cdot (\underline{r} \times \underline{u}_2)|} \quad (5.17)$$

where Ω is the volume of the unit cell. If $N > 0$, the jogs produced are interstitial forming; if $N < 0$ the jogs are vacancy forming. In

applying (5.17) to rocksalt structure alkali halide crystals, one must bear in mind that of the twelve possible intersections, while eight form single charged jogs, two form neutral double jogs and two form neutral double kinks so that the number of defects produced by non-conservative jog drag must sometimes be interpreted as defect pairs.

It should be noted here that if any of the jogs formed in a screw (or mixed) dislocation by intersections (a) or (b) is left behind instead of generating point defect strings, a pure edge dipole is drawn out normal to the Burgers vector. This dipole not only provides an obstacle to slip on the orthogonal or oblique systems, but can serve as a sink for point defects. Segmentation of these dipoles through periodic climb can lead to dislocation loops of vacancy or interstitial character. An alternative mechanism for dipole formation is multiple cross slip of screw dislocations, the mechanism by which multiplication and slip band broadening apparently takes place (Johnston and Gilman 1960; Mendelson 1962). In this case pinching off of dipoles can occur by glide (Tetelman 1962; Washburn 1963; Stokes and Olson 1963). The cross slip plane in the rock salt structure is $\{100\}$, on which slip is approximately four times more difficult than on $\{110\}$. In the symmetrical $|001|$ compression, however, there is no macroscopic resolved shear stress on $\{100\}$ whereas there is for $|011|$ compression. The $|011|$ orientation has been found to be harder than the $|001|$ orientation (Hesse 1965), which possibly correlates with a greater amount of debris where cross slip is easier.

Identical slip geometry and dislocation interactions obtain in either case.

A number of theories of work hardening have been formulated to explain the origins of three stage hardening in alkali halides. Davidge and Pratt (1964) have attributed Stage I hardening to long-range elastic interactions in the primary glide systems (Taylor hardening). Hesse (1965) has cited the immobility of sessile jogs, while Evans and Pratt (1970) have considered both bowing out at sessile jogs formed by multiple cross glide and forest hardening from blocking obstacles formed by oblique intersections; in particular, the apparent ease of multiple cross slip distinguishes Stage I in alkali halides from that in f.c.c. metals (e.g. Hazzledine 1967). Frank (1970) has stressed the importance of point defect production during deformation, which he shows explains the exceptional volume expansion during deformation measured by Davidge and Pratt, and also accounts for the thermally activated contribution to the flow stress.

Davidge and Pratt (1964) attribute Stage II to dislocation debris on the primary system, principally dipoles, which form a forest for oblique slip. Gilman and Johnston (1960) and Gilman (1962) have considered dipole hardening as a special case of precipitate hardening. Chen, Gilman and Head (1964) have considered instead the elastic interaction between dislocations and dipoles and advanced a theory of multipole hardening. Kroupa (1962) and Makin (1964) have discussed interaction between dislocations and prismatic dislocation loops, in this case formed by the thermally-assisted break-up of dipoles into strings of prismatic loops. Such interactions have been observed in

MgO by Stokes and Li (1964). Evans and Pratt (1970) suggest that increased debris in planes inclined to the principal slip plane accounts for Stage II hardening; this can come about only by oblique reactions of the form (5.14) above.

Stage III has been the subject of investigation by Davis and co-workers (Davis and Gordon 1969; Aladag, Davis and Gordon 1970; Davis 1971) and by Haasen and co-workers (Matucha and Haasen 1967; Fontaine and Haasen 1969; Haasen et al. 1970). In particular Stage III hardening in NaCl is believed to be controlled by the thermally-activated stress-assisted cross slip of screw dislocations, which is made easier with the application of pressure through an increase of stacking fault energy with pressure (Fontaine 1968).

It is clear from this very brief review that the detailed distribution of dislocations and debris cannot be unambiguously inferred from the work hardening behaviour. This information can be derived only from the sort of transmission electron microscopy described below. However, it is abundantly evident that closer attention should be paid to the deformation conditions effected in colour centre studies and the deformation parameters more accurately established, in the absence of subsequent detailed microscopical examination, if they are to assist in a meaningful interpretation of the spectroscopic results.

5.6.1.3 Electron microscopical observations

Deformed specimens intended for electron microscopical examination were sectioned along active {110} slip planes, as indicated by the stress birefringence patterns, using the string saw described in §3.2.2. In

Some cases sections were obtained parallel to the orthogonal or oblique systems, or parallel or normal to the compression axis. These sections were mounted, polished and examined at liquid helium temperature. Particular caution was observed to avoid any incidental deformation during sectioning or mounting.

Micrographs comprising fig. 5.36 illustrate several deformation features in four alkali halides deformed to Stage II and sectioned parallel to the primary (101) slip plane from regions in the centres of deformed crystals. The KCl, KI and NaBr were deformed in $|001|$ compression; the NaCl crystal illustrated was deformed in $|011|$ compression by Hesse. Diffracting conditions such that $g = \bar{2}02$ were maintained because in this reflection all dislocations are in contrast, including the reaction product dislocation in (5.14), save those in the orthogonal system normal to the foil plane; the latter are in strong residual contrast. In fig. 5.36a in KCl, we find a feature which is relatively common in all alkali halide deformations, viz. small loops (circled) with apparent axis along $|010|$. These are almost certainly a product of dislocation jog formation, viz. clusters of point defects from non-conservative jog motion or break-up of edge dipoles drawn out from sessile jogs. A second common feature, illustrated in fig. 5.36b in KI, is the formation of dense networks from primary-oblique interactions of the sort (5.14). Fig. 5.36c, of NaCl deformed in $|011|$ compression, indicates the result of putting resolved shear stress on the (010) cross slip plane; cross slip occurs readily and many widely spaced edge dipoles are formed. Fig. 5.36d, of NaBr deformed in $|001|$ compression, illustrates narrow edge dipole formation where there is

no macroscopic stress on the cross slip plane. Similar dipoles, though not nearly so pronounced, are also seen in NaCl under $|001|$ compression.

5.6.2 Deformation and Colour Centres

5.6.2.1 Deformation followed by irradiation

Almost all the experiments dealing with the effect of deformation on subsequent colour centre production have been conducted by deforming crystals a few percent in compression (or sometimes bending), then investigating an enhancement of early stage F colouration. Most studies (see Schulman and Compton 1962) have considered that an increase in anion vacancy concentration is associated with plastic deformation; recently, however, some indications of the propensity of dislocations or dislocation debris for hole trapping or interstitial stabilisation have emerged. Both roles are important for explaining enhanced first stage colouration.

(i) Formation of anion vacancies

It has now been fairly well established (Crawford 1968) that radiolysis is a bulk crystal process and does not occur preferentially at defect sites such as along dislocations existing within a crystal. Even so, Bauer and Gordon (1962) claimed to have evidence supporting the view that F centre enhancement due to plastic deformation arises from F centre production at dislocation lines. The work of Crawford and Young (1960) and Geudeke and Burgers (1963), providing no evidence of climb in heavily irradiated NaCl ($F > 10^{18} \text{ cm}^{-3}$), is often cited to discount preferential F centre production along dislocations; this

evidence is, however, macroscopic, and it is shown in §5.6.3 that dislocations do indeed climb with irradiation on a scale detectable by electron microscopy. Nevertheless, we still consider that direct production of F centres at dislocation sites (e.g. the Seitz mechanism) does not represent the mechanism of coloration enhancement, although there may be preferential survival of F centres produced near dislocation lines (see §5.2.4).

An alternative mechanism is the production of anion vacancies arising from the motion of dislocations. One possibility, suggested by Nowick (1958) and reiterated by Roshchina and Klyukvian (1966) is that moving dislocations disperse precipitated impurities which sensitise early stage F centre production, causing their redissolution on an atomic scale. A more likely interpretation (Mitchell, Wiegand and Smoluchowski 1963; Royce and Smoluchowski 1964) is that a source of extra anion vacancies is the debris resulting from dislocation interaction. Considerable experimental support for this arises from the work hardening studies of Davidge and Pratt (Davidge, Silverstone and Pratt 1959; Davidge and Pratt 1963, 1964) and the electron microscope observations cited in §5.6.1 which emphasise the role of dislocation dipoles and non-conservative motion of jogs formed by repeated dislocation intersections or as a result of slip band broadening by multiple cross glide. Davidge and Pratt's measurements of bulk density change with plastic deformation indicate that the dislocation content alone cannot account for the observed density changes and that the equivalent (in dislocation dipoles, clusters of point defects or individual point defects) of 10^{18} vacancy pairs cm^{-3} are produced by

10% compression. Clearly these concentrations are more than adequate to sensitise early stage coloration. Both Chang (1965) and Fröhlich and Grau (1965) have presented evidence supporting this view; in fact Chang (1965) has found anomalies in the β band consistent with the location of a deformation-induced F centre within a few Burgers vectors of an edge dipole core.

One problem in this interpretation (Sibley, Nelson and Crawford 1965) is that a mechanism must exist for transformation of anion-cation vacancy pairs or vacancy pair clusters, which are the products of non-conservative jog motion or edge dipole climb and annihilation, into single F centres. Significantly, Sibley et al. (Sibley, Nelson and Crawford 1965; Sibley and Russell 1967) have shown that prior plastic deformation increases the M/F and R/F ratios in crystals subsequently irradiated over those ratios obtaining in undeformed irradiated crystals; this effect is particularly striking in very pure samples. Very recent studies (Camagni, Boni and Giani 1968; Boni and Camagni 1971; Levy, Mattern and Lengweiler 1970) have confirmed this excess F aggregate population in a variety of deformed alkali halides (KCl, NaCl, LiF).

Additional evidence for the production of vacancy defects derives from the observations of Serughetti et al. (1967 and their other publications referenced therein) that deformation produces marked changes in the optical absorption spectra of electron excess centres. Observed thermoluminescence (Clark and Newman 1969, 1971b) and thermally stimulated currents (Hirai and Scott 1966; Clark and Newman 1969), induced by low temperature deformation and subsequent anneal of crystals previously irradiated, halogenated or additively coloured,

suggest that up to four new sorts of electron trap arise from plastic deformation. These traps are apparently populated from ionization of existing colour centres by passing dislocations, and the electrons released from these traps during anneal apparently recombine at interstitial sites to give rise to observed luminescence. Butler (1966) has shown that deformation luminescence is intimately connected with anion vacancy defects, particularly M centres; however, the traps observed by Clark and Newman are stable only in their ionized form at room temperature and so cannot be associated with F or M centres and must be some new electron trap introduced by plastic deformation. An extra exciton band is also produced, which anneals in the same temperature range as the α band (Clark and Newman 1971a), suggesting that anion vacancies are produced in some form; Clark and Newman point out, however, that the isolated anion vacancy is mobile below room temperature, whereas their traps are stable and favour instead cation-anion vacancy aggregates formed by non-conservative jog motion, some of which should be positive and charged and could trap electrons. Indeed, Ueta and Künzig (1955) pointed out some time ago that irradiated alkali halide crystals bleached more rapidly after plastic deformation and attributed this behaviour to electron traps (but not isolated anion vacancies) which stabilised the electrons released from F centres during bleaching.

(ii) Stabilisation of interstitials

A second interpretation of enhanced coloration is that plastic deformation stabilises hole excess centres such as halogen interstitials. This approach largely derives from a suggestion of Sibley and Russell

(1967) that dislocation dipoles may stabilise interstitial defects, and some experimental observations by Ishino, Mitchell and Clark (1967) and Clark and Newman (1971a) on the effect of plastic deformation on the V absorption spectra. Many earlier observations went unnoticed because the nature of the centres responsible for V band absorption (§2.6.4.2) was largely speculative. For example, both Sibley (1964) and Chang (1964) noticed that the region of the V_2 band was affected in much the same ways as the F band by plastic deformation. Sibley, Nelson and Crawford (1965) found that a centre apparently introduced by plastic deformation of KCl absorbing in the V_2 region did not seem to be the usual V_2 centre. Wiegand, Turner and Smoluchowski (1966) similarly found a trapped hole band in deformed LiF.

The comprehensive study of Ishino et al. (1967) of V bands in KBr established much more firmly the effects of plastic deformation on the hole-excess centres, in particular finding a deformation-induced anisotropy in the V_2 region. This they ascribed to a separate new band, the V_x band, exhibiting $|100|$ dichroism in a crystal showing primarily $|\bar{1}01|$ (101) slip, and thus arising from defects with either $|110|$ or $|100|$ axes. A parallel observation was an increase in absorption in the V_2 band region and a decrease in the V_3 band region. Similar changes were found both for crystals plastically deformed and subsequently irradiated and for crystals irradiated and subsequently plastically deformed. A preliminary assignment for the V_x band involved the reorientation of a non-symmetric defect in the strain field surrounding screw dislocations, chiefly because Gilman and Johnston (1959) reported that edge dislocations have a greater mobility than

screw dislocations in LiF, and more of the latter would presumably remain in a deformed crystal.

Clark and Newman (1971a) have recently extended this work to encompass both KCl and low temperature deformation. They show that the V_x band is not associated with the isolated point defects or dislocation dipole products of deformation because of its stability in annealing (the evidence of Davidge and Pratt 1963 suggests that dipoles anneal out at 500 K in NaCl due to vacancy mobility; the V_x band in KBr is stable to > 670 K), and from additional stress birefringence observations conclude that the V_x band is associated with an interstitial trapped at the dislocations themselves. The V_x band in KBr is shown to have two components (but only one in KCl) which are explained by postulating two different trapping environments (edge and screw dislocations); the larger edge: screw velocity ratio in KCl is invoked to explain the single V_x band in KCl. They also observe another band, labelled the V_s band, which exhibits no dichroism and which they attribute to an interstitial stabilised at a dispersed impurity. They also observed depression of V_3 band absorption which they interpret as the cutting of interstitial clusters (to which they ascribe the V_3 band) by mobile dislocations during deformation.

If this trapping role of dislocations is correct (somewhat different models to that of Clark and Newman are proposed in §5.7.2 to account for observed dislocation climb), it suggests that a major role of dislocations in coloration enhancement may be the stabilisation of anion interstitials (either at dislocation cores or at debris). Such stabilisation might be expected to reduce vacancy-interstitial

recombination and thus enhance F centre production. Both Sibley and Russell (1967) and Royce and Smoluchowski (1964) have shown that liquid nitrogen temperature coloration of deformed alkali halides results in an increase in F colorability and not the M centre enhancement observed at room temperature; this suggests that thermal activation is necessary for the M centre formation observed at room temperature, and is consistent with the continuing effectiveness of interstitial traps even to low temperatures, where the interstitial is still mobile (§2.6.1). A requirement of this mechanism (at least on the athermal model, §2.7) is that dislocations serve as sinks as effective as interstitial clusters; this will be demonstrated in §5.6.3.

5.6.2.2 Irradiation followed by deformation

The most striking effect of irradiation on subsequent deformation behaviour is a marked increase in yield stress over that in unirradiated material. Most well annealed alkali halides generally yield plastically in the region $20\text{--}50 \text{ g mm}^{-2}$ (see §5.6.1) whereas those irradiated to an F centre concentration $\sim 10^{18} \text{ cm}^{-3}$ typically exhibit yield stresses exceeding $10^{-3} G$ where $G \equiv (C_{11} - C_{12})/2$ is the shear modulus $\sim 10^6\text{--}10^7 \text{ g mm}^{-2}$). Whapham and Makin (1960) found in LiF that hardening increased with irradiating dose up to about $5 \times 10^{23} \text{ eV cm}^{-3}$ where the hardening finally saturated; their hardening curves closely resemble F centre saturation curves, and it is evident from other data (§2.7) that a dose of $5 \times 10^{23} \text{ eV cm}^{-3}$ corresponds roughly to F saturation. Indeed, Nadeau (1962, 1963, 1964) in LiF and Sibley and Sonder (1963) in KCl, found that this increase in flow stress, $\Delta\tau$, was proportional to the

square root of the F centre concentration. F centres themselves do not introduce appreciable hardening, as indicated by the additive colouration experiments of Suzuki and Doyama (1959). Therefore the induced hardening was ascribed to interstitials and has been interpreted on the solution hardening model of Fleischer (1962) for point defects inducing tetragonal strains. In this case the isolated H centre was considered the likely entity, and Fleischer's theory has often been invoked to confirm the presence of stable interstitials at higher temperatures. On Fleischer's model the flow stress increase is given by

$$\Delta\tau = (G/n) c^{\frac{1}{2}}, \quad (5.18)$$

where c is the atomic concentration of strain centres, in the case of isolated defects equal to the F centre concentration. n is a parameter describing the interaction of a dislocation with a strain centre which has been found consistently in the region 10 - 12 for KCl (e.g. Sibley and Russell 1965, Sonder et al. 1967), in accord with Fleischer's estimate for tetragonal strain centres. For an F centre concentration $\sim 10^{-4}$ ($\sim 10^{18} \text{ cm}^{-3}$), $\Delta\tau \sim 1 \text{ Kg mm}^{-2}$ which is close to what is observed.

However, we now know from the electron microscopical observations of §5.3 and §5.4 that considerable interstitial clustering occurs at all temperatures, and that at room temperature these clusters are quite large and account for nearly all interstitials produced by irradiation. Therefore, a far better approach to an analysis of the hardening is to consider the hardening introduced by prismatic dislocation loops (e.g. Silcox and Hirsch 1959, Kroupa and Hirsch 1964), planar precipitates

(e.g. Kelly and Nicholson 1963, 1971) or forest dislocations (Basinski 1959, Saada 1960).

Each of these approaches results in an expression for the flow stress of the form

$$\Delta\tau = \frac{GR}{kL} \quad (5.19)$$

where R is the displacement vector of the loop/precipitate/forest dislocation, L is the average distance between obstacles threading the slip plane, and k is a constant reflecting the interaction between a mobile dislocation on the slip plane and the obstacle. An early application of forest hardening theory to loops (Silcox and Hirsch 1959) gave $k \sim 2\pi$, while Kroupa and Hirsch (1964) have derived $k \sim 8$. Saada (1960) has considered forest interactions of the same type which occur in the NaCl system and derived $k \sim 2.5$ for attractive interactions and $k \sim 5$ for repulsive interactions. Kelly and Nicholson (1963) have applied Saada's approach to planar precipitates (e.g. shearable Guinier-Preston zones in Al-Cu).

It is first instructive to consider cluster geometry and distribution. We shall assume for the loop that $\underline{R} \approx a/2 \langle 110 \rangle$, and that any one glide dislocation with $\underline{b} = a/2 \langle 110 \rangle$ can interact with six different types of loops. For one of these the Burgers vector of the dislocation and the displacement of the loop will be nearly identical, and part of the loop will combine with the dislocation, in this case forming a large jog. In another case the two displacements will be orthogonal and lead to no net elastic attraction. Of the remaining four oblique interactions, two will be strongly attractive and two strongly repulsive.

The analogous dislocation reactions which result in work hardening were delineated in §5.6.1.2. In the case of loops, of course, the long-range elastic interaction is smaller and shorter range elastic interactions predominate. The actual nature of observed interactions is discussed later in §5.6.3. Averaging over those interactions likely to raise serious obstacles for passage of the dislocation, we shall elect to use a value $k = 4$.

We first consider the case of KCl where we have seen (§5.3.1, §5.4.3) that the interstitial clusters are elongated platelets with length $\ell \sim 100$ nm and width $d \sim 10$ nm at saturation lying along $\langle 100 \rangle$. If N_v is the number of clusters per unit volume, the average number of clusters N_s intersecting a unit area of slip plane is

$$N_s = (\sqrt{2}/3) N_v \ell, \quad (5.20)$$

where ℓ is the average length of a cluster. The average distance between clusters intersecting a slip plane is then

$$L = N_s^{-1/2} \sim N_v^{-1/2} \ell^{-1/2}, \quad (5.21)$$

and we have from (5.21)

$$\Delta\tau \sim \frac{Gb}{k} \ell^{1/2} N_v^{1/2} \quad (5.22)$$

For KCl, $G = 1.7 \times 10^6$ g mm⁻² and $b = 0.45$ nm. From low temperature observations of KCl externally irradiated to saturation at room temperature ($F = 10^{19}$ cm⁻³, §5.4.3), we estimate $N_v \sim 10^{15}$ cm⁻³, $\ell \sim 100$ nm, and using $k = 4$ find

$$\Delta\tau_{\text{sat}} \sim 1700 \text{ g mm}^{-2}, \quad (5.23)$$

in excellent agreement with the extrapolated results of Sonder et al. (1967).

At lower doses we have one low temperature observation (§5.4.3) for KCl irradiated externally to $F \sim 5 \times 10^{17} \text{ cm}^{-3}$ for which $N_V \sim 3 \times 10^{14} \text{ cm}^{-3}$ and $\ell \sim 20 \text{ nm}$. We calculate $\Delta\tau \sim 460 \text{ g mm}^{-2}$, again in good agreement with the data of Sonder et al. (1967). It has been noted (§5.4.3) that the number of clusters N_V remain relatively constant throughout irradiation; we therefore expect $\Delta\tau \propto \ell^{\frac{1}{2}}$.

We should point out that (5.22) can be arranged to reflect a dependence with F centre concentration similar to (5.18). We must first assume that nearly all interstitials are contained in the clusters (we have confirmed this from the measurements of §5.4.3). The number of interstitials associated per cluster, n_c , on the most probable models subsequently discussed in §5.7 is

$$n_c = 4 d\ell/a_o^2, \quad (5.24)$$

where d and ℓ are the length and width of an elongated cluster. The relationship between density of F centres and density of cluster is

$$\begin{aligned} F &= N_V n_c &&) \\ \text{or } N_V &= F/n_c = a_o^2 F/4 d\ell. &&) \end{aligned} \quad (5.25)$$

(5.22) then becomes

$$\Delta\tau = \frac{Gb}{8} a_o (F/d)^{\frac{1}{2}}. \quad (5.26)$$

Rendering (5.26) in the same form as (5.18) we have

$$\Delta\tau = (G/n') c^{\frac{1}{2}}, \quad (5.27)$$

$$\text{where } n' = 8d^{\frac{1}{2}}/a_o b\sqrt{N_o} \quad (5.28)$$

for N_o = the total ion density ($\sim 3 \times 10^{22} \text{ cm}^{-3}$ for KCl).

We note from (5.28) that n' depends upon the width of the cluster, which might not be expected to remain constant with dose. However, there is considerable indication (§5.3.1) that clusters in KCl (and also LiF: Mannami, Akisue and Tanaka 1967) grow primarily by elongation along a $\langle 100 \rangle$ axis. In this case we can assume an approximately constant width which must be $d \sim 6$ nm to obtain $n' = 12$ and thus agreement with the data of Sonder et al. (1967). This is not an unreasonable width for the dose range measured, although the electron microscopy suggests a value closer to ~ 10 nm for defect concentrations nearer saturation. Of course the present model does not take into account other hardening mechanisms, such as source hardening, hardening by isolated interstitials, etc. For example, if as few interstitials as 1/10 of the total interstitial population remained as isolated halogen molecules, they could contribute as much as half the total hardening on Fleischer's (1962) model. Thus, the hardening will be sensitive to the distribution of interstitials, which is easily altered by impurity doping. Sibley and Russell (1965) actually observed that in KCl irradiation hardening decreases with divalent impurity doping; this may be explained in two ways. First, the cation vacancies created by divalent doping provide strain-relieving interstitial traps (H_V centres, §2.8.3) and lower the total strain inducing interstitial population. Second, the availability of closely spaced interstitial traps early on in the irradiation depresses the isolated interstitial (or interstitial molecule) population. Both effects should lead to a reduction in hardening. A similar effect for irradiation at 80 K followed by room temperature anneal (Sonder et al.

1967) can be explained by a similar argument based on the availability of closely spaced interstitial traps upon annealing from low temperature irradiation.

For alkali halides such as KI which (at least in the later stages of irradiation) exhibit more nearly circular clusters, the form of (5.26) will be somewhat different. In this case, for a cluster radius r_o we find

$$\Delta\tau = \frac{Gb}{8} a_o (F/\pi r_o)^{\frac{1}{2}} \quad (5.29)$$

Alternatively, we can express (5.29) in terms of N_V and F and find

$$\Delta\tau = \frac{Gb}{4} \left\{ \frac{N_V a_o^2}{\pi} \right\}^{\frac{1}{4}} F^{\frac{1}{4}} . \quad (5.30)$$

Since we know that N_V remains relatively constant during the irradiation, we expect $\Delta\tau \propto F^{\frac{1}{4}}$, rather than the $\sqrt{F}$ dependence of KCl, and of course, the overall hardening should be considerably less. For example, for KI externally irradiated to $F \sim 3 \times 10^{18} \text{ cm}^{-3}$ $r_o \sim 80 \text{ nm}$ and $\Delta\tau \sim 200 \text{ g mm}^{-2}$ (cf. KCl, $\Delta\tau \sim 800 \text{ g mm}^{-2}$). Recent compression tests on externally γ irradiated KI (D. G. Howitt, private communication) confirm this predicted behaviour; irradiation induces considerably less hardening in KI than in KCl, and the induced hardening begins to saturate much earlier on in the irradiation. This result suggests that hardening is attributable chiefly to the interstitial clusters and not to isolated interstitials, as the distribution of the latter would be expected to be similar in both KCl and KI, while the morphology of the former is clearly observed to differ widely in the two crystals.

5.6.3 Interaction of dislocations and irradiation defects

Two principal observations were made in this study of the interaction of dislocations and irradiation defects: first, the effect of irradiation on existing dislocations during irradiation of a previously deformed crystal; and second, the interaction of glide dislocations with large interstitial clusters during subsequent deformation of a previously irradiated crystal. Both effects illustrate what we believe to be in large part responsible for the influence of deformation in spectroscopic measurements, and in addition they reveal vital information about the interstitial aggregation process.

5.6.3.1 Deformation followed by irradiation

Dislocations were rarely seen to survive in KCl or NaCl foils irradiated in situ at room temperature in the microscope. In NaBr, where the defect production rate is orders of magnitude smaller, they are seen to survive, and we indicated in §5.3.1.4 that dislocations near screw orientation are observed to climb perceptively into helices (fig. 5.6b). In KI irradiated at room temperature in the microscope, fig. 5.37a, we have the observation that in those regions with a large existing dislocation density, the normal distribution of large interstitial clusters is replaced with a fine distribution of small clusters. The dislocations themselves appear to be heavily decorated with small clusters, and in the case of the edge dislocations illustrated, to disintegrate under the heavy irradiation involved. Such behaviour suggests that dislocations provide an effective sink for interstitial defects produced during irradiation. Izumi (1969) observed that in NaCl

and KCl irradiated in the microscope, defect clusters were often seen to nucleate in straight lines along $\langle 100 \rangle$, suggesting decoration of dislocations or point defect trails.

A more dramatic effect is seen for the case of screw dislocations in crystals externally irradiated. A KI crystal ~ 1 mm thick was bent to introduce dislocations and irradiated at room temperature with 400 keV electrons to a dose of 1000 MRad and an F centre concentration $\sim 2 \times 10^{18} \text{ cm}^{-3}$. In this case dislocations predominately near screw orientation were seen to climb into helices (A, fig 5.37b) suggesting condensation of irradiation defects at dislocation cores. In some cases, these helices were even seen to have degenerated into strings of loops (B, fig. 5.37b). Again, the large interstitial cluster density in the vicinity of dislocations was smaller than in undeformed regions (cf. fig. 5.20a).

The number of defects condensing can be calculated by measuring the mean radius r and pitch of the helical turns. The number of defects condensed per turn is then

$$n_t = \frac{r^2 b}{(\Omega/4)} = 3 \times 10^3 \text{ defects turn}^{-1} \quad (5.31)$$

where Ω is the volume of the unit cell; (5.31) assumes a defect of strength b , for example a cation-anion vacancy or interstitial pair or an interstitial halogen molecule for reasons which will become evident in §5.7. The mean pitch p measured is 43 nm turn^{-1} , so we calculate the linear density of condensation

$$N_\ell = n_t/p = 7 \times 10^8 \text{ defects cm}^{-1}. \quad (5.32)$$

A foil thickness ~ 300 nm was assumed, and from this a dislocation density

ρ of $\sim 10^9$ cm cm⁻³ estimated. Therefore the total number of defects condensed per unit volume was

$$N_v = N_\ell \rho = 7 \times 10^{17} \text{ defects cm}^{-3}. \quad (5.33)$$

The average number of stable Frenkel pairs N introduced by irradiation was $\sim 2 \times 10^{18}$ cm⁻³. The volume from which these defects condense per unit length of dislocation line is then

$$v_c = N_\ell / N \sim 4 \times 10^{-10} \text{ cm}^3, \quad (5.34)$$

which corresponds to a capture radius $r_c \sim 120$ nm about each dislocation.

This is an exceptionally large distance from which to draw vacancy defects at room temperature, but is of the same order as the normal spacing between interstitial loop clusters in undeformed material. Furthermore, the concentration of condensed defects is $\sim$ the measured F centre concentration (within a factor of 3), and while at the same time the number of interstitial clusters is reduced in the deformed crystal. From this evidence we conclude that interstitial defects are responsible. The mechanism by which interstitials might induce climb relates to the formation of interstitial loops and is discussed in §5.7.

It is, of course, the edge components that climb, turning a screw dislocation with thermal jogs into a helix. This can be seen from the diagram in fig. 5.38. In (a) we indicate the FS/RH convention for interstitial climb of an edge dislocation. In (b) we show a screw dislocation, either right-handed or left-handed, on which we can imagine thermal jogs. The sense of climb for each edge component, above or below the slip plane, is indicated for interstitial condensation. We note that the sense of the helix depends on the sign of the screw dislocation (i.e. the direction of $\underline{b}$) as well as the sign of the condensation (i.e. vacancy or interstitial).

The geometric and contrast properties of a helix provides us with a way to distinguish between interstitial and vacancy helices. A regular helix laying normal to the electron beam should project as a smooth sinusoidal curve (Thomas and Whelan 1959). Deviations from this form arise from inside/outside image contrast behaviour as discussed for loops (§5.5.3), which distorts the normal symmetrical projection, and from constraints introduced by crystal symmetry (Forty 1961). A smooth helix requires prismatic glide as well as climb (Amelinckx et al. 1957), and where the former is difficult a rather angular helix results. A regular helix viewed obliquely (for example the helix inclined to the foil in fig. 5.37b) projects as a looped configuration, fig. 5.38d. The form of the projection depends on the angle from which the helix is viewed and whether it is right-handed or left-handed. Provided the sense of inclination is known, and the looped structure can be distinguished from the cusped contrast geometry (see below), the sense of the helix may be determined by inspection. The Burgers vector of the helix, which for a given sense of helix determines its character, may be ascertained from the contrast behaviour of the untilted helix, fig. 5.38e. Because their normals project alternately into regions of normal and reverse contrast (see §5.5.3), adjacent half-turn loops of the helix appear in alternate inside and outside contrast, imparting a characteristic cusped form to the image. Taken together, the sense of the helix and the sense of $\underline{b}$ specify the helix character. An analysis was attempted on the helices appearing in fig 5.37b, but the small radii of the helices made a character assignment difficult. Nevertheless, it is felt that the evidence

cited above rather convincingly supports the mechanism of interstitial condensation.

Four points derive from this conclusion with regard to colour centre studies. First, it is clear that dislocations themselves are effective sinks for the point defect products of irradiation. In particular, the observations of climb strongly suggest a model for the V_x band of Ishino, Mitchell and Clark (1967) and Clark and Newman (1971a). Furthermore, it is not necessary to invoke debris as sites for interstitial stabilisation; dislocations themselves are clearly adequate sinks.

The second point concerns the enhancement of early stage coloration. It would be expected that the presence of so strong an interstitial trap would alter local recombination conditions, particularly in the early stages of coloration when interstitial concentration is not large enough to result in large interstitial clusters. As indicated in §5.5 the number of interstitial clusters remains relatively constant throughout irradiation; these clusters simply grow in size with continued irradiation and thus increase their cross sections (actually, perimeters) for interstitial capture. It is probable that during the early stages of irradiation in undeformed material a substantial number of interstitials remain in isolated or di-interstitial form and considerably increase the available recombination volume (as in the low temperature case). The provision by prior deformation of an interstitial sink as effective as large interstitial clusters early on in the irradiation undoubtedly alters the recombination kinetics and leads to an increase in stable Frenkel pair concentration. The dislocation sink should have

progressively less effect as irradiation proceeds, i.e. as the defect concentration increases to that point where large interstitial clusters would have formed anyway.

The third point relates to irradiation hardening mechanisms. Clearly, irradiation of previously deformed material should induce appreciable subsequent hardening because the condensed defects may effectively pin existing dislocations; this is consequently an effective source-hardening mechanism. Both Ishino, Mitchell and Clark (1967) and Clark and Newman (1971a) discovered that an irradiated crystal which is subsequently deformed also acquires a V_x band. The implication is that a dislocation in moving through the crystal either sweeps up isolated interstitials or, in intersecting or passing near larger clusters, disperses interstitials which then condense on (or are swept up by) that or subsequent dislocations. This sort of mechanism should evidently be included in any proposed hardening model. In particular, the latter may effectively render interstitial clusters particularly "hard" obstacles.

Finally, and probably most important, the climb of a perfect $a/2$ $\langle 110 \rangle$ dislocation by interstitial condensation implies that some form of interstitial incorporation can produce a lattice strain very close to a perfect lattice translation, which of course is the same problem with interstitial loop formation.

5.6.3.2 Irradiation followed by deformation

A similar conclusion about the form of interstitial incorporation in the large interstitial loops can also be made from observation of the interaction between perfect glide dislocations and interstitial loop clusters. Fig. 5.39 illustrates an (001) KI foil prepared from a crystal γ irradiated in bulk at 1000 MRad, cleaved to ~ 1 mm thickness and deliberately bent to introduce simple glide dislocations. Two sorts of interaction are indicated: at A it appears that the dislocation has looped around a large loop cluster, showing that the latter is an effective obstacle to dislocation motion; at B it appears that a dislocation has actually joined with and incorporated a loop as part of its own line (this same sort of interaction has been observed in deformed MgO by Stokes and Li 1964 between glide dislocations and prismatic loops). Since the loop does not lie on the $\{110\}$ slip plane (but instead about 90° from it), incorporation into the dislocation line introduces a large jog in the latter, which appears evident from fig. 5.39. This observation suggests that the displacement vector of the loop and the Burgers vector of the dislocation are the same or very nearly the same in both magnitude and direction. Such an observation also lends support to the hardening model developed in §5.6.2.2.

5.7 Models for Interstitial Aggregates

It is clear that the exact nature of interstitial aggregates in alkali halides cannot be ascertained solely from the electron microscopical analysis of §5.3, §5.4 and §5.5. Certainly, however, the electron microscopy does establish some rather stringent conditions for any potential aggregate model: the loops must be interstitial and planar with habit plane between $\{110\}$ and $\{100\}$ and have a displacement vector R close enough to $a/2 \langle 110 \rangle$ to preclude fault contrast. In addition, perfect dislocations must interact rather completely with the loops and must be made to climb during irradiation by some process analogous to interstitial aggregate formation. Clearly, a perfect $a/2 \langle 110 \rangle$ dislocation loop satisfies these criteria and in a simple single species material would prove an acceptable and probable interpretation. While in the present case there is no specific evidence (fault contrast, displacement fringes, precipitate contrast) to confirm that the observed loops are other than simple planar dislocation loops, nevertheless, several morphological features (manner of growth, morphology differences, nucleation below 30 K, irregularity of loop edges, etc.) and a considerable amount of non-microscopical evidence (principally spectroscopic) suggest that the distribution of interstitial defects is considerably more complex than in the sort of simple interstitial loops encountered in single species materials, e.g. metals. Therefore, we shall first consider the additional non-microscopical evidence that casts doubt on the simple interpretation, then proceed to consider a

number of alternative models, two of which at least appear to conform closely to most of the available evidence.

5.7.1 Spectroscopic evidence

The principal contribution of spectroscopy has been to uncover virtually no direct evidence for the involvement of the cation sublattice in the fundamental irradiation damage process, while abundant evidence has emerged to confirm and even demonstrate the nature of damage in the anion sublattice. The experiments of Ueta et al. (1969), for example, indicate that the fundamental products of the creation process are the F centre and an interstitial halogen atom, the H centre, formed within about 20 nsec of an electron-hole recombination. The F centre halogen vacancy species is stable even above room temperature, and it remains relatively isolated in which state it is easily detected optically. On the other hand, paramagnetic resonance spectra attributable to a single interstitial halogen species have not been observed in alkali halides irradiated at room temperature (cf. H centre EPR obtained by Klnzig and Woodruff 1958, 1961 at liquid helium temperature). Absence of such spectra has impeded positive confirmation of the fate of the halogen interstitial at room temperature, but is consistent with chemical stabilisation of the interstitial not involving an atomic (i.e. H centre) aggregate, for example formation of halogen molecules. What relevant spectroscopic information there is is that obtained from optical absorption bands, which is far less specific. The H band is known to saturate at liquid helium temperature and disappear at temperatures much above 50 K (Itoh and Saidoh 1969).

It is also well known that room temperature irradiation produces V bands (e.g. Ishii and Rolfe 1966) which grow with increasing dose, but the detailed structure is complicated by the breadth of the V bands (see fig. 2.2) and the temperature and dose dependence of the spectra (see §2.6.4.2). Nonetheless, information from a number of recent experiments has clarified certain aspects of V band absorption.

For example, it is now clear that the main V bands produced by ionizing radiation at room temperature are in the region of the V_2 and V_3 bands and are similar to those produced by additive coloration in halogen gas (Ishii and Rolfe 1966). In KI, Hersh (1957) and Konitzer and Hersh (1966) have concluded that the positions of these bands are fairly well correlated with bands associated with molecular iodine in solution. Specifically, they suggest that the V_2 and V_3 bands arise from a single centre, and they assign the observed optical transitions to an $|I_3^-|$ molecular ion. Irradiation of KI at room temperature, indeed, produces a broad V band covering the V_2/V_3 region, which Konitzer and Hersh assign to aggregated molecular iodine centres. Ishii and Rolfe (1966) have come to similar conclusions for KBr. Significantly, Winter, Wolfe and Christy (1969), in a study of six alkali halides, indicate that V band positions depend primarily on the anion species and only marginally on the particular cation species.

The sequence of V band development (with continued irradiation or increasing irradiation temperature) also suggests growth of halogen molecular aggregates. At low temperatures the V_4 band develops out of the H' band (Itoh et al. 1967) as the H band disappears, and is

consistent with formation of isolated halogen molecules from the reaction of two H centres. With continued irradiation or increasing irradiation temperature, the V_2 band develops at slightly higher energies (i.e. greater perturbation from the environment). With further irradiation, the absorption shifts to still shorter wavelengths and broadens into the wide V_3 band. Such a sequence suggests that the molecular environments change in at least three stages, ending with a complex mixture of molecular perturbations. This sort of sequence is consistent with molecular aggregation on at least two models advanced later.

The V_x band of Ishino, Mitchell and Clark (1967) and Clark and Newman (1971a), which has been attributed to defect condensation at or near dislocation cores, falls between the V_2 and V_3 bands nearest the V_2 absorption. This specific ascription suggests that V_2 absorption may arise similarly from the presence of halogen interstitial molecules near the edge of a growing aggregate whose surrounding strain field resembles that of perfect dislocations.

Hermann and Pinard (1970b, 1971) have recently extended the earlier work of Christy and Phelps (1961) and Goldstein (1969) in KCl and NaCl to show that the V_3 band grows in proportion to the F band up to saturation ($\sim 10^{19}$ defects cm^{-3}), suggesting that it arises from a complement of the F centre. The proportionality factor is not known, but assuming a one-to-one correspondence between this species and the F centre, they calculate oscillator strengths of 0.24 and 0.20 for the V_3 bands in KCl and NaCl (cf. F band oscillator

strengths of 0.90 and 0.81). Since the oscillator strength cannot exceed ~ 1 , at the very least a large proportion of the complementary interstitial defects must be contributing to V_3 absorption. The intrinsic nature of the V_3 band has also been demonstrated in other potassium and rubidium halides (Winter, Wolfe and Christy 1969) and in LiF (Mayhugh and Christy 1970). Although this information cannot in itself establish the identity of the centre responsible for the V_3 band, it does have considerable significance for the constitution of the interstitial clusters observed by electron microscopy, since we know (from §5.4) that nearly all interstitials are stabilised in these clusters at room temperature. It is thus natural to connect the observed clusters with their optical manifestation in the V bands.

5.7.2 Inducing the required displacement

In evaluating alternative interstitial loop models, it is instructive to consider first the ways in which the necessary observed $a/2 \langle 110 \rangle$ displacement can be generated. A revealing exercise is to consider initially the ways in which we can make a perfect $a/2 \langle 110 \rangle$ edge dislocation climb interstitially. In fig. 5.40 we reproduce one of the two possible equilibrium positions (fig. 1.2) for an $a/2 \langle 101 \rangle$ edge dislocation in the NaCl structure, viewed in the (100) plane perpendicular to the dislocation line; we investigate how this dislocation can be extended to the next (101) slip plane below.

5.7.2.1 Conventional climb

Clearly, the simplest way to effect this extension (i.e. to

create an interstitial doublejog) is to condense an extra interstitial anion-cation pair at the point marked x in fig. 5.40a, reproducing the perfect lattice and resulting in the configuration shown in fig. 5.40b. This process requires, in addition to a supply of anion interstitial ions, a source of cation interstitials. It also requires conversion of an H centre (the normal halogen interstitial form) to an interstitial ion with the attendant loss of a hole. If the cation interstitial can be derived from the lattice, no other source being apparent in the pure crystal, this hole should be trapped in the resulting cation vacancy to produce a paramagnetic centre. It is also clear that if the anion supply is the H centre, which presumably initially condenses at the dislocation core to relieve strain, conversion of the halogen atom and supply of the cation interstitial to the core must be effected simultaneously to maintain charge neutrality. Otherwise, a cation-anion interstitial pair must somehow arrive at the core together from their respective sources. Such a pair is not normally envisaged (see e.g. Barr and Lidiard 1970), and an apparently simple climb mechanism becomes in reality rather complex. As an alternative, we consider means of utilising only the interstitial halogen defects which are known to be produced in the radiation damage process.

5.7.2.2 H centre condensation

One possibility is that the single halogen interstitial migrates to and stabilises at the point marked x in fig. 5.40a. As discussed in §2.3.3.2 the single interstitial halogen atom takes the form of an H

centre, a $|X_4^{3-}|^0$ molecule occupying three anion sites along a $\langle 110 \rangle$ direction. The $\langle 110 \rangle$ orientation arises from the gain in quantum mechanical energy achieved by delocalising its hole (Dienes, Hatcher and Smoluchowski 1967; Bachmann and Peisl 1970). H centres are extremely mobile along $\langle 110 \rangle$, can easily reorient along any of the six equivalent $\langle 110 \rangle$ directions, and are undoubtedly the mobile entity in some way initially responsible for loop nucleation and growth as evidenced in low temperature loop nucleation experiments, §5.4. There are two problems in utilising the H centre alone. The first is that the elastic distortions associated with the H centre are too small to reproduce anything like a displacement with magnitude $\sim a/\sqrt{2}$. Table 5.6 contains simple estimates of the displacement which is likely to result for the potassium halides observed in this study; the $|X^-|$ ion radii in these estimates are those derived by Tosi and Fumi (1963) and Fumi and Tosi (1964); the $|X^0|$ atomic radii are assumed to be one-half the molecular bond length; the $|X^{-\frac{1}{2}}|$ radii are taken simply as the mean of r_{X^-} and r_{X^0} . The magnitude of the displacement R caused by the H centre is then

$$R = \frac{4r_{X^{-\frac{1}{2}}} + 2r_{X^-} - \sqrt{2} a}{a/\sqrt{2}}, \quad (5.35)$$

expressed in units of the perfect lattice shear. It is clear from Table 5.6 that these displacements are small fractions of what is required to reproduce the required $a/\sqrt{2}$ displacement, and it is unlikely that any stable arrangement of H centres (e.g. H_2 : Dienes, Hatcher and Smoluchowski 1970) would induce the required strains. (The negative displacements in Table 5.6 are an anomaly of the simplistic hard sphere

model; Bachmann and Peisl 1970 calculate a $\langle 110 \rangle$ displacement of 0.08 in units of $a/\sqrt{2}$ for an H centre in KBr.) This result derives, of course, from the small size of the halogen atom compared to the ion. The second problem is that it is not altogether clear whether even the $\langle 110 \rangle$ displacement direction would be preserved during H centre condensation at a dislocation core. Fig. 5.40c and d reproduce the two equilibrium edge dislocation positions depicted in fig. 1.2 with an H centre precipitated at the core. It is not immediately evident, at least in (c), that given the small strain of the H centre and its preference for hole delocalisation, a $\langle 110 \rangle$ orientation is necessarily preferred. Near $\langle 100 \rangle$ orientations straddling the slip plane are also conceivable.

5.7.2.3 Halogen molecule condensation

The next possibility arises from interaction of two H centres stabilised at the dislocation core to form an $|X_2^0|$ interstitial molecule. The probable stable orientation of an isolated halogen molecule in otherwise perfect lattice occupies two interstitial sites along $\langle 100 \rangle$ as depicted in fig. 2.4f (White and Greene 1969). However, at a dislocation core much of the considerable strain from the isolated molecule can be relieved by alignment along $\langle 110 \rangle$ between the two neighbouring anions immediately below the slip plane, at x in fig. 5.40e and f. The additional stabilisation probably necessary for this orientation might derive from the quantum mechanical delocalisation of the two holes along the $\langle 110 \rangle$ line of anions to form an $|X_4^{2-}|$ configuration.

The estimated magnitude of displacement from such a configuration is given by

$$R = \frac{4r_{X^0} + 2r_{X^-} - a/\sqrt{2}}{a/\sqrt{2}}, \quad (5.36)$$

in units of $a/\sqrt{2}$. Table 5.6 shows that the $\langle 110 \rangle$ displacement is likely to be at least of the order $a/\sqrt{2}$, though by no means exactly. The hard sphere model is, of course, notoriously unreliable for an ionic lattice, and the actual displacements obtaining (after inclusion of polarisation effects, quantum mechanical stabilisation, etc.) could well be closer to (or farther from) $a/\sqrt{2}$ than indicated in Table 5.6. However, it is unlikely that in all alkali halides a stable molecular displacement exactly $a/\sqrt{2}$ would be sustained.

5.7.2.4 Induced crowdion motion

A third possibility involves rearrangement of the lattice near a dislocation core in the presence of substantial strain arising from a nearby isolated halogen molecule incorporated interstitially. The mechanism is illustrated in fig. 5.40g and h. An $|X_2|$ molecule forms some distance from a dislocation core in (g) and aligns interstitially along $\langle 100 \rangle$; the attendant strain causes crowdion displacement, in (h), of a cation-anion pair to the nearby dislocation core, relieving much of the molecular strain and extending the perfect dislocation. The molecule then more comfortably occupies the cation-anion vacancy pair left behind, and probably aligns along $\langle 100 \rangle$. A requirement of this model clearly is that a molecule must form near but not at the dislocation core; this appears likely only if an H centre does not have sufficient

time to diffuse to the dislocation core before meeting another H centre, or if a mechanism exists to remove a molecule condensed at the core. The likelihood of the former happening is relatively small and is discussed together with the latter in §5.7.5.

Each of these models (with the exception of the H centre precipitation) provides a mechanism for the dislocation climb observed in §5.6.2. Since the displacement from the interstitial clusters analysed in §5.5 is also $a/2 \langle 110 \rangle$, these models likewise provide mechanisms for growth of interstitial clusters. We therefore investigate the implications of extending these growth modes to interstitial aggregate formation. In particular we have the requirements of observed unfaulted displacement and the complex V band behaviour.

5.7.3 Simple dislocation loop

We first suppose that the defects discussed in §5.5 consist of planar unfaulted interstitial dislocation loops with Burgers vector $a/2 \langle 110 \rangle$ made up of extra planes of anions and cations. This structure, illustrated in fig. 5.41a, would give the required displacement vector and would exhibit the observed unfaulted behaviour. Such a dislocation loop can also explain observed loop orientation. For simplicity, consider a pure edge square loop with $\underline{R} = \langle 101 \rangle$. For a large loop in isotropic material, the minimum energy configuration has the loop plane normal to the displacement vector, i.e. a pure edge loop. For loops of the size observed by electron microscopy ($< 1 \mu\text{m}$), significant deviations from the pure edge orientation can occur for both isotropic (Bullough and

Foreman 1964) and anisotropic (Bacon, Bullough and Willis 1970) material. The glide cylinder (actually a parallelepiped) for such a loop consists of one set of parallel (101) primary slip planes and an orthogonal set of parallel (010) cross slip planes. Since slip is comparatively difficult on the latter (see §1.4), we should expect the loop to tilt so that slip occurs for those loop segments lying in (101). This means that the loop normal n and R define an (010) plane, and the loop plane tilts about an $|010|$ axis towards (001) as observed. It is, however, difficult on this model to explain why an (001) loop plane should obtain in (001) foils, and it is also difficult to explain the widely differing loop morphology in different alkali halides. There are, in addition, a number of fundamental difficulties inherent in this model.

First, there is the question of nucleation. In simple species crystalline materials (e.g. f.c.c. metals, Mazey and Barnes 1968; b.c.c. metals, Eyre and Bullough 1965; Bullough and Perrin 1968), interstitial nucleation begins on the closest packed planes ($\{111\}$ in f.c.c. and $\{110\}$ in b.c.c.), altering the stacking sequence and introducing a faulted loop. This subsequently shears to remove the fault, then rotates by glide and self-climb to establish loop orientation appreciably removed from the initial faulted habit plane. A corresponding sequence in the NaCl structure involves $\{222\}$ planes populated alternatively by all cation and all anion species. There is no indication, even in the early stages of loop formation, that a defect with $\langle 111 \rangle$ displacement field is nucleated, and the resulting ionic fault would be of extremely high

energy electrostatically and unlikely to form. Other difficulties attend unfaulted precipitation on $\{110\}$ and $\{100\}$, both of which entail two extra $\{220\}$ or $\{200\}$ half planes of mixed anion/cation population. Electrical neutrality requires that both half planes be nucleated and further that a cation-anion constituent interstitial pair be nucleated simultaneously. It is difficult to envisage how this could occur unless a cation-anion interstitial pair forms a mobile entity (for example, the double crowdion discussed for fig. 5.40h). A similar difficulty does not arise for the case of vacancy loops formed by quenching from high temperatures (for example, see the work of Groves and Kelly 1963b on vacancy loops in MgO), since the divacancy pair is a known mobile entity.

Second, the introduction of conventional perfect interstitial dislocation loops in alkali halides requires a source of both anion and cation interstitials or sinks for both kinds of vacancies. The evidence derived from point defect measurements is now overwhelmingly in favour of the irradiation damage process occurring predominantly on the anion sublattice (Crawford 1968; §2.5), producing F centres and complementary interstitial halogen atoms. The number of sites involved in the interstitial clusters seen in this work is always very close to the number of F centres produced and measured by optical absorption. Even if the cation sublattice damage rate were finite (for example, for electron displacement damage above the ~ 0.4 MeV threshold), it is still unlikely to be large enough to permit formation of dislocation loops containing essentially all the anion interstitials. Even if equal numbers of anion

and cation interstitials could be initially produced (this condition is virtually unobtainable, since ionization damage on the halogen sublattice is always vastly greater than displacement damage, even for neutral particle irradiations; the one exception might be low energy, ~ 5 keV, ion bombardment where sufficient energy may not be transferred to an electron to activate even the Pooley-Hersh mechanism), it is most unlikely that both interstitial species would exhibit sufficiently similar mobility and proclivity for stabilisation to result in similar recombination kinetics, and thus in similar concentrations at any point in the irradiation. A similar problem was encountered by Groves and Kelly (1963a) in explaining interstitial loops in neutron-irradiated MgO.

The only alternative to cation interstitial production is a sink for cation vacancies. The latter are created if the perfect lattice acts as the only other source of cation interstitials. If interstitial halogen were incorporated into a normal dislocation loop as halide ions (at formation they are H centres, i.e. halogen atoms) and a nearby cation drawn from its lattice site to occupy an adjacent interstitial site, the resulting hole from the halogen atom would be trapped at the cation vacancy. Such a centre is paramagnetic and is apparently observable by EPR in crystals doped with divalent impurities (Känzig 1960, Schoemaker 1965), where it resembles a V_k centre distorted by an adjacent cation vacancy, but it has never been detected in irradiated alkali halides. Since isolated cation vacancies are not detected, the cation vacancy must then either diffuse away to some unspecified vacancy sink, be left aggregated in the centre of the expanding loop, or find

camouflage in some obscure way. A large sink for cation vacancies should be seen in the microscope, but no other large cluster is observed (except at temperatures higher than room temperature in KCl and NaCl). A sheet of cation vacancies (with trapped holes) left in the centre of the loop would be expected to induce sufficient relaxations to produce an observable fault.

A further problem is accounting for the V bands associated with the interstitial halogen species at room temperature. It was noted in §5.4.3 that the loop clusters formed in externally irradiated crystals account for nearly all the interstitials formed during irradiation, from comparison with measured F centre density. The scale of the absorption indicates that most interstitials must be contributing to the V_3 absorption band, since the oscillator strength cannot exceed ~ 1 , and assuming that every interstitial contributes results in a computed oscillator strength $\sim 0.2 - 0.3$. Furthermore, the proportionality between the V_3 and F bands over a wide range up to saturation shows that if interstitials in these loops give rise to the V_3 band, interstitials in the body of the loop as well as at the bounding dislocation core must contribute to the absorption; if only interstitials at the core contribute, then as the loop grows in size with irradiation (which is demonstrated in §5.4), the proportionality would be lost. Thus, these observations could not be explained if most interstitial anions became incorporated into normal perfect interstitial dislocation loops, since all those in the centre of the loop would be accommodated as perfect lattice and could contribute neither the

required number of absorbing species nor the proportionality in absorption to the F band. We therefore feel that, while a simple dislocation loop by itself satisfies the basic electron microscopical criteria of §5.5, an unfaulted interstitial dislocation loop, constructed only from extra planes of anions derived from the irradiation process and cations derived from the lattice is not only improbable, but does not satisfy additional evidence. This is not to say that a perfect dislocation loop in conjunction with some other radiolytic defect might not satisfy available criteria. Such a mechanism is, in fact, indicated in §5.7.5.

5.7.4 $|X_2^0|$ molecular precipitate

An alternative is to sustain the required lattice displacement solely with interstitial halogen irradiation products in the form of interstitial halogen molecules as discussed in §5.7.2. A possible configuration for a planar precipitation of $|X_2|$ molecules deriving from H centre-H centre interactions is illustrated in fig. 5.41b, extending the condensation process envisaged in fig. 5.40 into a planar loop. On this model, molecules are accommodated along $\langle 110 \rangle$ between neighbouring $|X^-|$ ions and aligned in parallel fashion, though not necessarily all in the same plane; a staggered array, fig. 5.42, could provide a pseudo-planar precipitate on planes other than $\{110\}$. This precipitate provides a displacement close to $a/2 \langle 110 \rangle$ and utilises only the interstitial halogen primary irradiation products.

Apart from the magnitude of the displacement involved, there are other experimental observations consistent with this model which can be justified in terms of the elastic interaction between $|X_2|$ molecules regarded as elastic point dipoles. The elastic interaction is particularly important since the quantum mechanical energy per $|X_2|$ molecule is expected to be roughly constant, provided the molecule is accurately aligned between the two neighbouring halide ions, since the bounding dislocation line energy depends primarily on the displacement vector and core length and only secondarily on the detailed loop shape.

The elastic interaction energy between two parallel point force dipoles is given by (e.g. Stoneham and Bullough 1970)

$$E = \frac{A}{r^3} \{15 \ell^4 - 6 \ell^2 - 1 + 4\nu (1 - 3\ell^2)\} \quad (5.37)$$

where r is the interdipole distance and $\ell \equiv \cos \theta$ is the direction cosine of the vector joining adjacent dipole centres with respect to the dipole axis. Poisson's ratio ν is not well defined for cubic crystals; usually the Voigt average ν_V (1.3) is used. For KI, $\nu_V = 0.2516$, but in fact (5.37) is not very sensitive to ν in the region $0.2 < \nu < 0.3$. The behaviour of the interaction given by (5.37) is illustrated in fig. 5.43, which indicates that there is a maximum attractive interaction for $\theta = 60^\circ$, contributing significantly to the stability of a structure in which $\theta = 60^\circ$ interactions predominate. The value of A , of course, is not well defined for application of (5.37) on an atomic scale. An attempt was made to estimate this parameter (M. Stoneham, private communication), which is reflected in interaction energy values tabulated in Table 5.7. However, it would be foolish to take these values

as anything approaching absolute, and for the most part we shall try to utilise only the qualitative trend of relations such as (5.37). Furthermore, the qualitative predictions of nearest neighbour interactions are unlikely to differ appreciably from those of the more correct but more involved consideration of the interaction of a force dipole and the full dislocation loop.

The three nearest neighbour interactions for various planar growth configurations are given in Table 5.7, where it is assumed that the loops lie near (001) with displacement vector along $|101|$, as illustrated in fig. 5.27. A total interaction energy for additional molecules added in the several modes of possible growth has also been calculated. It is apparent from the latter values that planar growth on (001) along $|100|$ or along $|010|$ are equally likely as far as the elastic dipole interactions are concerned. The dipole-dipole interactions are therefore unable to account for the directed growth observed in the early stages of cluster growth (or always in KCl); in fact, initial elongation along $|010|$ always occurs, rather than along $|100|$ as might be marginally predicted from Table 5.7. However, in later stages of growth in some alkali halides (e.g. KI, KBr), growth can be relatively unidirectional, suggesting that preferential growth results from some constraint which depends more critically on ion species.

Table 5.7 also shows that (001) planar growth along $|100|$ is likely to be energetically very similar to growth generally along $|100|$ but out of the (001) plane so as to tilt the loop normal towards the

displacement vector, i.e. so that the loop acquires pure edge character. For these two cases the only difference is that a $\theta = 45^\circ$ interaction at $r = a$ is replaced by a $\theta = 90^\circ$ interaction at $r = a/\sqrt{2}$, leading to only small differences in total interaction energies.

We can explain observed loop orientations by considering the smallness of this difference in intermolecular interactions in conjunction with the increase in dislocation line energy with the addition of interstitial molecules to the loop. For simplicity we consider a square loop lying in (101) with sides of length L along $|010|$ and $|101|$ and displacement vector R normal to the plane of the loop, along $|101|$. In the limit of very large L this pure edge orientation will be the minimum energy configuration. However, for L in the region of interest ($L < 1 \mu\text{m}$), elastic interactions between opposite sides of the loop will alter both the total elastic line energy and the minimum energy orientation position. We are faced with two possible modes of molecular growth along the segments initially lying along $|10\bar{1}|$: continued pure edge growth along $|101|$ or growth instead along $|100|$, increasing the line length and altering the character of the $|101|$ segment from edge to mixed. The total elastic energy of a pure edge square loop (in the limit of isotropic elasticity) has been calculated by Bullough and Foreman (1964) by a method including core surface tractions and is of order

$$E_L \sim \frac{GR^2}{\pi(1-\nu)} \ln \frac{L}{R}, \quad (5.38)$$

where G is the shear modulus ($G = 1.1 \times 10^{11}$ dynes cm^{-2} in KI) and R

is the magnitude of the loop displacement vector. This amounts to an energy component

$$E_s \sim \frac{GR^2}{4\pi(1-\nu)} \ln \frac{L}{R} \quad (5.39)$$

for each side of the loop, corresponding to about 8×10^7 eV cm⁻¹ or 4 eV per interstitial molecule added along $|10\bar{1}|$. The calculations of Bullough and Foreman (1964) and Bacon, Bullough and Willis (1970) indicate that an energy minimum can exist for a non-edge orientation; for their specific calculations $\underline{n}$ is rotated $\sim 15^\circ$ from $|101|$ towards $|001|$ for $L \sim 200 R$ ($L \sim 100$ nm in KI). The smaller the loop, the further displaced towards an (001) loop the minimum energy configuration becomes. For $L \sim 200 R$ the difference between this energy minimum and a (001) loop does not exceed $0.02 E_L$. (Bullough and Foreman consider rotation about the loop diagonal, while in the present case we consider $|010|$ as the rotation axis; this difference will alter energy profiles somewhat, but probably not by an order of magnitude). We therefore expect that the line energy difference in placing $|101|$ aligned interstitial molecules along $|100|$ and along the minimum energy direction (somewhere between $|10\bar{2}|$ and $|10\bar{3}|$) amounts to about 0.1 eV per molecule.

From Table 5.7 we see that the decrease in elastic interaction energy between molecules for the three principal interactions introduced by each additional molecule amounts to 0.58 eV per molecule for growth along $|100|$ and 0.53 eV for growth along $|101|$, or about 0.05 eV difference. We therefore expect that the line energy difference (~ 0.1 eV) will be of the same order as the elastic intermolecular

interactions (0.05 eV) and loops will tend to grow inclined to the (001) habit plane at some minimum energy position between (001) and (101). The smallness of these differences suggests that influences such as image forces in thin films, defect supersaturation at high irradiation rates, etc., can greatly influence loop orientation with respect to the $|010|$ axis, and this is consistent with the observation that tilt occurs in large crystals externally irradiated in bulk but not in thin films irradiated in situ. Image forces, for example, are expected to lower the longer range line energy, while short range intermolecular interactions remain relatively unaffected, with the result that a habit plane closer to (001) obtains during loop growth in this foils.

Tilt of the loop normal from $|001|$ to a direction away from the displacement vector involves a strongly repulsive $\theta = 0$ molecular interaction at $r = a/\sqrt{2}$ instead of a $\theta = 45^\circ$ interaction at $r = a$. This tilt is grossly unfavourable, as shown in Table 5.7, and is never seen. Growth exactly along $|010|$ is much more favourable than tilted growth in this general direction, i.e. tilt of the loop about $|100|$, since the tilted growth involves a repulsive $\theta = 30^\circ$ interaction instead of an attractive $\theta = 60^\circ$ interaction. In this case, growth exactly along $|010|$ is preferred by about 0.4 eV per molecule, and this large energy differential is unlikely to be offset much by a gain of ~ 0.1 eV from a line energy decrease resulting from tilted growth. Therefore, little deviation from an $|010|$ growth axis should result, and experimentally little tilt about the $|100|$ axis is

observed (§5.5.1). Thus growth by molecular precipitation is not inconsistent with observed loop morphology.

This model can also explain the behaviour in very thin foil regions during in situ irradiation. It was indicated in §5.3.1 that only planar defects lying normal to the foil were sustained in thin (001) KCl foils, and that the projection of their displacement vectors R on the foil plane lies along $\langle 100 \rangle$. We can use the $|X_2|$ model to demonstrate that in the presence of strong image forces arising from nearby foil surfaces, nucleation of planar defect lying normal to the (001) foil surface is the favoured configuration, and that for such a defect with trace along $|010|$ the expected displacement vector is directed along $|101|$, consistent with observation. The sorts of planar defect normally observed in thicker (001) foils are absent in thin regions, viz. those lying normal to the foil plane with R along $|101|$ out of the foil plane (orientation A in fig. 5.2).

In fig. 5.44 we have illustrated a cross section of a thin (001) foil region sustaining a single halogen molecule nucleus and a further precipitated molecule in equivalent orientations A, B and C (corresponding to halogen molecular precipitate clusters of the orientations illustrated in fig. 5.1a). In the first two orientations, the molecular axis lies inclined to the foil plane and the loop elongation axis in the foil plane; in the third the molecular axis lies in the foil plane and the loop elongation axis normal to the foil plane. Orientation C is likely to be the higher energy configuration, because in orientations A and B strain energy arising from the halogen

molecule will be partially reduced by surface relaxation, and it is unlikely that a molecular axis as depicted in C would nucleate in very thin foils. On the other hand, the $|101|$ molecular axis for A and B is energetically favourable, and of these two possibilities B is of lower energy in the presence of the image forces indicated.

In a wedge-shaped (001) foil, then, we expect first a region in which no stable defects are sustained, where image forces are large enough to remove all interstitials from the foil; next a thicker region in which only defects in orientation B are sustained, where the image forces remain large enough to favour a single orientation of least energy; last the thicker regions in which planar defects in orientation A can nucleate planar loops lying parallel to the foil plane. Even in thick regions, straightforward defects in orientation C are still less probable, since the long axis for the equilibrium defect size in these regions is of the order of the foil thickness; it is indeed possible that the surface-relaxed defects D in fig. 5.1a represent such orientations. Defects of type B are expected to remain small in extent in very thin foils or near the surfaces of thicker ones because of the interstitial depletion in these regions. It is worth noting here that similar arguments can be put forward on the perfect dislocation model of §5.7.3 in the presence of substantial image forces.

The sequence of V band development during prolonged irradiation or with increasing temperature is also compatible with the halogen precipitate model. In very small precipitates formed at an early stage of irradiation or at low temperature, most of the molecules will find

themselves close to the edge of the precipitate (i.e. at the core of the dislocation loop); we suggest that these molecules could give rise to V_2 absorption in much the same region as the V_x band arising from molecular precipitation at a dislocation core. As irradiation progresses, the loops grow in size, and optical absorption will be dominated instead by molecules in the body of the precipitate (the number of sites in the interior grows as r^2 , those at the edge only as r , for a cluster of radius r), which experience a different environment from that near the perimeter; these, we suggest, give rise to V_3 absorption, which will increase roughly in proportion to the F band. A similar explanation has been advanced by Sonder et al. (1967). A difficulty with the precipitate model is that it does not explain the breadth of the V_3 band; most of the molecules in the interior of the cluster would be expected to experience rather identical surroundings which should produce a well defined V_3 optical transition.

However, the principal difficulty in explaining the experimental results in terms of a planar precipitate of halogen molecules is the absence of fault contrast (§5.5.2). It is highly unlikely that these molecular precipitates would lead to displacements near enough $a/\sqrt{2}$ and near enough to the $\langle 110 \rangle$ direction to give truly unfaulted behaviour. The magnitude of the expected fault, indicated in Table 5.6 for the three potassium halides studied, should be observable for KBr, if not for KI. However, it is worth noting that in the one potassium halide for which these effects should be most pronounced, KCl, the defects remain rod-like and do not extend into planar loops. The same result obtains in KBr and KI in the earliest stages of loop growth, and KBr is

more reluctant to open out into loops than is KI, which most nearly approaches the perfect $a/2 \langle 110 \rangle$ lattice shear. This behaviour may imply a relationship between growth morphology and presence of a fault (or some other constraint); in any event it does mean that for loops like those in KCl, the straightforward $\langle 110 \rangle$ molecular precipitate cannot definitely be ruled out solely on the basis of fault contrast criteria, as it appears to be for KI and KBr.

A possible way in which a molecular precipitate could be retained without inducing observable fault contrast would be to distribute the molecules regularly but non-uniformly within the loop plane. Such a distribution could give rise to the discrete lattice equivalent of a Somigliana dislocation in an isotropic continuum (Somigliani 1914, 1915; R.Bullough, private communication).

In the case of a round loop, as in KI, the non-uniform distribution might be in the form of concentric rings of molecular precipitates. Most of the interstitials would gravitate towards the edge of the precipitate, since in a collection of n parallel elastic dipoles occupying $n+m$ ion sites within a confined planar area, the occupation density would tend towards unity at the edge and zero at the centre. Certainly the width of the outermost ring would have to be $\sim$ the observed dislocation image width, but the variation of the resulting inner distribution could be sufficient to prevent the phase difference ultimately responsible for fault

contrast from every building up to observable proportions over sufficiently large an area. The required driving force for distributing n molecules over $n+m$ rather than just n sites is not immediately apparent. However, the differences in displacement energy (ostensibly the energy in separating the $\{110\}$ surfaces by the molecular dimension) might explain differences in loop morphology, since where the displacement is smallest (e.g. KCl) a single linear strip might nucleate, whereas where the displacement is largest (e.g. KI) the molecules may minimise the displacement energy by arranging in circular zones.

5.7.5 Molecule-induced perfect dislocation loop

A final model is based by extension on the anion-cation crowdion mechanism induced by strains arising from halogen molecule accommodation, as discussed in §5.7.2. Fig. 5.4lc illustrates a cross section of an entire loop produced by this mechanism. Here halogen molecules occupy scattered anion-cation vacancy sites in the vicinity of the dislocation core. Such a loop model satisfies many of the requirements cited above. It generates a perfect unfaulted interstitial dislocation with the required displacement vector. The dislocation is not firmly pinned to a precipitate as in the molecular precipitation model, and habit plane adjustments are possible as well as complete interaction with intersecting dislocations. The broad V_3 band is immediately explained by the multiplicity of possible molecular environments available.

In fact, if a single environment obtains, as for example a single sheet of molecules above or below the slip plane, a displacement fault would return since the molecule is not the same size as the divacancy it inhabits; as long as the molecules in their divacancy sites remain randomly distributed the fault problem is obviated. The exact distribution of the molecule in the vacancy pair is unclear; almost certainly a hard sphere molecule would not be expected. Chemically the configuration is an H_V (or Hayes-Nichols, fig. 2.4) centre with an extra trapped hole, i.e. $|H_V^+|^0$, and how the two holes would localise is open to speculation. There is some evidence (Känzig 1960) to show that a hole trapped at a single cation vacancy localizes as a V_K centre perturbed by the cation vacancy; however, if the molecule-divacancy centres are to account for V_3 absorption, a molecule-like optical transition must somehow be retained, and some $|X_3^-|$ character must persist.

There is very recent evidence for such a model from the apparent existence of electrically dipolar defects involving both ionic sublattices inferred from measurements of ionic thermal currents in irradiated high purity KCl (Stott and Crawford 1970, 1971). By applying an electric field (at around 250 K) following irradiation at various temperatures from 80 K to 350 K, then cooling to 77 K and annealing, Stott and Crawford found depolarization currents consistent with a large number of dipolar defects. Since no conceivable defects existing solely on the anion sublattice are likely to be dipolar,

these depolarization currents were ascribed to cation-anion vacancy pairs, the number of which then had to be extraordinarily large to account for the observed dipole loss, viz. one-fifth the number of F centres produced by irradiation at 250 K. Four principal ITC peaks were found at 125 K, 145 K, 160 K and 190 K, which altered only in overall (but not relative) strength for different irradiation temperatures; all peaks also annealed at the same rate and were stable for several weeks at room temperature. However, no spectra were obtained for irradiation at 80 K or at 350 K.

Provided these thermal current measurements are not spurious (for example, originate in electronic rather than ionic polarization; their reproducibility makes this unlikely), the molecule-divacancy centre satisfies the observed behaviour extremely well. The numbers are certainly right to describe sites involved in the interstitial clusters, and the temperature range over which the dipolar defects are produced ($80\text{ K} < T < 350\text{ K}$) coincides with the range of stable production for large interstitial clusters. Addition of the molecule to the ^dvacancy undoubtedly lowers its electric dipole moment somewhat, with the result that even more dipoles are required than estimated by Stott and Crawford, producing closer to the expected one-to-two correspondence between dipolar defects and F centres for irradiation.

It is instructive to consider reorientation modes of the molecule-divacancy centre. The likely mechanism is that of electron transfer to the molecules along $\langle 110 \rangle$ from a neighbouring halogen ion (five halogen ions surround the cation vacancy part of the centre).

This reorients the dipole by 90° via the same hole jump path as for the 60° reorientation of a V_k centre. In fact, the temperature at which such a transfer is thermally activated is likely to be similar to that for V_k reorientation (Table 2.6; ~ 165 K in KCl), viz. just in the region of the major ITC peak. 54° jumps (from $\langle 100 \rangle$ to alignment along $\langle 111 \rangle$) are also possible by the same mechanism, but undoubtedly require more activation if they occur, since the molecular bond is stretched. Bulk diffusion is only possible in the region where the cation vacancy is mobile, provided some mechanism exists to effect the interchange between cation and that half of the molecule residing in the cation vacancy. The activation energy for single cation vacancy mobility in KCl is ~ 0.7 eV (Barr and Lidiard 1970) which implies diffusion only at or above room temperature. During anneal to this temperature region, Stott and Crawford found continuous ITC activity, while for irradiation at 350 K no ITC peaks were found. This result has real implications for the large spherically symmetrical defects (§5.3.4) produced during irradiation above room temperature, i.e. where the neutral cation vacancy might be mobile, and is discussed further in §5.7.6. The broadness of the ITC peaks and the fact that they cannot be fitted to Arrhenius-type plots to determine unique activation energies suggest that a variety of environments obtain; certainly, ease of reorientation in the double defect illustrated at the top of fig. 5.41c, for example, would be different from that of any relatively isolated one.

The presence of the molecule also means that the cation vacancy will not normally be observable by EPR as a cation vacancy-trapped hole

defect, and this may explain the absence of evidence for defects on the cation sublattice. However, the centre might prove convertible to $|H_V^0|^0$ by brief irradiation at low temperature, which is the familiar Hayes-Nichols centre. Similarly, annihilation of half the molecule by an F centre should produce a cation vacancy with trapped hole, a paramagnetic centre which has been observed by EPR in impure LiF (Künzig 1960) and Pb^{2+} doped NaCl and KCl (Schoemaker 1965). These may represent the confirmatory experiments necessary to identify the molecule-divacancy defect.

The chief problem with this model is the nucleation. It appears unlikely that a molecule should form at some distance from the loop dislocation core rather than at the core, since the precursor H centre is probably stabilised initially at the core, and the probability of two H centres interacting at room temperature at other than a stabilising site is negligible, provided suitable stabilising sites are available. This may be seen from consideration of the irradiation rates employed for H centre production and the diffusion rate of the H centre at room temperature. The highest irradiation rates employed (viz. high dose rates in the electron microscope) are $\sim 10^{24}$ eV cm⁻³ sec⁻¹, which in the most efficient alkali halides correspond to creation of $\sim 5 \times 10^{20}$ H[•] cm⁻³ sec⁻¹. A typical athermal aggregation radius is ~ 10 lattice sites, and if the distance the H centre migrates before joining a cluster is $\sim$ the cluster spacing (~ 500 nm; this assumes that clusters are effective strain-relieving

sinks), the available aggregation volume per interstitial is $\sim 10^{-17}$ cm³. With an activation energy for motion ~ 0.1 eV, and assuming a jump frequency $\nu \sim 10^{13}$ sec⁻¹, the H centre reaches a cluster in $\sim 10^{-8}$ sec, and the probability of creating another H centre in this volume during this time is $\sim 5 \times 10^{-5}$. We therefore conclude that if existing clusters are effective stabilising sites for subsequent interstitial production, most molecular production should occur very near the dislocation core surrounding the cluster.

A possible explanation for the nucleation is that the precipitated halogen molecule is actually unstable at the core, i.e. the quantum mechanical stabilisation envisaged in fig. 5.40f or fig. 5.41b is not sufficient to stabilise this molecular orientation, and the more stable arrangement of fig. 5.40h is somehow achieved. A mechanism can be envisaged in which, near a dislocation core, the molecule can transport itself in crowdion fashion as a $|X_3^-|$ molecular ion along $\langle 110 \rangle$ just above the slip plane, accompanied at each stage by adjacent action motion in the opposite direction. The molecule stabilises as an $|H_V^+|$ centre by eventually relaxing into the resulting cation vacancy at some distance from the dislocation, leaving behind an extra anion and cation at the core. This sequence is illustrated in fig. 5.45; the process would be expected to occur randomly on either side of the dislocation.

5.7.6 High temperature molecular aggregation

The result that massive ITC activity is observed in annealing above 250 K and that no ITC spectrum is produced by irradiation above 350 K suggest that on the molecule-divacancy model the centre is mobile at these temperatures, diffusing probably by cation vacancy motion. If the molecule is predominantly bound to the anion vacancy side of the divacancy, mobility of the centre might be little different from straightforward cation vacancy mobility, which has an activation energy typically $\sim 0.6-0.7$ eV. If sufficient numbers of these centres aggregate, the result is a halogen gas-filled void; furthermore, once the void becomes large enough that the halogen molecules are no longer firmly bound to the lattice, the void becomes a high pressure halogen gas bubble and would be expected to produce an outward strain, as observed for the large spherical clusters in KCl, §5.3.3. It was indicated there that formation of these clusters correlates with onset of vacancy mobility and also involves a large number of defect sites.

Knutson, Hooper and Bray (1966) claim to have detected NMR spectra from bulk molecular $^{19}\text{F}_2$ in cavities produced by neutron irradiation of LiF, indicating that 1-2% of all fluorine in the sample is ultimately trapped. This result is consistent with the large number of sites involved in the spherical clusters observed in §5.3.3, viz. $\sim 3 \times 10^{20} \text{ cm}^{-3} = 2\%$. If this amount of halogen is indeed being stabilised externally to the lattice (but

inside the crystal), there must be a considerable overabundance of alkali metal, which may well precipitate to form the colloidal alkali apparently detected by other means (see §2.6.5.2; ^7Li metal was also detected along with $^{19}\text{F}_2$ in the NMR measurements of Kuntson, Hooper and Bray 1966). This may be seen as follows. The production of the halogen molecule (formed from two H centres) requires initial creation of two F centres. The induced crowdion mechanism, §5.7.5, produces (essentially) an anion interstitial and a cation interstitial. If the molecule then occupies the resulting divacancy, and these aggregate to form gas-filled voids, we are left with two F centres, an anion interstitial and a cation interstitial (the latter are available for annihilation, however, only at the dislocation loop core). Subsequent annealing will produce a cation interstitial, an F centre and an electron; ultimately, aggregation of each species (cation interstitial + electron; F centre) leads to formation of alkali metal collids. Nucleation may well take place at the interstitial dislocation loops (possibly free from their molecule-divacancy atmospheres) which would explain their disappearance during anneal when F centres annihilating at the loop produce alkali atoms.

The expected strain ϵ induced by a spherical cluster of halogen molecule-divacancy defects may be calculated by the inhomogeneous inclusion treatment of §5.3.3.4. In this case the transformation strain v^* may be derived from the difference in volume per molecule provided by the cation-anion vacancy and that required for a molecule in a molecular fluid, given the density of the fluid. The molecular

fluid was presumed to be liquid, since it is shown below that sufficient pressure exists to compress the halogen molecules to a liquid state (only fluorine gas is above its critical temperature at room temperature). Accordingly, compressibilities (or bulk moduli) and densities for the liquefied gases were utilised. Data for the former exist only for Cl_2 and Br_2 , and then only at low pressure (< 300 atm), although B^* for most liquefied gases is $\sim 10^{10}$ dynes cm^{-2} , and this was used arbitrarily for F_2 and I_2 .

Table 5.3 lists the calculated results for ϵ , assuming these values. It is readily apparent that (because of the high compressibilities of the halogen liquids) agreement between the strain predicted for such inclusions and the measured strain (§5.3.3.2) is scarcely better than for alkali colloids (Table 5.3), and actually worse for KCl. However, it should be recognised that the bulk moduli B^* of the halogen liquids begin to increase with increasing pressure for sufficiently high pressures, and $\epsilon \propto B^*$ until $B^* \sim Y$, after which a limiting value $\epsilon \sim 0.2-0.3 \nu^*$ is reached. The hydrostatic pressure inside the inclusion is given via (5.3) by

$$\begin{aligned} P &= (\alpha-1) \nu B &&) \\ &= 3B\epsilon (1-\alpha)/\alpha &&) \quad (5.40) \end{aligned}$$

For Cl_2 in KCl, assuming the value of ϵ calculated in Table 5.8 using B^* for the liquid at zero pressure, we have

$$P = 1700 \text{ atmospheres.}$$

It is highly unlikely that the value of B^* measured at zero pressure

would obtain at such high pressures, and a much larger value of B^* is expected. Accordingly, considerably larger values of ϵ are expected than listed in Table 5.3, approaching more closely to the measured values.

This mechanism for formation of voids under high pressure may well explain the large internal cavities universally observed by electron microscopy (e.g. Ilibi and Yada 1960) and even by optical microscopy (e.g. Whapham and Makin 1960) in very heavily irradiated alkali halides. Also, the large ($\sim 1 \mu\text{m}$) apparently edge-on lenticular defects observed lying along $\langle 100 \rangle$ after heavy electron or oxygen ion bombardment in the electron microscope (Carroll and Birnbaum 1965; Russell, Martin and Bowen 1970 who attributed these to Li or Li_2O precipitates) may well be internal cleavage cracks nucleated by the high pressure of occluded halogen gas. Significantly, Russell et al., although detecting Li and Li_2O in their diffraction patterns, found no difference between selected area diffraction patterns from those regions containing the defects and those not; it is probable that halogen desorption from the foil surfaces was responsible for their Li and Li_2O (from residual microscope O_2) production.

5.8 Suggestions for Further Work

Since few previous electron microscopical studies of alkali halides have achieved the sort of success enjoyed by the present study, there are clearly large numbers of electron microscopical experiments now made possible which should be attempted. For example, the low temperature techniques described have already enabled unimpeded investigation of the deformation and work hardening behaviour of alkali halide crystals on a microscopical scale hitherto unavailable. Important segregation or precipitation processes can likewise be followed from the earliest stages in heavily doped or mixed alkali halides. We feel, however, that the greatest impact on alkali halide studies will continue to be in the field of radiation damage and colour centre defects, and we shall confine our remarks here to a number of further critical experiments, similar to those already described in §§5.3, 5.4 and 5.5, which should be attempted to elicit the maximum microscopical information about the character and stability of radiation-induced defect aggregations.

5.8.1 Primary interstitial clusters

The primary problem here is the precise model for interstitial stabilisation, the crucial information being the strength of the displacement vector and the apparent absence of fault contrast in interstitial loop clusters. A distinction between the molecular precipitate and the induced crowdion models relies on the precision

of this information. A study similar to that performed in KI should be attempted in KBr, the only other alkali halide studied so far to exhibit large round interstitial loops, in order to ascertain with certainty that no fault contrast arises for interstitial loops in this structure. Other alkali halides having similar cluster morphology should also be found; RbI is a probable candidate. An attempt should be made to correlate probable molecular displacement on the precipitate model with cluster growth morphology in a large number of alkali halides in an attempt to discover the driving force for the transition between narrow and round clusters and to obtain additional evidence on which to base a growth model which accounts for these morphological differences. For example, a careful study of the transition between elongated growth and circular growth modes might reveal evidence supporting a precipitate model in initial stages of growth and dislocation breakaway (i.e. induced crowdion motion) in the later stages.

Next, further evidence should be sought regarding the interaction of dislocations and defect clusters in several alkali halides with different cluster morphology in an attempt to determine more exactly the magnitude of the principal loop displacement vector and the nature of the loop. Further systematic dislocation climb experiments should be performed to obtain more information about this important mechanism and to search for evidence of debris left behind in climb.

Finally, electron microscopical examination should be made

in crystals externally irradiated and annealed above room temperature to investigate the stability of primary interstitial clusters under non-irradiating conditions. At the same time, certain crucial spectroscopic experiments should also be initiated to search for the evidence of the halogen induced divacancy $|H_V^+|$, e.g. the cation vacancy + trapped hole centre (called the V_F centre by Känzig 1960) resulting from recombination of $|H_V^+|$ with F centres. Optical bleaching after external room temperature irradiation followed by short x-irradiation at low temperatures should produce this classic antimorphic species which should be detectable by EPR. Similarly, short low temperature irradiation following extensive room temperature irradiation should produce $|H_V|$ centres which have a known optical absorption somewhat removed from the V bands. Further ionic thermal current experiments might be conducted in materials other than KCl, particularly in a material exhibiting a different cluster morphology (e.g. KI).

5.8.2 Vacancy related clusters

The basic question here is whether the spherical clusters observed in KCl, LiF (and NaCl at elevated temperatures) represent colloidal alkali metal or the high pressure halogen bubbles suggested by the halogen molecule-divacancy model for interstitial stabilisation. Further measurements should be made on symmetrical clusters occurring in as many alkali halides as possible to

ascertain with which model the magnitude and direction of the measured strain are in every case consistent. For example, in NaCl an outward strain is expected on the halogen (liquid) inclusion model, whereas an inward strain is predicted for Na colloid formation. In addition, further electron microscopical examination should be made of crystals externally treated to induce the colloid characteristics evidenced by other techniques. In particular, it must be ascertained if large spherically symmetrical cluster formation is a thin foil anomaly. Besides the obvious externally irradiated crystals, crystals additively coloured with halogen gas and slowly cooled might also be examined to ascertain if occlusion of molecular halogen results in similar spherical clusters (or even planar loops).

5.8.3 Irradiation hardening

The basic question here is whether the large interstitial clusters observable by electron microscopy are alone responsible for irradiation hardening in irradiated alkali halide crystals, or whether single interstitials or small submicroscopical aggregates are contributing the largest portion of the flow stress increase. Preliminary experiments indicate that, as expected on the model introduced in §5.6.2.2, KI crystals with large round planar interstitial clusters are much less severely hardened by irradiation than crystals such as KCl, LiF, or NaCl with more nearly linear interstitial clusters. This suggests that the clusters, indeed, are primarily responsible for the observed hardening, and it also

suggests that few isolated interstitials are left in the lattice during room temperature irradiation, i.e. the large clusters account for all interstitial damage production. It would be helpful to sort out definitely the alkali halide hardening behaviour into two groups, one characteristic of alkali halides exhibiting round planar clusters and another characteristic of alkali halides exhibiting elongated clusters. Therefore, as large a range of irradiated alkali halides as possible should be tested and examined.

Deformation at temperatures below room temperature would be helpful in determining the temperature dependence of the hardening behaviour. This information should be able to sort out hardening due to small obstacles, such as single interstitials or small interstitial aggregates (or even small unobservable alkali colloids) and the much larger observable interstitial clusters. Finally, a detailed microscopical examination of the interaction of dislocations and the observable interstitial clusters should be made in several alkali halides to ascertain the probable strength of the obstacles, the mechanism of interaction, and the detailed distribution of dislocations in irradiated crystals compared with unirradiated material.

Table 5.1

Transition from Planar Loop to Spherical Cluster and Related
Behaviour

NaCl	KCl	KBr	KI	LiF
$1473^i(673^i)$	$1373^i(623^i)$			
$2573^i(673^i)$	$2423^i(573^i)$			
	$3553^a(623^a)$	$3423^a(523^a)$	3433^a	3373^i
$4473^a(623^a)$	$4423^a(573^a)$			
5473^a				
6573^i663^a				
				7473^i
				8473^i573^a

ⁱ by irradiation at temperature indicated, K

^a by anneal to temperature indicated, K

() temperature, K at which indication anneals out

¹This study (1967): thin foil electron microscopy ²Izumi (1969): thin foil electron microscopy ³Jain and Sootha (1968): colloid band
⁴Westervelt (1953): anneal of irradiation induced hardness ⁵Aerts, Amelinckx and Dekeyser (1959): anneal of irradiation induced hardness
⁶Yoshida and Ikeda (1957, 1958): colloid band ⁷Durand, Farge and Lambert (1969): small angle x-ray scattering of electron irradiated crystals
⁸Guinier and Lambert (1966): small angle x-ray scattering of neutron-irradiated crystals

Table 5.2

Analysis of R for Edge-On Planar Loops in KCl

(values in $\text{\AA}$ units)

data, this study (1967)

data, Izumi (1969)

2.34

2.64

2.48

2.80

2.16

1.98

2.64

2.18

average 2.40

average 2.40

Table 5.3

Analysis of Spherical Cluster Strain

<u>Data, KCl</u>	<u>Average Cluster Radius, nm</u>	<u>Measured Strain</u>	
		<u>ϵ,</u>	<u>%</u>
This study (1967)	52	+5.5	
Izumi (1969)	37	+6.3	
Kawamata and Hibi (1965)	115	+7.0	

Alkali Metal Colloidsexpected strain ϵ , %†

	<u>K in KCl</u>	<u>Na in NaCl</u>	<u>Li in LiF</u>
f.c.c.	+0.47	-1.7	+3.4
b.c.c.	+0.76	-1.3	+4.8
molten	+1.03	-0.61	+7.7

Halogen Liquid Inclusionsexpected strain ϵ , % *

<u>Cl₂ in KCl</u>	<u>Cl₂ in NaCl</u>	<u>F₂ in LiF</u>
0.30	0.82	1.2

† based on available compressibility data for b.c.c. metallic phase

* based on available compressibility data for halogen liquid below 300 atm.

Table 5.4
Energy Loss Data

<u>Investigator</u>	<u>Alkali halide</u>	<u>Energy Loss Peaks (eV)</u>		<u>F band (eV)</u>
Pradal and Gout (1964)	NaF	5.7	3.7	3.6
Creuzberg (1966)	NaBr	5.7	2.2	2.3
Creuzberg (1966)	NaI	5.7	2.1	2.1
Creuzberg (1966)	KF	3.8	2.3	2.7
Creuzberg (1966)	KI	3.7	~1.8	1.8
Creuzberg (1966)	RbF	3.5	2.1	2.4
this study (1971)	KCl	3.5	-	2.2

Table 5.5

Comparison of Low Temperature F centre Production Rate $\{\partial F/\partial E\}_0$
and Observable Damage Onset

	$\{\partial F/\partial E\}_0^\dagger$ (FeV^{-1})		Observa- tion time at 10 K (sec)	Time advantage over KCl at 10K	Expected advantage
	300 K	4 K			
KCl	5.5×10^{-4}	4.5×10^{-4}	20	1	1
NaCl	3.7×10^{-4}	6.3×10^{-6}	40	2	72
KI	1.3×10^{-4}	1.4×10^{-7}	60	3	3200
NaBr	5.4×10^{-6}	2.7×10^{-7}	>120	>6	1670
		$(2.1 \times 10^{-8} \text{ at } 77 \text{ K})$			

[†] data Hughes et al. (1967)

Table 5.6

Expected Displacement from Halogen Interstitial Precipitates in

Potassium Halides

X	r_{X^-}	r_{X^0}	$r_{X^{-\frac{1}{2}}}$	a_{KX}	Δ_H	Δ_{X_2}
Cl	1.66	0.99	1.34	6.30	-0.05	+0.64
Br	1.80	1.15	1.47	6.60	-0.20	+0.76
I	2.02	1.33	1.68	7.06	+0.15	+0.87

r_{X^-} from Fumi and Tosi (1964)

r_{X^0} assumed to be one half the bond length in the X_2 molecule

$r_{X^{-\frac{1}{2}}}$ assumed to be $\frac{1}{2} \{r_{X^-} + r_{X^0}\}$

$$\Delta_H = \frac{4r_{X^{-\frac{1}{2}}} + 2r_{X^-} - \sqrt{2} a}{a/\sqrt{2}}$$

$$\Delta_{X_2} = \frac{4r_{X^0} + 2r_{X^-} - a/\sqrt{2}}{a/\sqrt{2}}$$

Ionic radii and lattice parameters given in Angstrom units.

Table 5.7

Principal Elastic Dipole Interactions for a Planar X_2 Molecular Precipitate

The precipitate is assumed to lie near (001) with displacement vector $\underline{R}$ along $|101|$. The elastic dipole interaction is assumed to be of the form $E = \frac{A}{r^3} \{15 \ell^4 - 6\ell^2 - 1 + 4\nu (1 - 3\ell^2)\}$

Type of Growth	Number	ℓ	Principal Interactions	r	(units of A/a^3)	Principal Interaction Energy (eV, assuming $A/a^3 = 0.2$ eV)
1. Along $ 100 $, planar	2	$\frac{1}{2}$		$a/\sqrt{2}$	-8.1	-0.58
	1	$1/\sqrt{2}$		a		
2. Along $ 100 $, loop normal tilting towards $\underline{R}$	2	$\frac{1}{2}$		$a/\sqrt{2}$	-7.4	-0.53
	1	0		$a/\sqrt{2}$		
3. Along $ 100 $, loop normal tilting away from $\underline{R}$	2	$\frac{1}{2}$		$a/\sqrt{2}$	+9.6	+0.70
	1	1		$a/\sqrt{2}$		
4. Along $ 010 $, planar	2	$\frac{1}{2}$		$a/\sqrt{2}$	-7.4	-0.53
	1	0		a		
5. Along $ 010 $, tilted	1	$\frac{1}{2}$		$a/\sqrt{2}$	-2.8	-0.20
	1	$\sqrt{3}/6$		$\sqrt{5} a/2$		
	1	$\sqrt{3}/2$		$\sqrt{5} a/2$		

Fig. 5.1. (001) KCl foil irradiated and observed in the microscope at room temperature, showing elongated loop and other defects.

(a) First micrograph, 8 sec, $j = 6 \text{ mA cm}^{-2}$. Defects A, A', B, C(B'), D and E are discussed in §5.3.1.1.

(b) Second micrograph of area as in (a), $j = 12 \text{ mA cm}^{-2}$, illustrating growth of defects and dose rate dependence of defect growth.

(c) Very thin foil region, showing predominance of defects C(B'), imaged in strong diffraction contrast, g perpendicular to projected defect axis.

(d) Defects C(B') as in (c) imaged in residual contrast conditions, g parallel to projected defect axis.

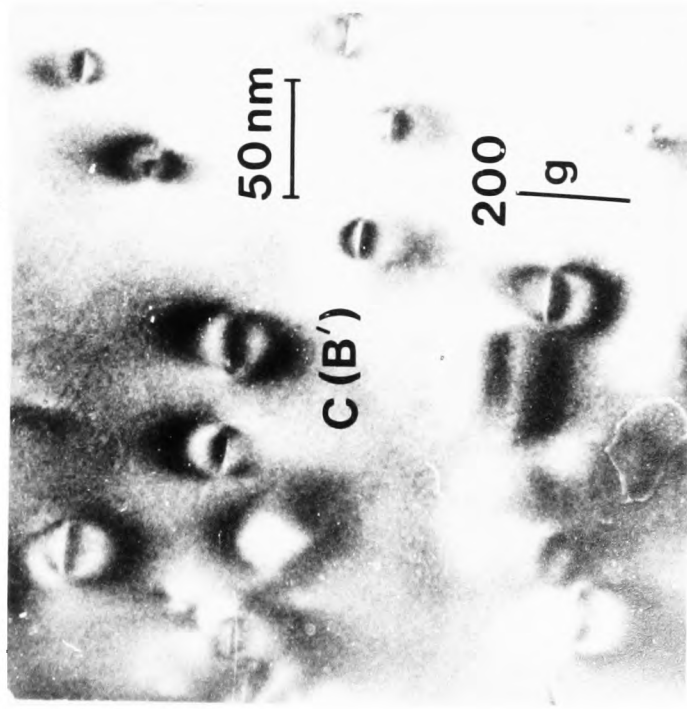


a



b

$s = 0$



d



Fig. 5.2. Schematic illustration of the equivalent orientations of narrow loop defects found in irradiated KCl. It is suspected that for thin foil in situ irradiations, defects C do not nucleate, and what appear to be end-on loops are actually small edge-on loops of type B.

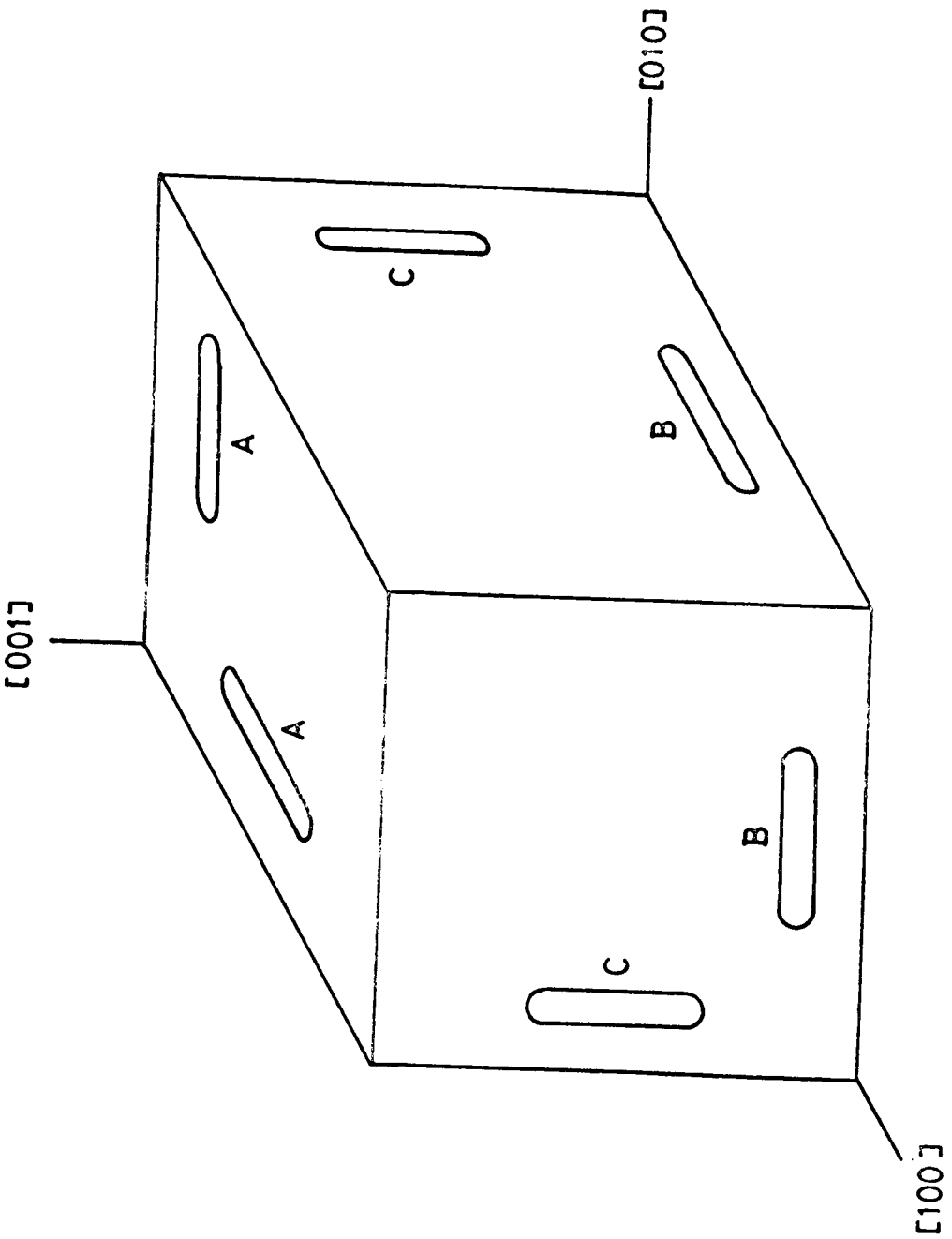
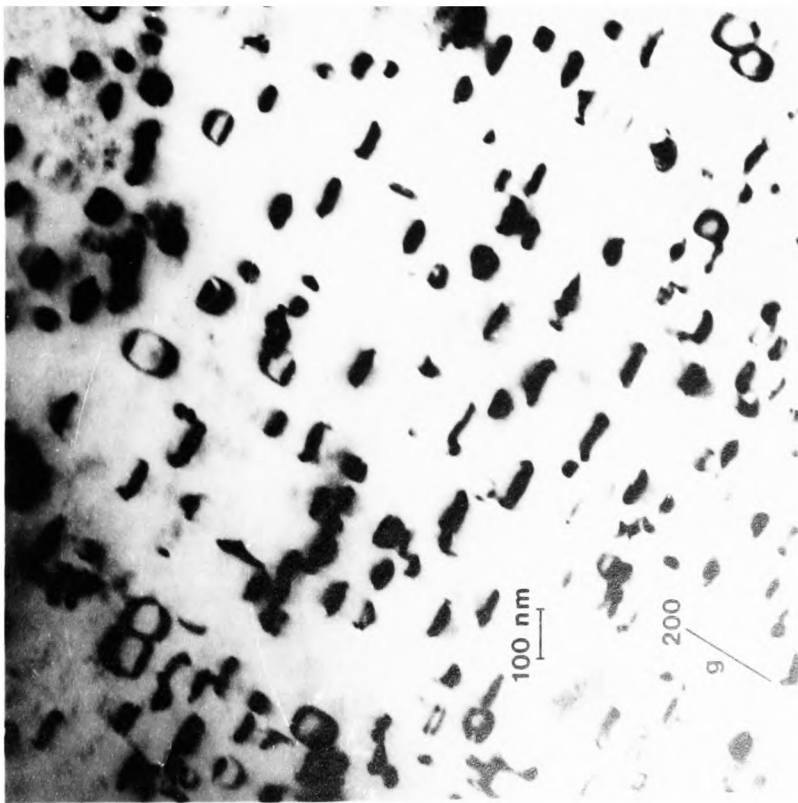


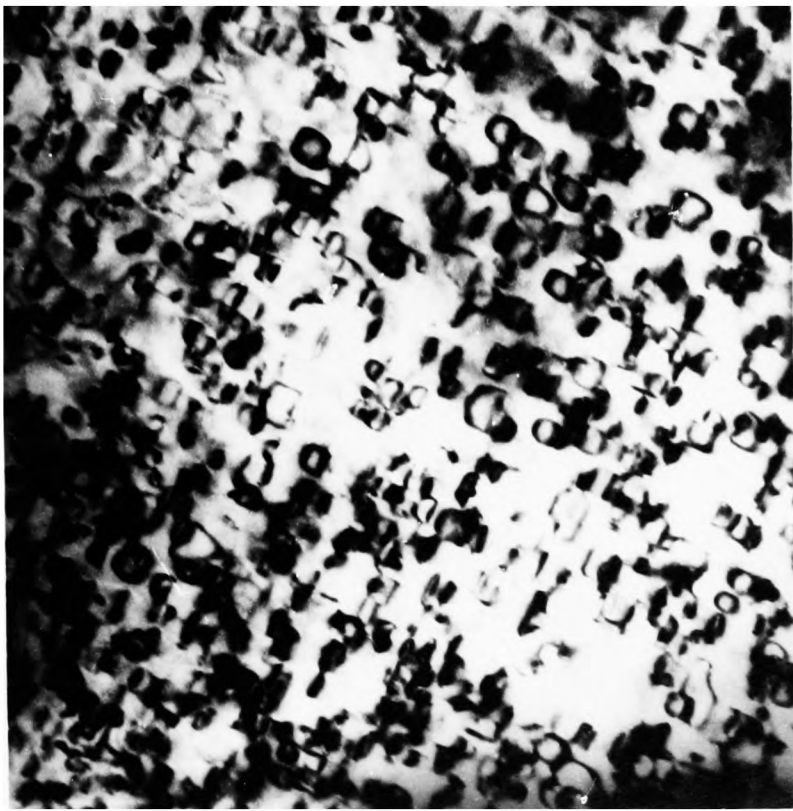
Fig. 5.3. (001) KBr foil irradiated and observed in the microscope at room temperature.

(a) $j = 5 \text{ mA cm}^{-2}$. Note that many of the defects extend along $\langle 100 \rangle$ and do not open out into large loops.

(b) $j = 10 \text{ mA cm}^{-2}$. Most defects have now opened out into square loops with sides along $\langle 100 \rangle$.



A

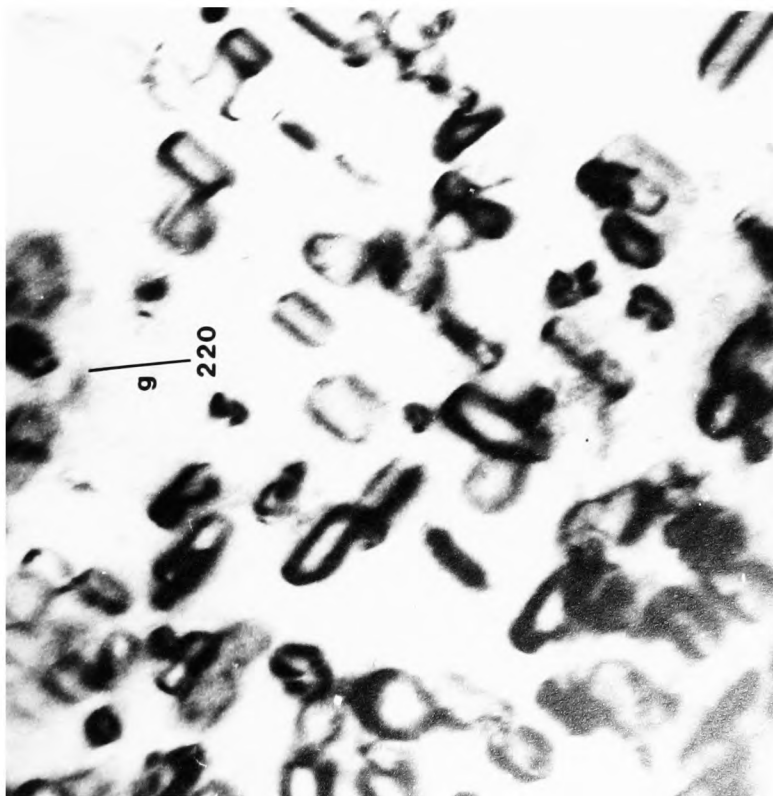


B

Fig. 5.4. (001) KI foil irradiated and observed in the microscope at room temperature.

(a) First 8 sec, $j = 5 \text{ mA cm}^{-2}$. Loops initially elongate along $\langle 100 \rangle$ within the first $\frac{1}{2}$ sec of irradiation, then slowly broaden with continued irradiation.

(b) Second 8 sec, $j = 5 \text{ mA cm}^{-2}$, same foil region as in (a). Loops have grown by broadening laterally, and some loops have intersected to form larger loops.



A



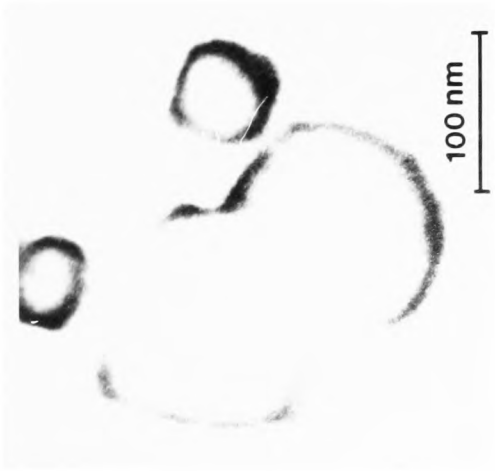
B

Fig. 5.5. Loop intersections in an (001) KI foil irradiated in the microscope at room temperature and observed at 10 K.

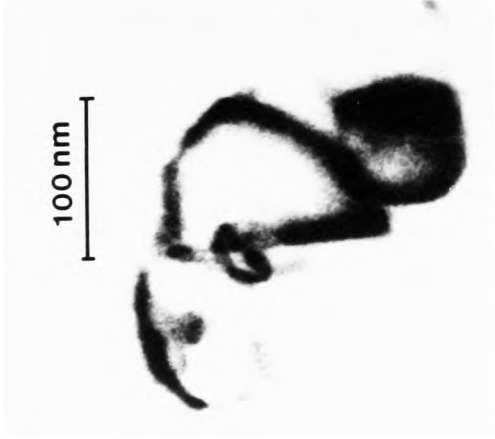
(a) Intersection of two loops of the same character and displacement vector.

(b) Interaction of two loops of the same character and opposing displacement vectors.

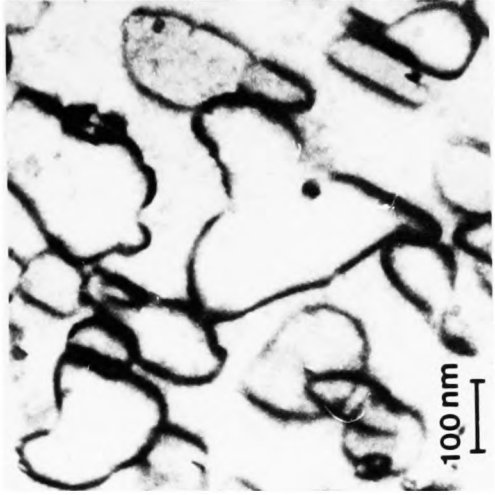
(c) Large irregular loop formed by repeated loop interactions of type (a) and (b).



A



B

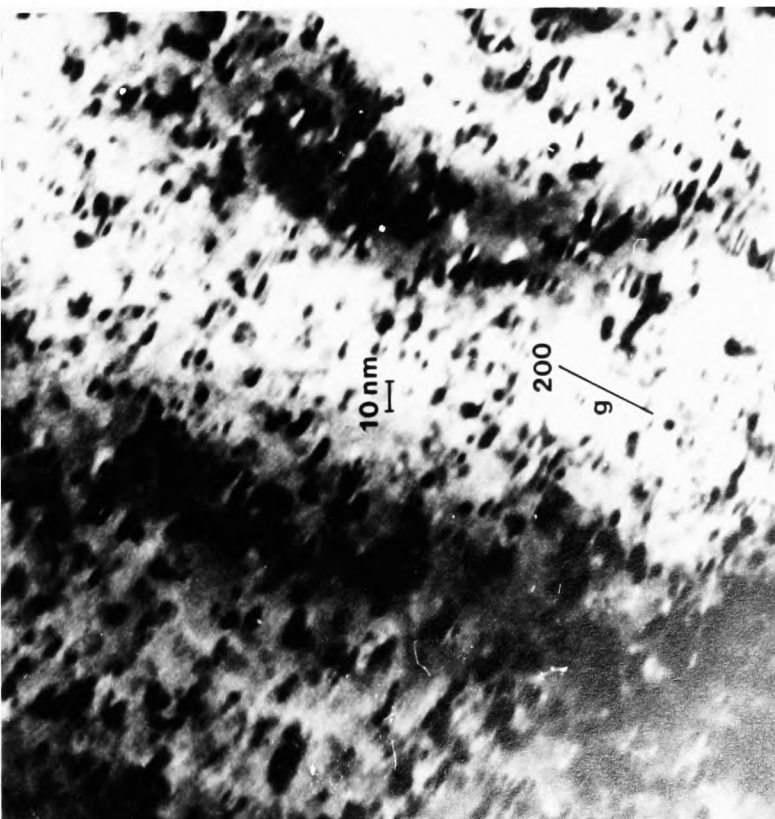


C

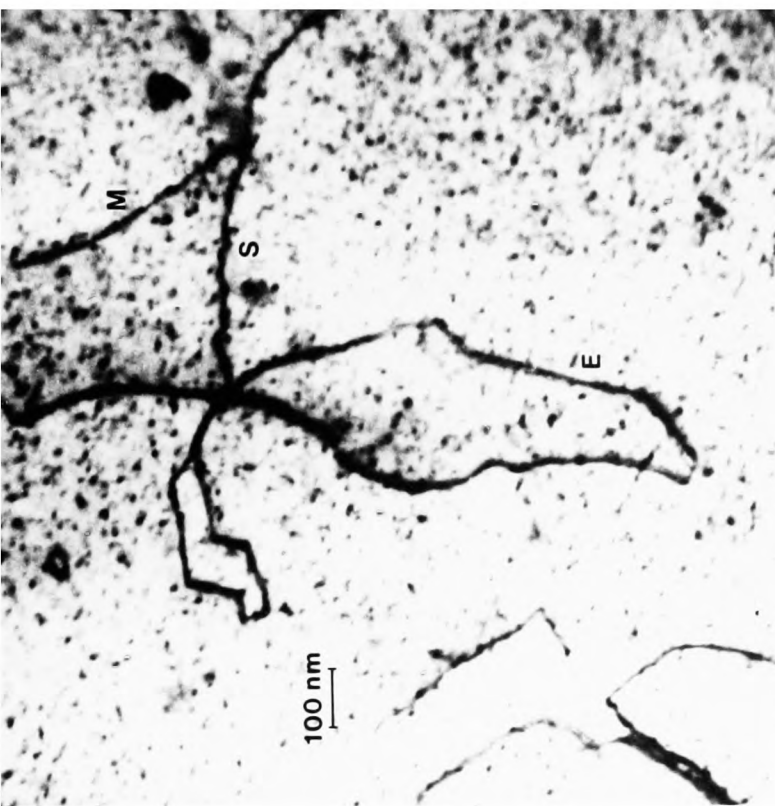
Fig. 5.6. (001) NaBr foil irradiated and observed in the microscope at room temperature, $j = 10 \text{ mA cm}^{-2}$.

(a) Small loop clusters elongate along $\langle 100 \rangle$ as in KCl, KBr and KI, but remain an order of magnitude smaller. Their formation is also considerably slower. Note that for $g = 200$ no defects are imaged with long axis parallel to $\langle 100 \rangle$ in common with the larger loops of other alkali halides.

(b) Dislocations introduced prior to irradiation (by compression of bulk crystal) surviving radiation damage at room temperature. Helical climb of dislocations in pure screw (S) or mixed orientations (M) can be just discerned.



A



B

Fig. 5.7. Continuous irradiation of an (001) KI foil in the microscope at room temperature, illustrating dose rate dependence of cluster growth and size.

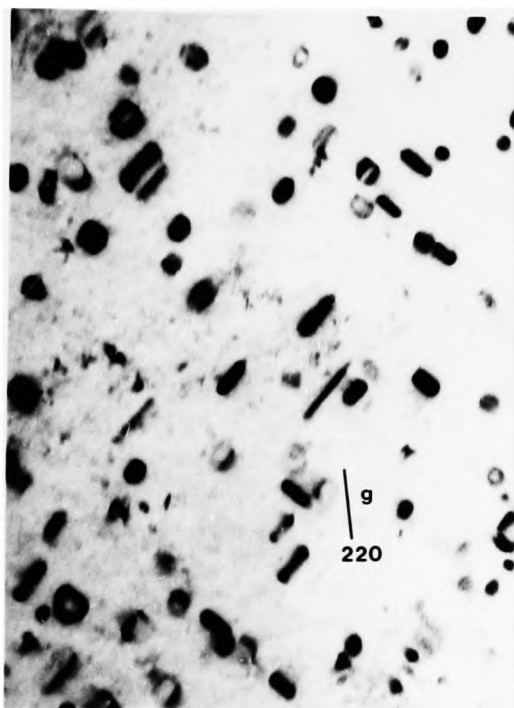
(a) After 10 sec, $j = 6 \text{ mA cm}^{-2}$. Initial nucleation and growth of defects to equilibrium cluster size takes place within first $\frac{1}{2}$ sec of irradiation.

(b) After 20 sec, $j = 6 \text{ mA cm}^{-2}$. Equilibrium cluster size is maintained, with small growth and shrinkage both present.

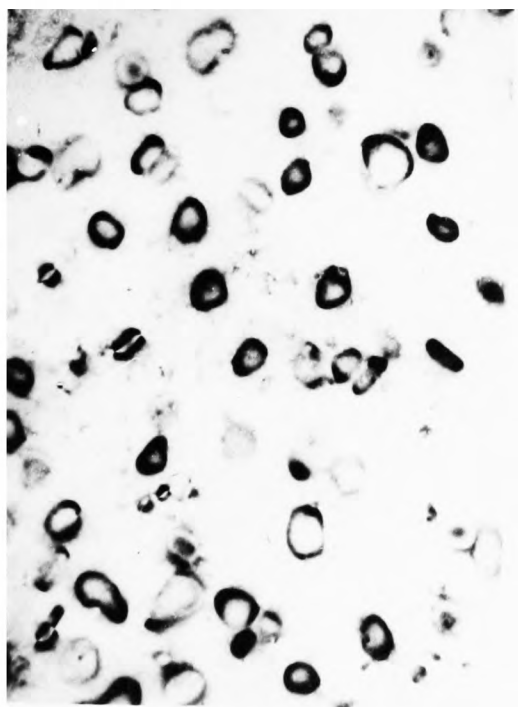
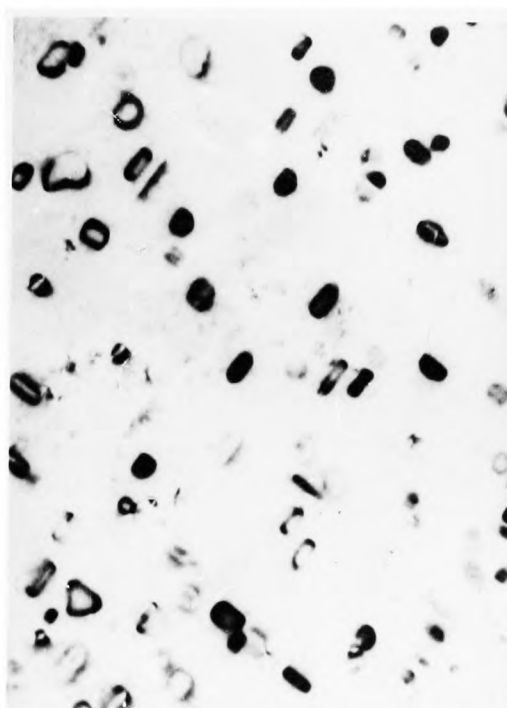
(c) After 30 sec, $j = 6 \text{ mA cm}^{-2}$, illustrating continued maintenance of an equilibrium cluster size.

(d) Immediately after doubling irradiating current density to $j = 12 \text{ mA cm}^{-2}$, showing that a larger equilibrium cluster size is established.

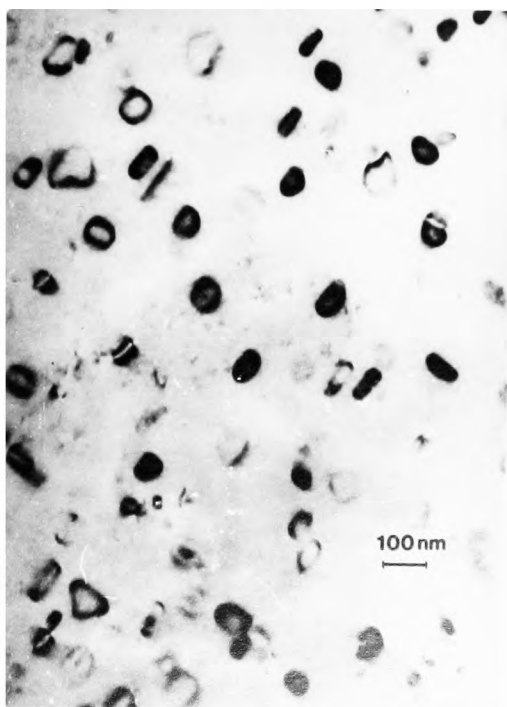
A



B



D



C

Fig. 5.8. Post-saturation behaviour in three alkali halides irradiated in the microscope at room temperature.

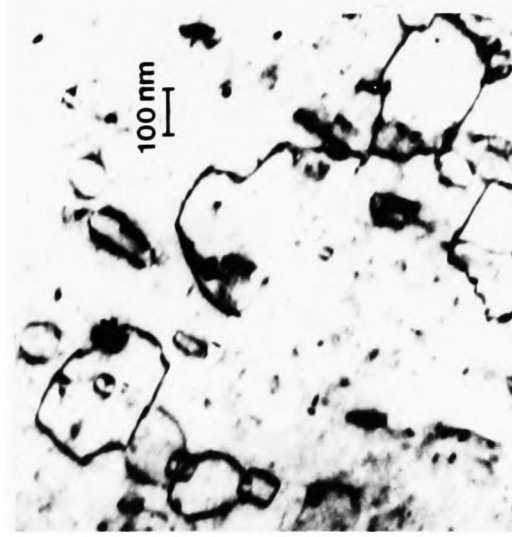
(a) Confused strain field contrast in an (001) NaCl foil resulting from a high projected cluster density in thicker foil regions.

(b) Large irregular loops in an (001) KI foil after prolonged irradiation at 10 mA cm^{-2} , some of which have intersected the surface.

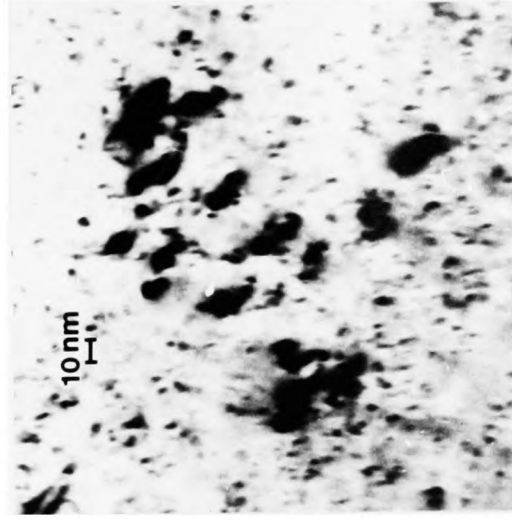
(c) Large clusters in an (001) NaBr foil after prolonged irradiation at 50 mA cm^{-2} , exhibiting elongated axes along $\langle 110 \rangle$.



A



B



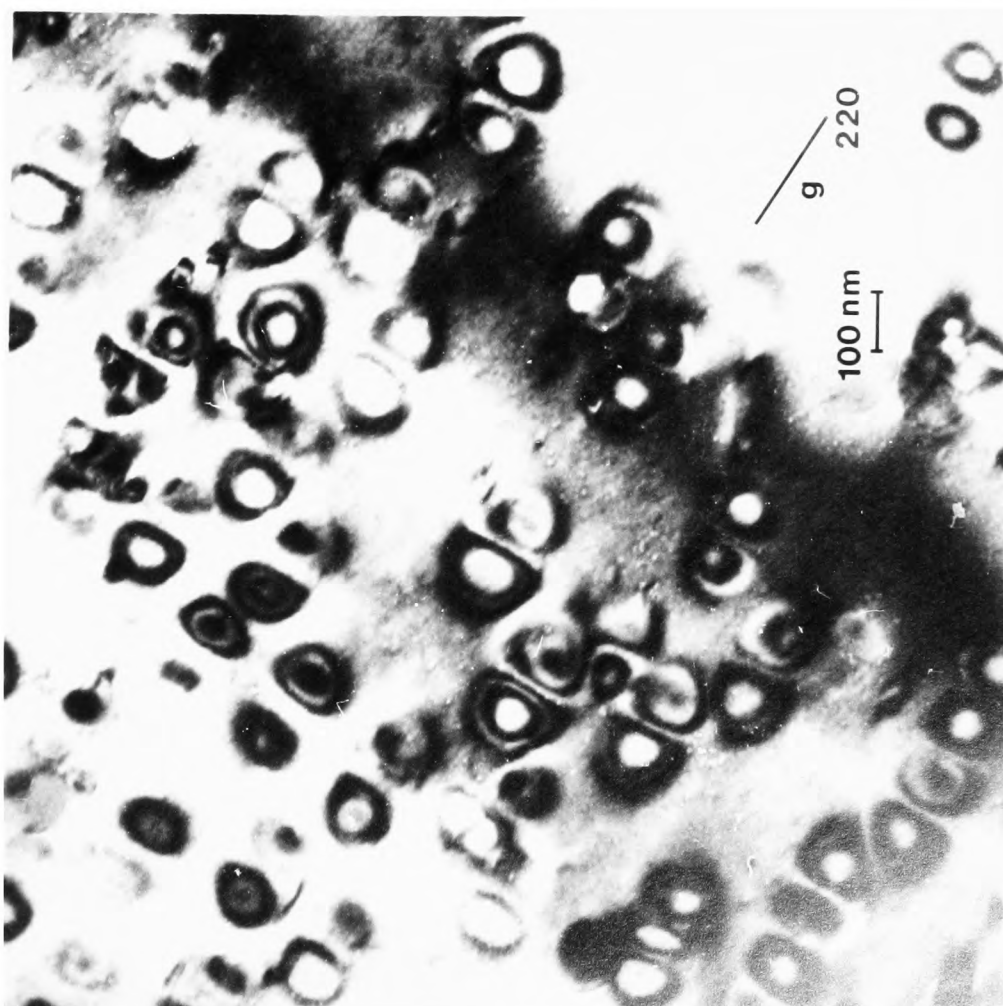
C

Fig. 5.9. Development of spherical clusters during irradiation in the microscope.

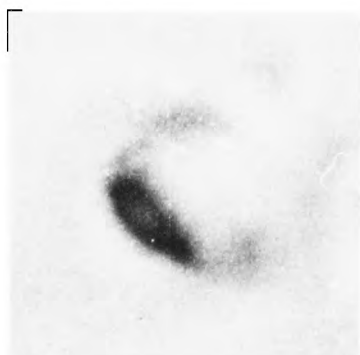
(a) Large spherical clusters in an (001) KCl foil after prolonged room temperature irradiation at $j = 20 \text{ mA cm}^{-2}$. Elongated clusters disappear and are replaced by a cluster having spherically symmetric strain field. The clusters illustrated have a diameter $\sim 100 \text{ nm}$ and density $\sim 4 \times 10^{13} \text{ cm}^{-3}$, and are shown in §5.3.3.2 to exhibit an outward strain $\sim 5\%$.

(b) Large dislocation ring in a thin region of an irradiated (001) KCl foil, shown to be the precursor of large spherical clusters illustrated in (a). The strain field is radially symmetric about the $[001]$ foil normal.

(c) Large spherical clusters forming in an (001) NaCl foil during irradiation at 473 K. These do not form at room temperature.



A



B



C

Fig. 5.10.

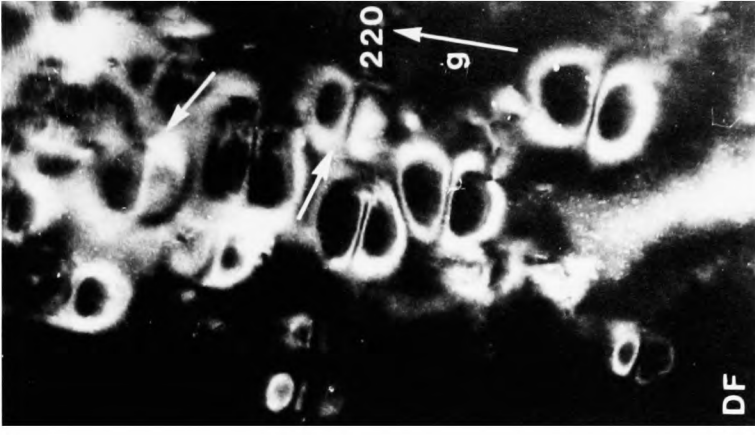
Determination of the sign of the lattice strain field surrounding spherical clusters in KCl.

(a) Bright field micrograph of large spherical clusters in an (001) KCl foil. Anomalous images due to clusters within $\xi_g/4$ of the foil surfaces are arrowed. Note that in bright field anomalous images can exhibit an intensity maximum on either side of $\underline{g}$, depending upon which surface they are nearest to.

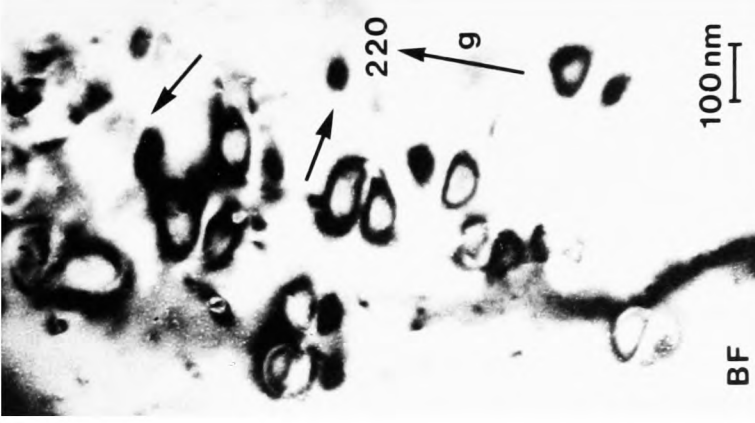
(b) Dark field $s = 0$ micrograph of the clusters in (a), showing that anomalous images exhibit an intensity maximum on the side of negative $\underline{g}$.

(c) Bright field micrograph of small spherical clusters in an (001) KCl foil reproduced from the study of Izumi (1969) showing at least one anomalous image.

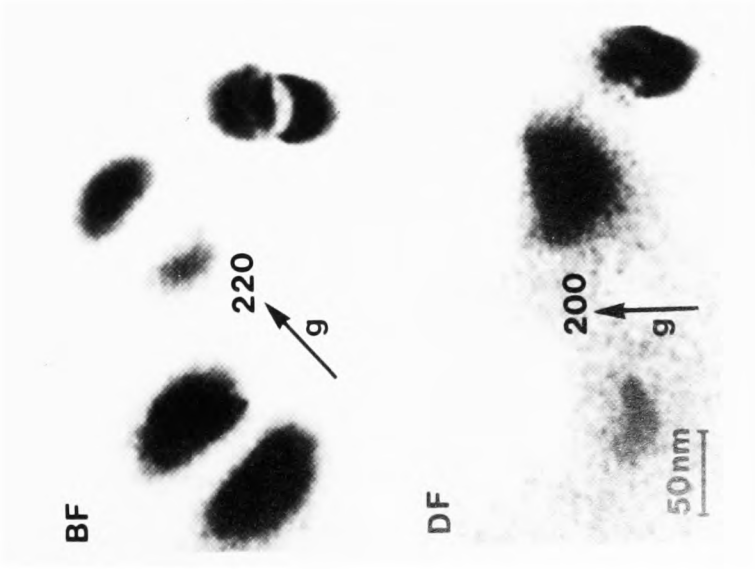
(d) Dark field s near 0 micrograph of the area in (c). Anomalous images exhibit an intensity maximum on the side of positive indicated $\underline{g}$. It is not known whether Izumi allowed for the 180° inversion of the micrograph and diffraction pattern in assigning the sense of $\underline{g}$. This allowance was made in (b).



B



A



C

D

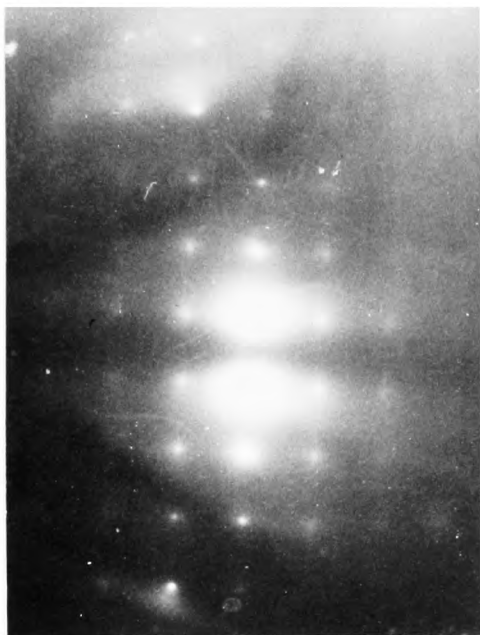
Fig. 5.11. Information deriving from diffraction patterns of alkali halide foils.

(a) Large diffuse scattering component obtaining during room temperature irradiation in an (001) KI foil. This component increases markedly in the first half second of irradiation, and obscures Kikuchi line contrast, making tilting experiments difficult.

(b) Adjacent area of the same KI foil as in (a) during irradiation at 10K showing marked reduction in diffuse scattering, far too much to be accounted for by reduction in phonon scattering. Kikuchi lines are prominent, and precise tilting experiments are easily performed. Streaks of unknown origin occur through $\langle 100 \rangle$ rows of diffraction spots and also midway between them.

(c) Diffraction pattern from neon condensed onto an (001) KI foil, indicating that temperatures below 10K can be attained in alkali halide foils.

A



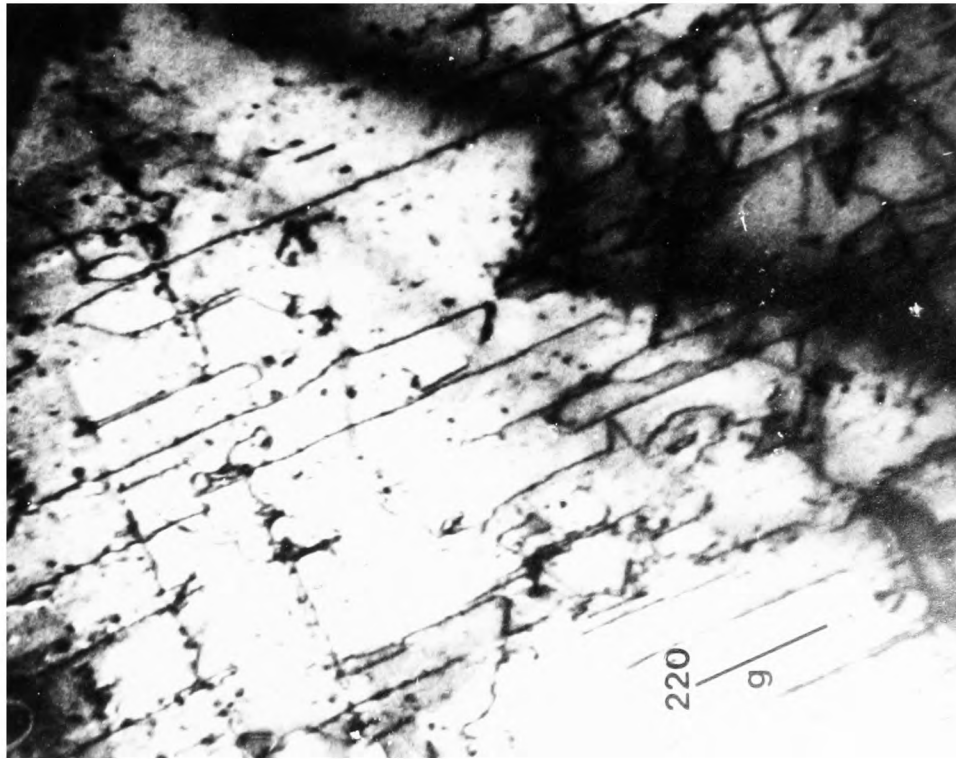
B



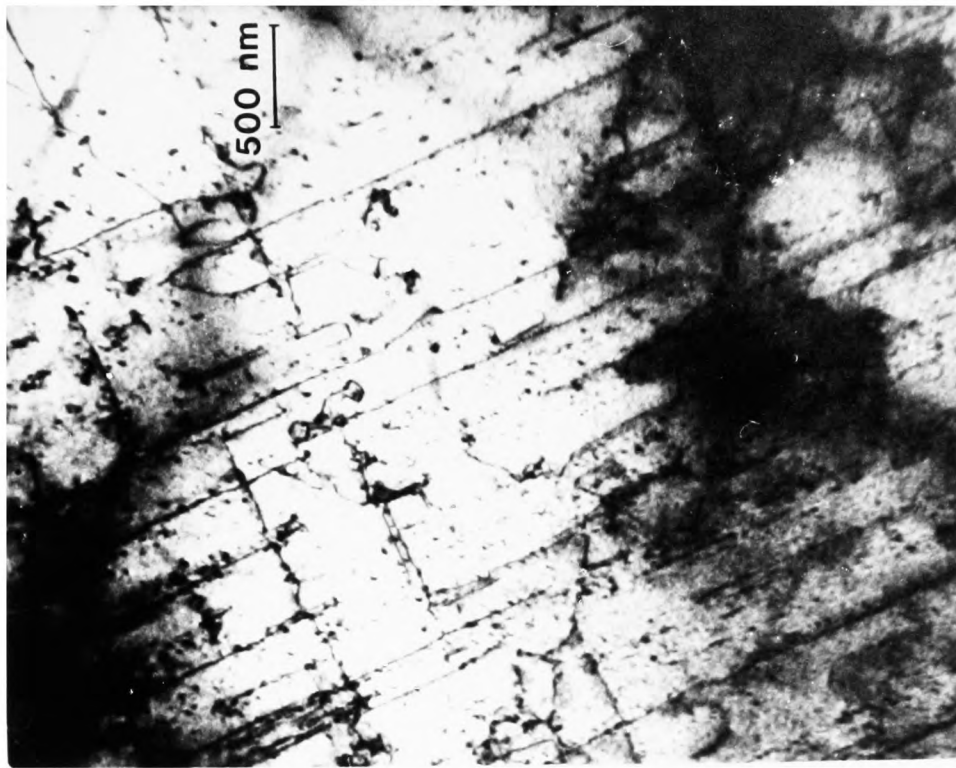
C



Fig. 5.12. Consecutive 10 sec micrographs of an (001) KCl foil thinned from a cleaved section and examined at 10 K with $j = 5 \text{ mA cm}^{-2}$. Dislocation arrays introduced into the foil by cleavage are clearly seen and survive at least 20 sec irradiation before being masked by fine scale low temperature defect clustering.



A

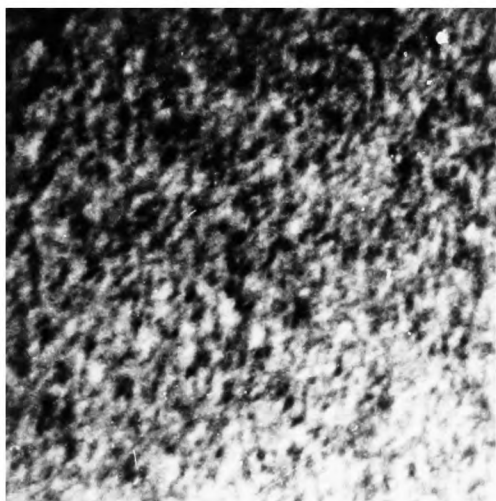


B

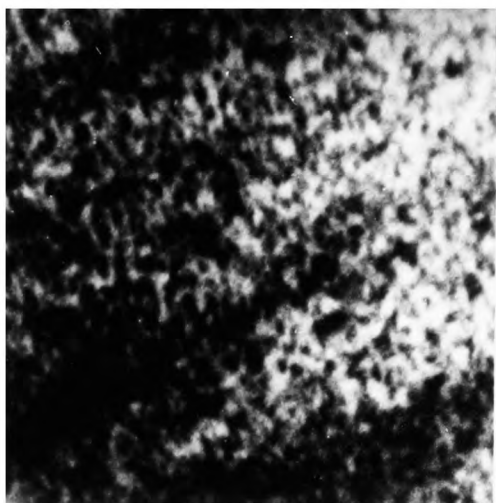
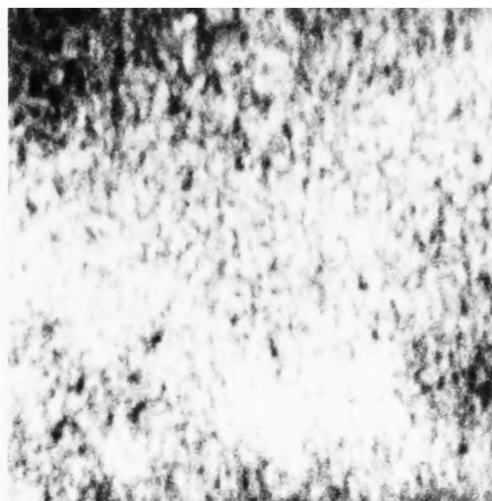
Fig. 5.13. Defect clusters formed in thin foils at 10 K by irradiation in the microscope. Clusters $\sim 5\text{--}10$ nm in size, often exhibiting black/white contrast, are created at densities $\sim 10^{16} \text{ cm}^{-3}$ at defect saturation for irradiation temperatures below the bulk interstitial mobility threshold.

- (a) (001) foil of KCl.
- (b) (101) foil of NaCl.
- (c) (101) foil of KI.
- (d) (101) foil of NaBr.

A
KCl

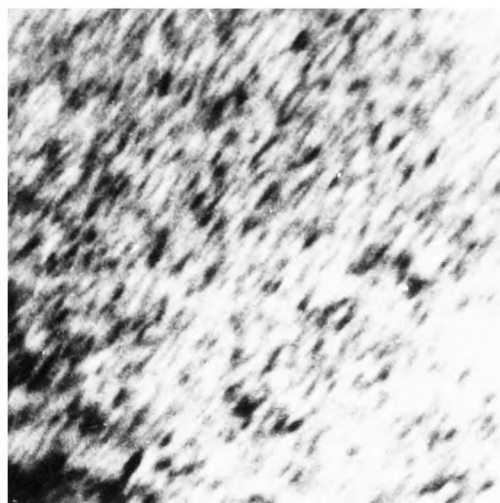


B
NaCl



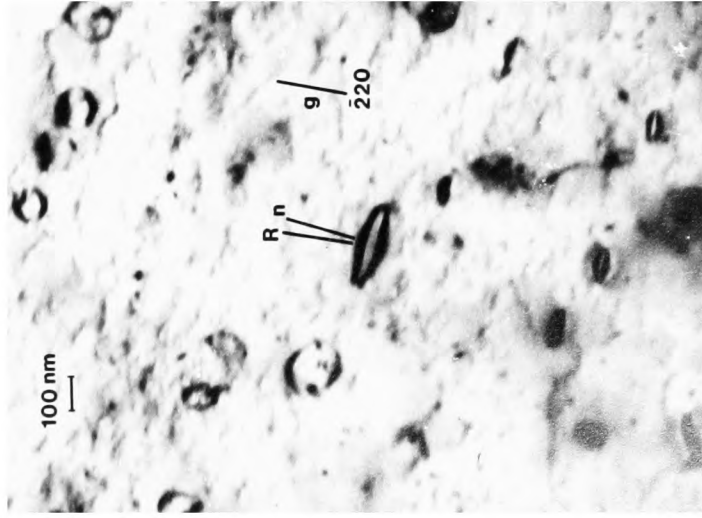
KI
C

50 nm
└─┘

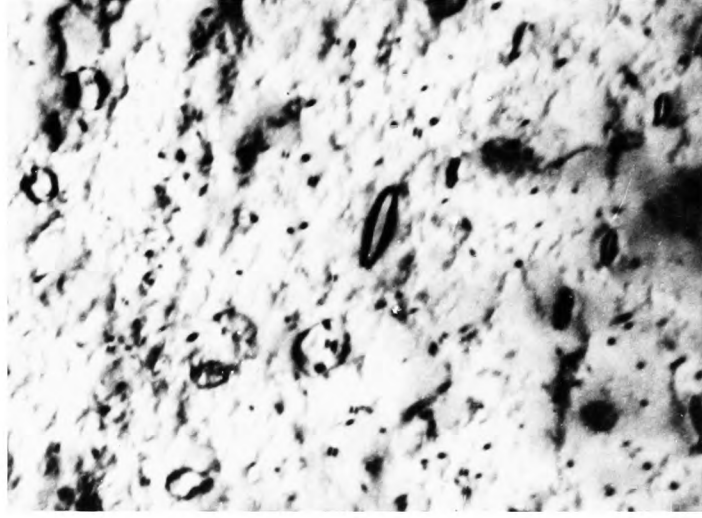


NaBr
D

Fig. 5.14. (001) foil of KI irradiated in the microscope at 10 K, $j = 13 \text{ mA cm}^{-2}$, micrographs at 30 sec intervals, illustrating onset of low temperature clustering. Large clusters were formed by prior external γ irradiation in bulk.



A



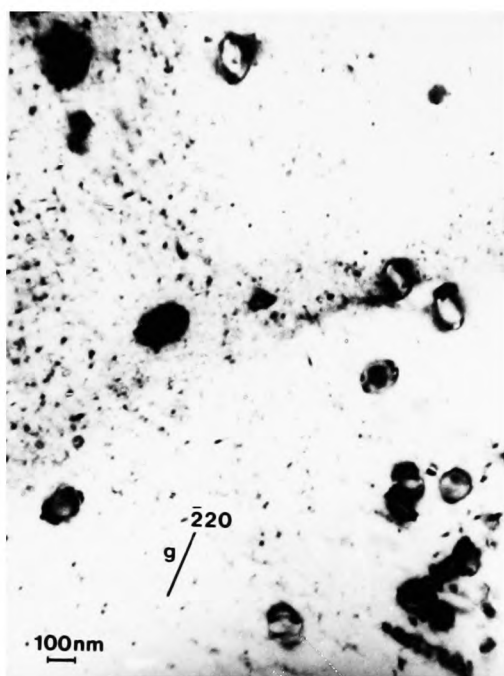
B



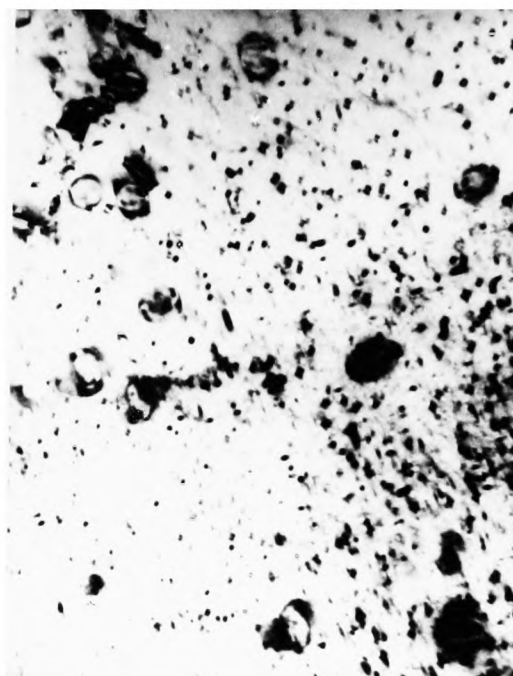
C

Fig. 5.15. Same (001) KI foil as in Fig. 5.14 but different area irradiated in the microscope at 35 K, $j = 13 \text{ mA cm}^{-2}$, micrographs at 30 sec intervals, illustrating the acceleration of defect clustering over irradiation at 10 K.

A



B



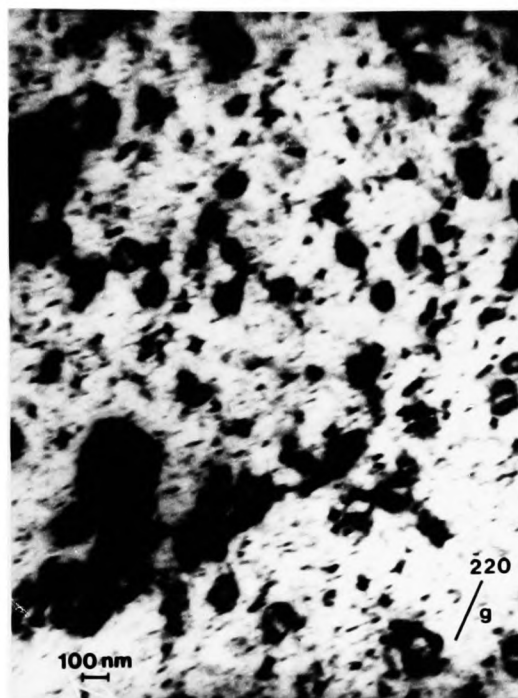
D



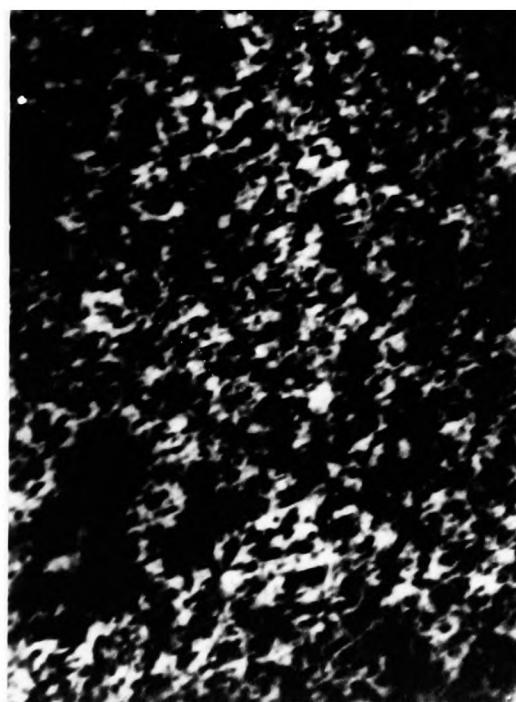
C

Fig. 5.16. Same (001) foil as in Fig. 5.14 but different area₂, irradiated in the microscope at 65 K, $j = 13 \text{ mA cm}^{-2}$, micrographs at 30 sec intervals, illustrating the rapid clustering and impossibility of microscopy at this temperature.

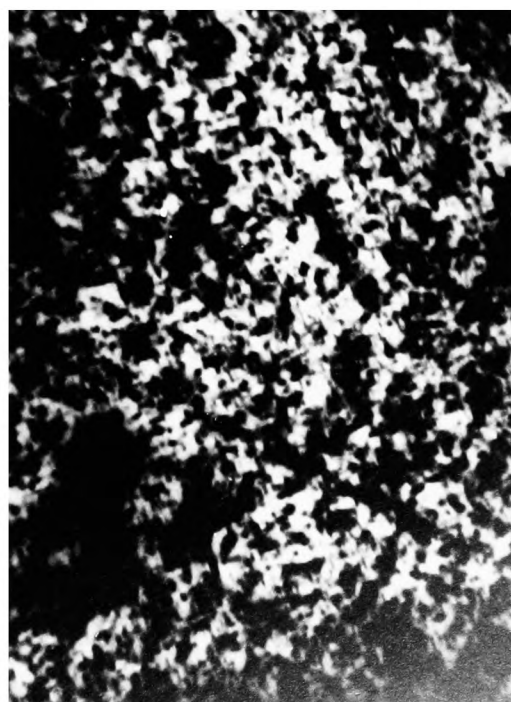
A



B

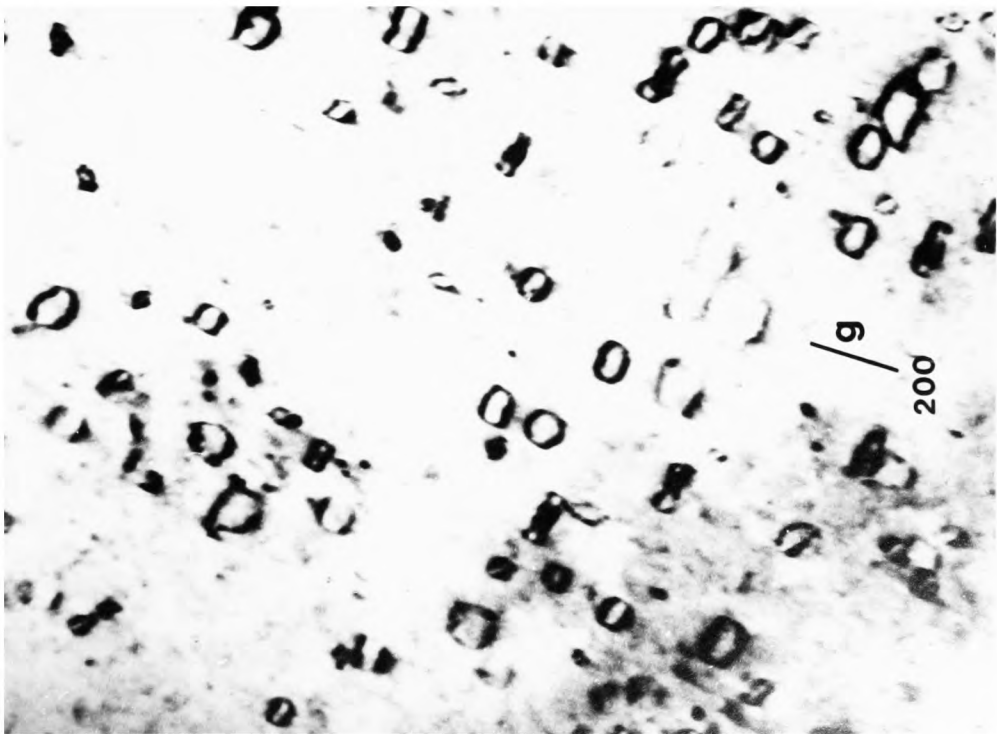


D

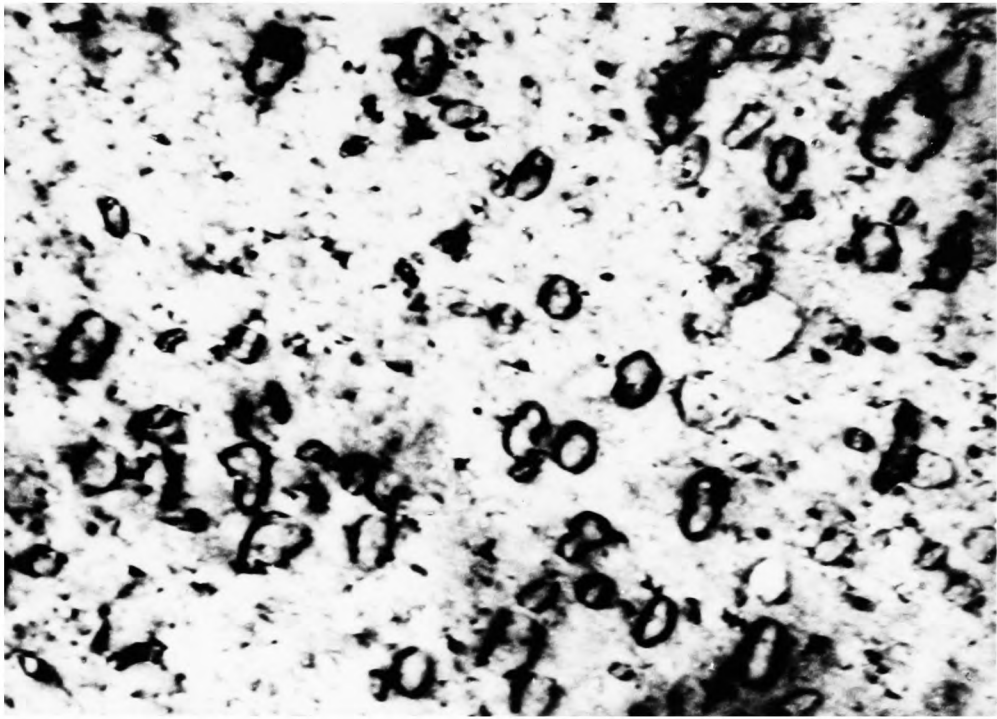


C

Fig. 5.17. (001) KI foil first irradiated at room temperature in the microscope to produce large loop defects, followed by brief examination at 10 K recorded (a) in the first micrograph. The foil was then annealed to room temperature without further irradiation and cooled to 10 K before re-examination, recorded in (b) the second micrograph. New clusters form during anneal of defects introduced during the brief low temperature irradiation, and all existing clusters are seen to grow appreciably. This KI foil contained 200 ppm Na⁺ which can be shown to affect only low clustering behaviour below 30 K.



A

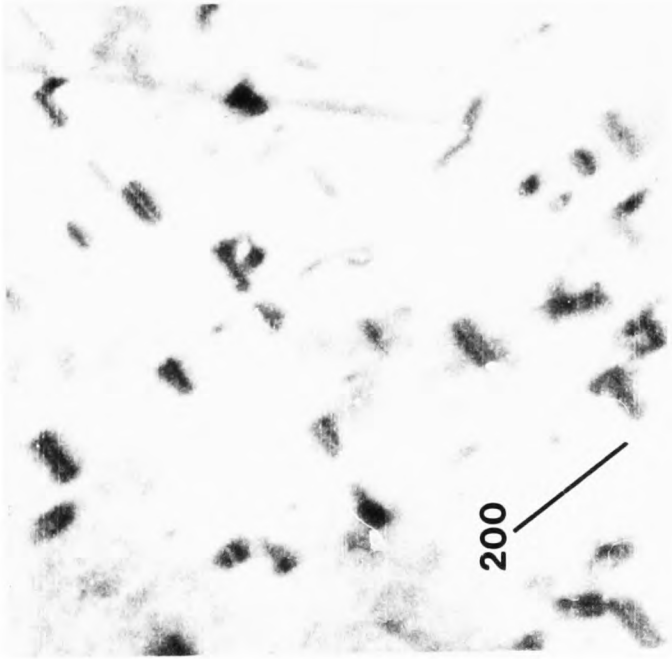


B

Fig. 5.18. Elongated loop clusters in electron irradiated KCl.

(a) (001) foil prepared from bulk crystal irradiated externally at room temperature with 4 MeV electrons to the total dose of 1000 MRad ($\sim 10^{19}$ F cm⁻³) and observed at 10 K. Insets indicate isolated larger loop occasionally observed, some of which do not retain the usual $\langle 100 \rangle$ elongation direction. Image quality in (a) is poorer than in low temperature examination of previously unirradiated material, because low temperature damage accumulates more quickly in previously irradiated material.

(b) (001) foil irradiated in situ in the microscope at room temperature, for comparison in cluster size and distribution with (a). A higher cluster density obtains during thin foil irradiation, but cluster morphology is identical.



A



B

100 nm

Fig. 5.19. (001) KCl foil prepared from bulk crystal irradiated externally with 400 KeV electrons to a total dose ~ 10 MRad ($\sim 5 \times 10^{17}$ F cm $^{-3}$) and observed at 10 K, showing small clusters exhibiting black/white streaking along $\langle 100 \rangle$. More time is available for observation of previously irradiated crystals at low temperatures if the defect clusters are appreciably smaller than those obtaining at saturation. This foil is at $\sim 1/20$ saturation defect density.

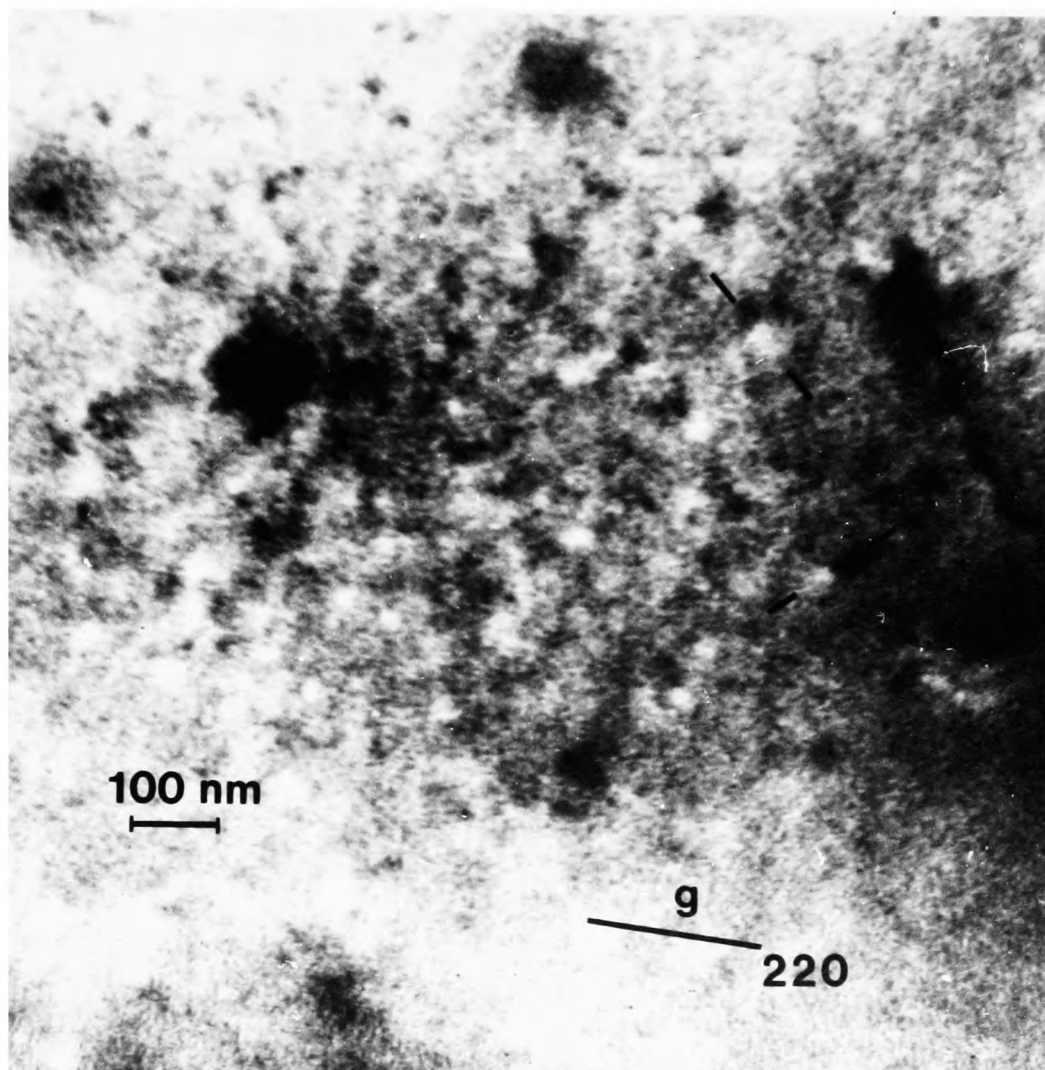
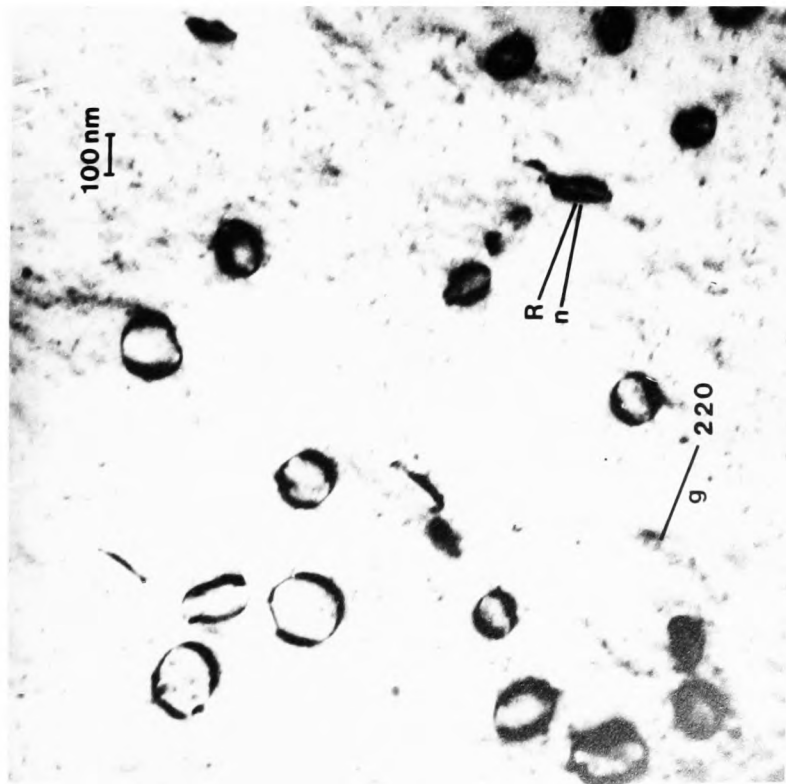


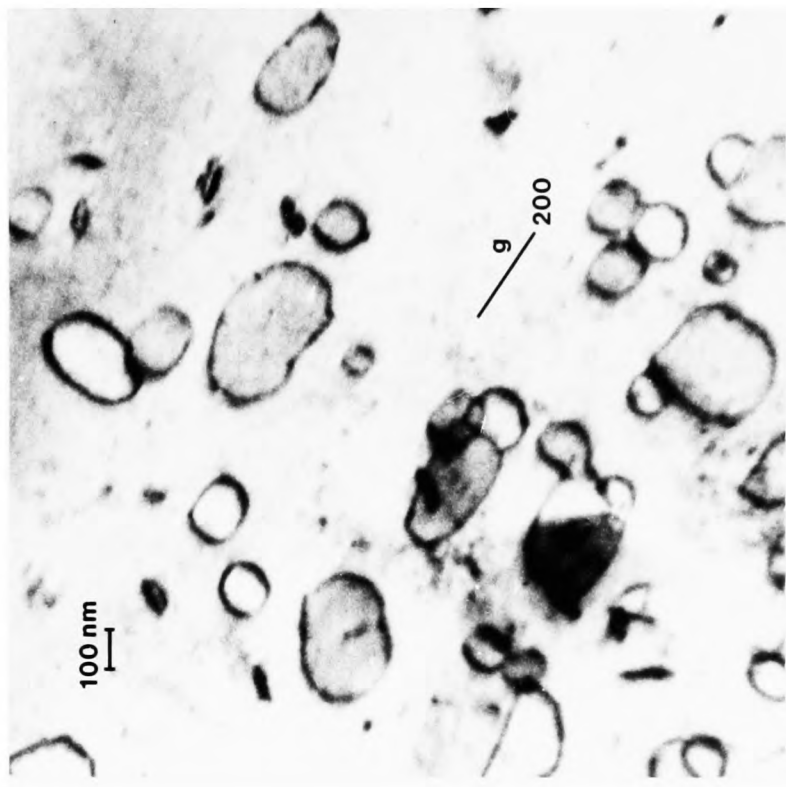
Fig. 5.20. Large plan r loop clusters in irradiated KI.

(a) (001) foil prepared from bulk crystal irradiated externally with 0.8 MeV γ irradiation at room temperature to a total dose of 1000 MRad (1.9×10^{18} F cm⁻³) and observed at 10 K. The number of sites involved in the loops is within a factor of two of the number of F centres, suggesting that these loops account for the fate of nearly all of complementary halogen interstitials.

(b) Similar distribution in an (001) foil briefly irradiated in situ in the microscope at room temperature and observed at 10 K. The density of loop clusters in foils irradiated in the microscope is somewhat larger than in crystals irradiated externally in bulk at lower dose rates.



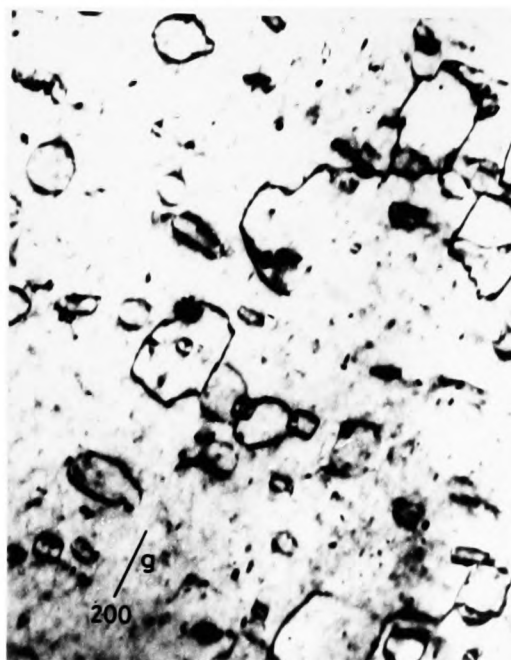
A



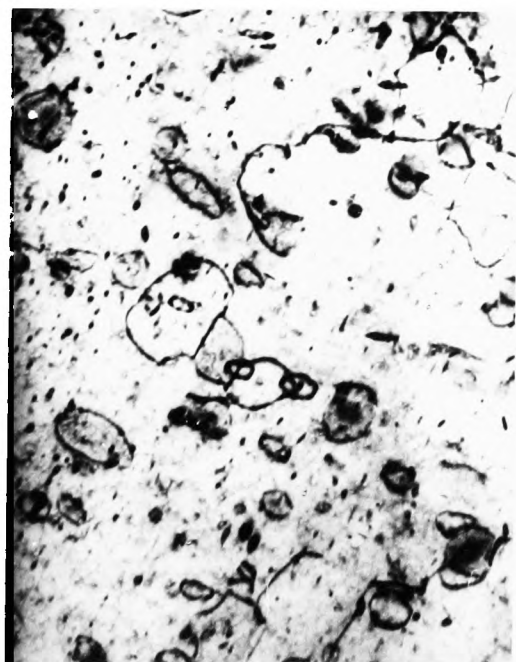
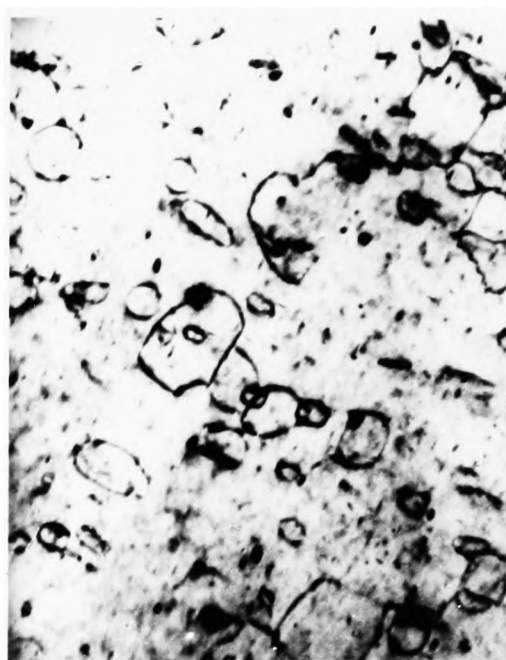
B

Fig. 5.21. (001) foil of KI: 200 ppm Na^+ previously irradiated in situ at room temperature and observed at 5 min intervals (a), (b) and (c) at 20 K with $j = 20 \text{ mA cm}^{-2}$. The absence of new defect cluster nucleation even after 15 min is to be compared with Fig. 5.14 for pure KI after only 30 sec irradiation, and is consistent with interstitial stabilisation as H_A or I_A^- centres. Note, however, marginal growth of existing room temperature clusters during prolonged irradiation. Raising the foil temperature to 35 K during irradiation in (d) results in new cluster growth.

A



B

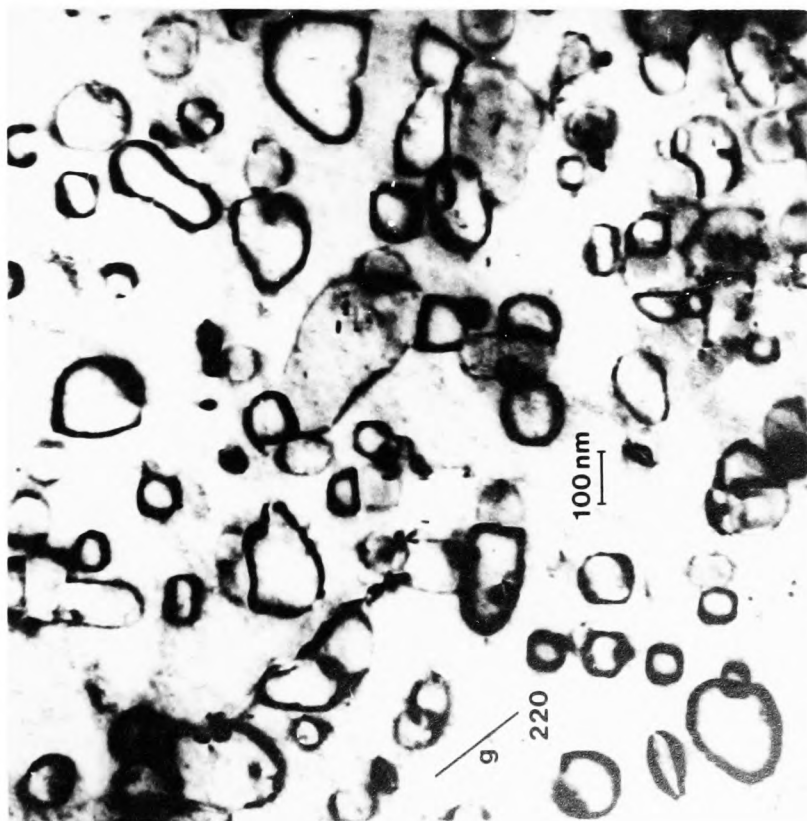


D

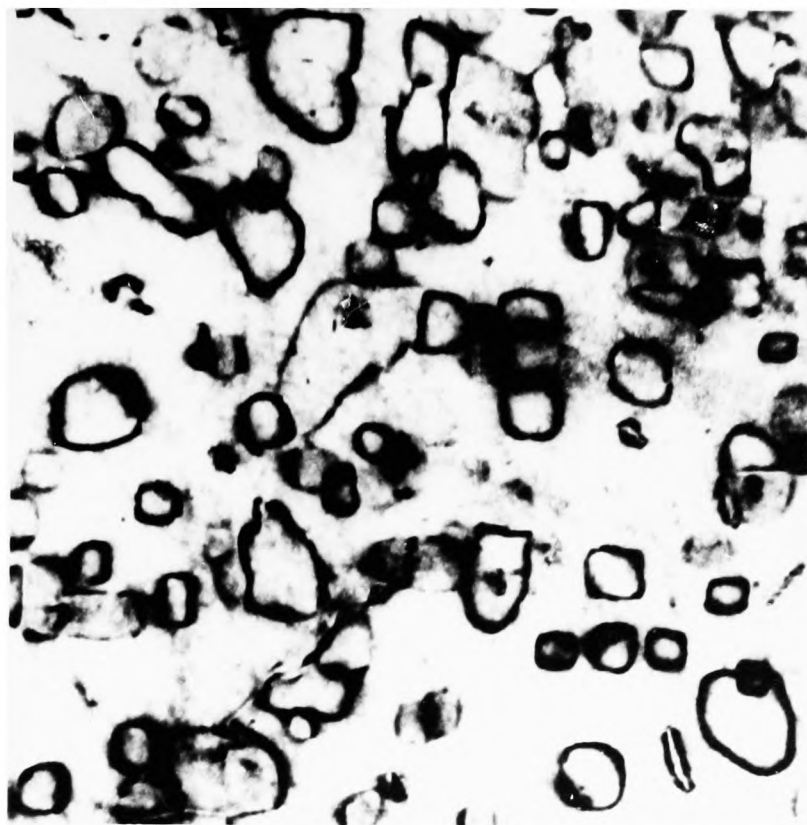


C

Fig. 5.22. Stereomicrographs of an (001) KI foil irradiated in situ at room temperature and examined at 10 K. (a) and (b) are tilted respectively $+8^\circ$ and -8° about 220 either side of the 001 pole. These micrographs indicate that the habit plane for planar loops produced in (001) foils internally in the microscope is close to (001).



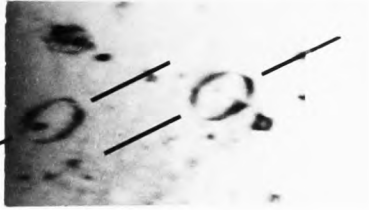
A



B

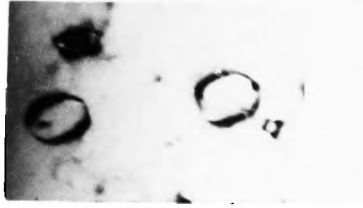
Fig. 5.23. Habit plane determination for planar loops in KI irradiated in bulk (γ , 1000 MRad), observed at 10 K in an (001) foil. (a) and (b) are a $\underline{g} = \pm 220$ pair for foil orientation $\underline{z}$ near $|001|$. (c) and (d) are a $\underline{g} = \pm 220$ pair for $\underline{z}$ near $|115|$. Projected major loop axes are marked. A stereographic analysis of these data appears in fig. 5.24.

A $z \sim 001$



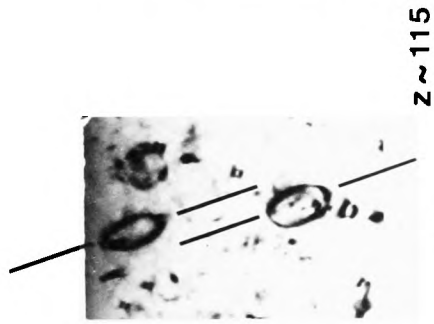
g
 $\bar{2}20$

B



g
 $2\bar{2}0$

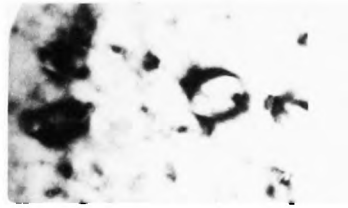
100 nm



$z \sim 115$

C

g
 $\bar{2}20$



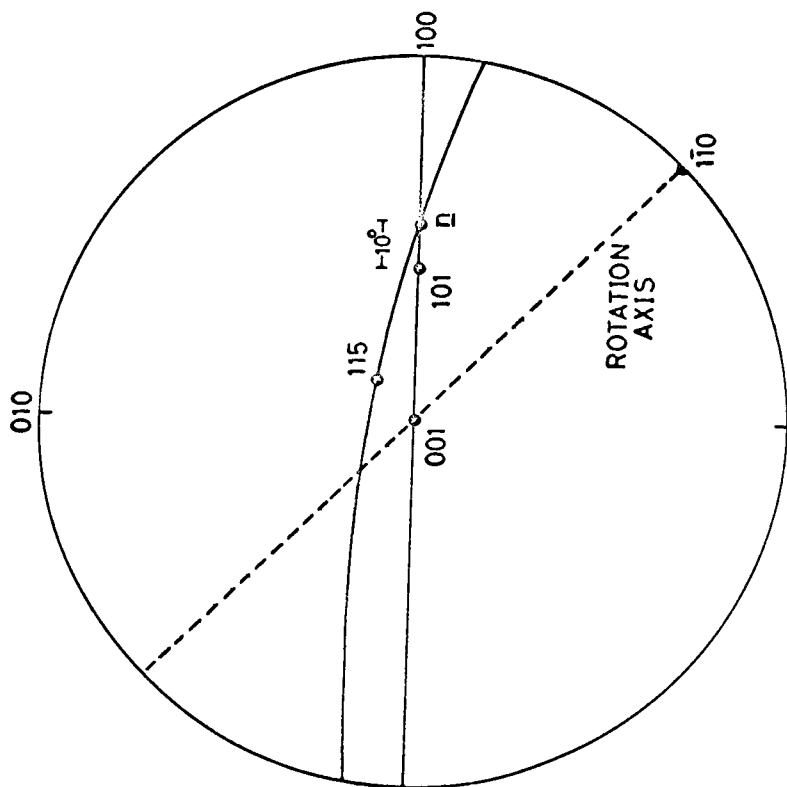
g
 $2\bar{2}0$

D

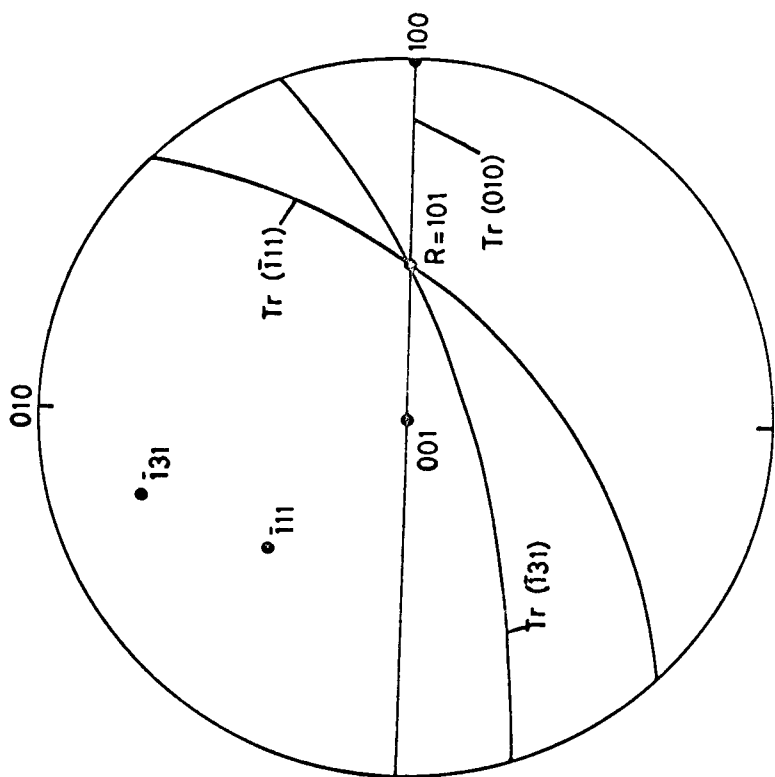
Fig. 5.24. Analysis of loop normal $\underline{n}$ and displacement vector $\underline{R}$ for planar loops in KI.

(a) Stereographic analysis of the loop normal in externally irradiated KI using the data of fig. 5.23 and the method of Maher and Eyre (1971). A loop normal $\underline{n}$ within 10° of $|101|$ is indicated.

(b) Stereographic analysis of the displacement vector using the data of fig. 5.25, 5.26 and 5.32. The displacement vector $\underline{R}$ lies along that $|101|$ direction closest to the loop normal $\underline{n}$ in (a) for externally irradiated KI.

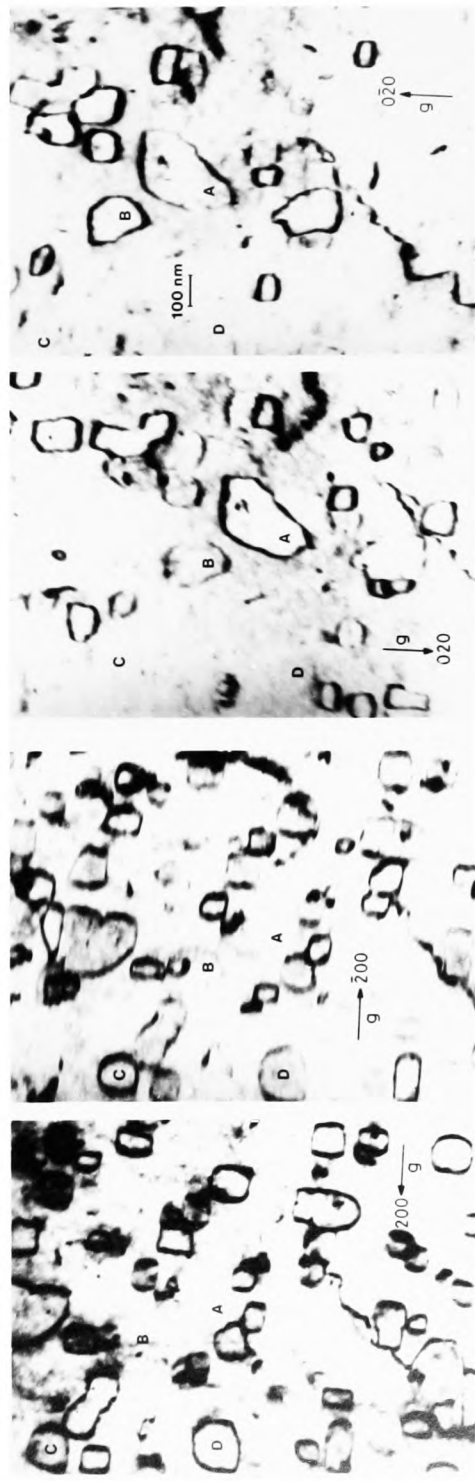
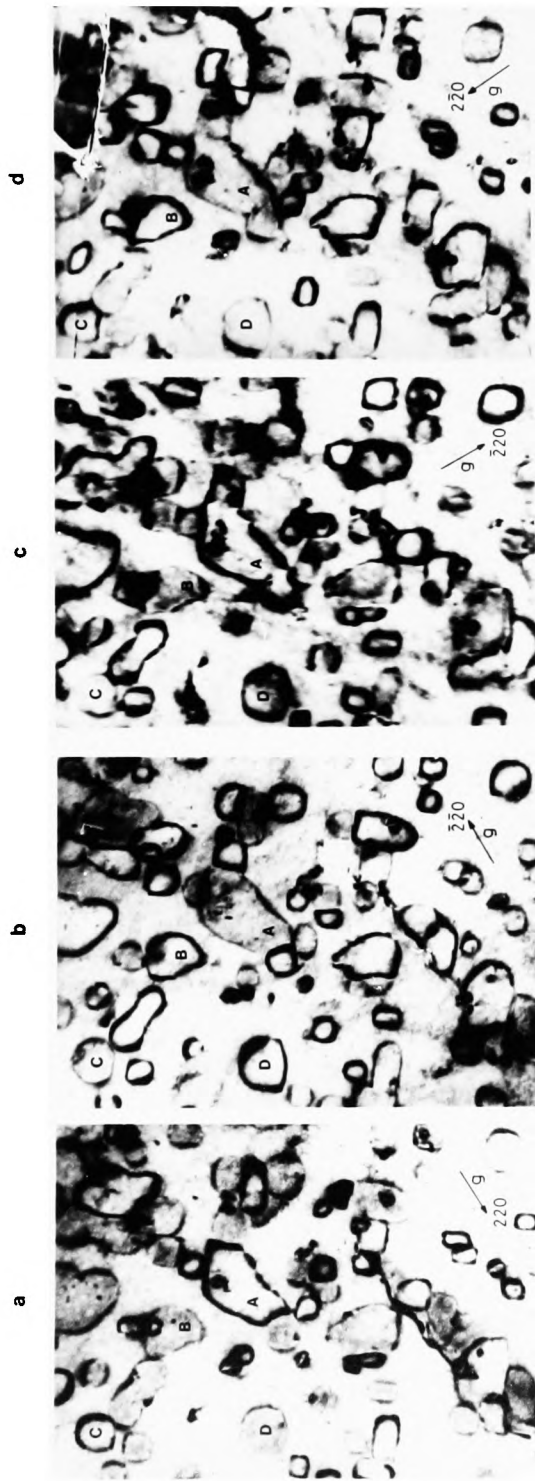


(a)



(b)

Fig. 5.25. Displacement vector analysis for planar loops in an (001) KI foil irradiated in the microscope, using eight co-planar reciprocal lattice vectors $\underline{g}$. The disappearance of loops in either $\underline{g} = \pm 200$ or ± 020 indicates the respective displacement vectors must lie in (100) or (010).



e f g h

Fig. 5.26. Displacement vector analysis for planar loops in a (101) KI foil irradiated in the microscope, using eight co-planar reciprocal lattice vectors $\underline{g}$. The disappearance of some loops in $\underline{g} = \pm 020$, $\pm 2\bar{2}2$ or ± 222 indicates that the respective displacement vectors must lie in (010), ($\bar{1}\bar{1}1$) or ($\bar{1}11$). (g) and (h) indicate the necessity of using $\pm \underline{g}$ pairs to distinguish between strong/weak inside/outside $\underline{g}$. $\underline{R} \neq 0$ contrast and a true $\underline{g}$. $\underline{R} = 0$ condition.

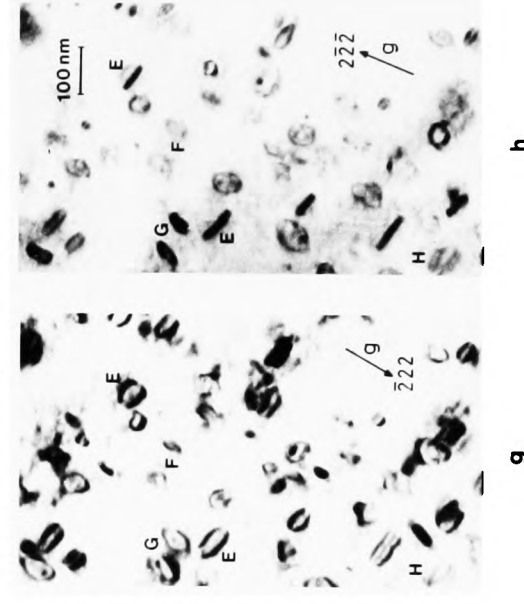
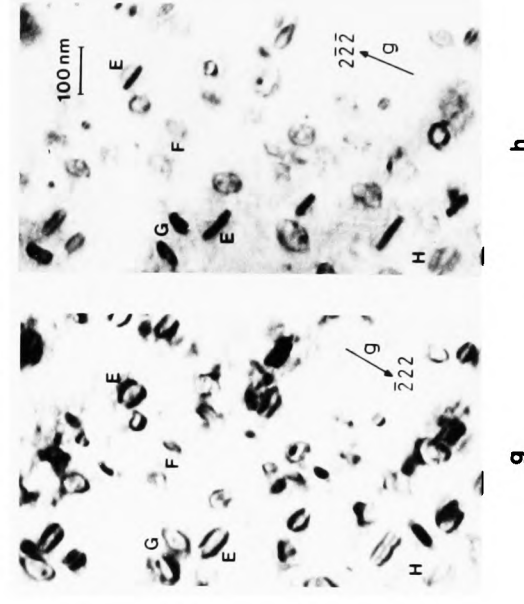
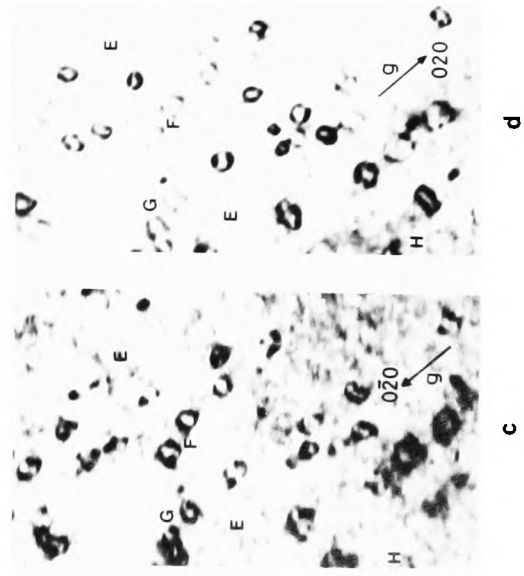
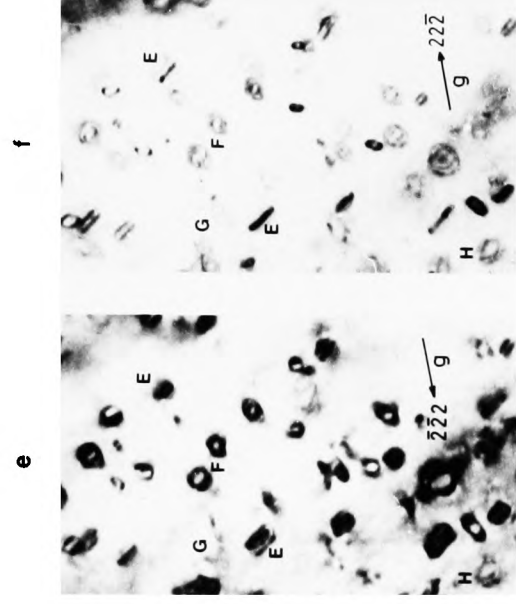
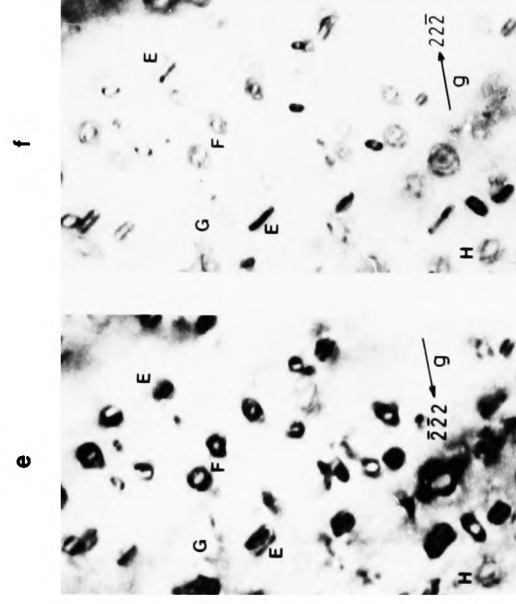
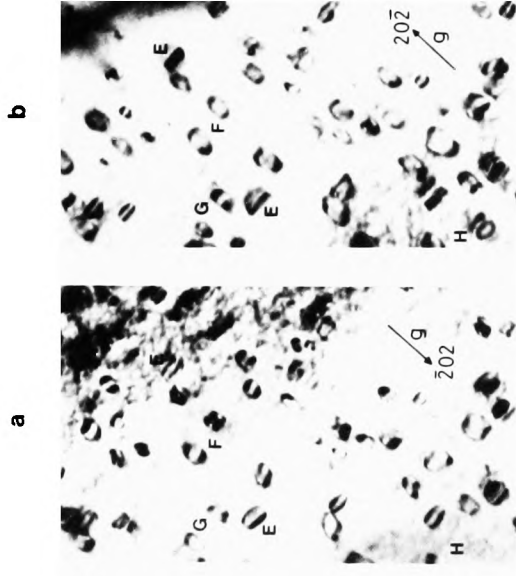


Fig. 5.27. Planar loop configuration in KI as indicated by the analysis of figs. 5.22 through 5.26. The loop displacement vector $\underline{R}$ is $|101|$. In externally irradiated crystals, the loop normal $\underline{n}$ lies within 10° of this $|101|$ direction; for in situ irradiation of (001) foils, the loop normal is closer to $|001|$.

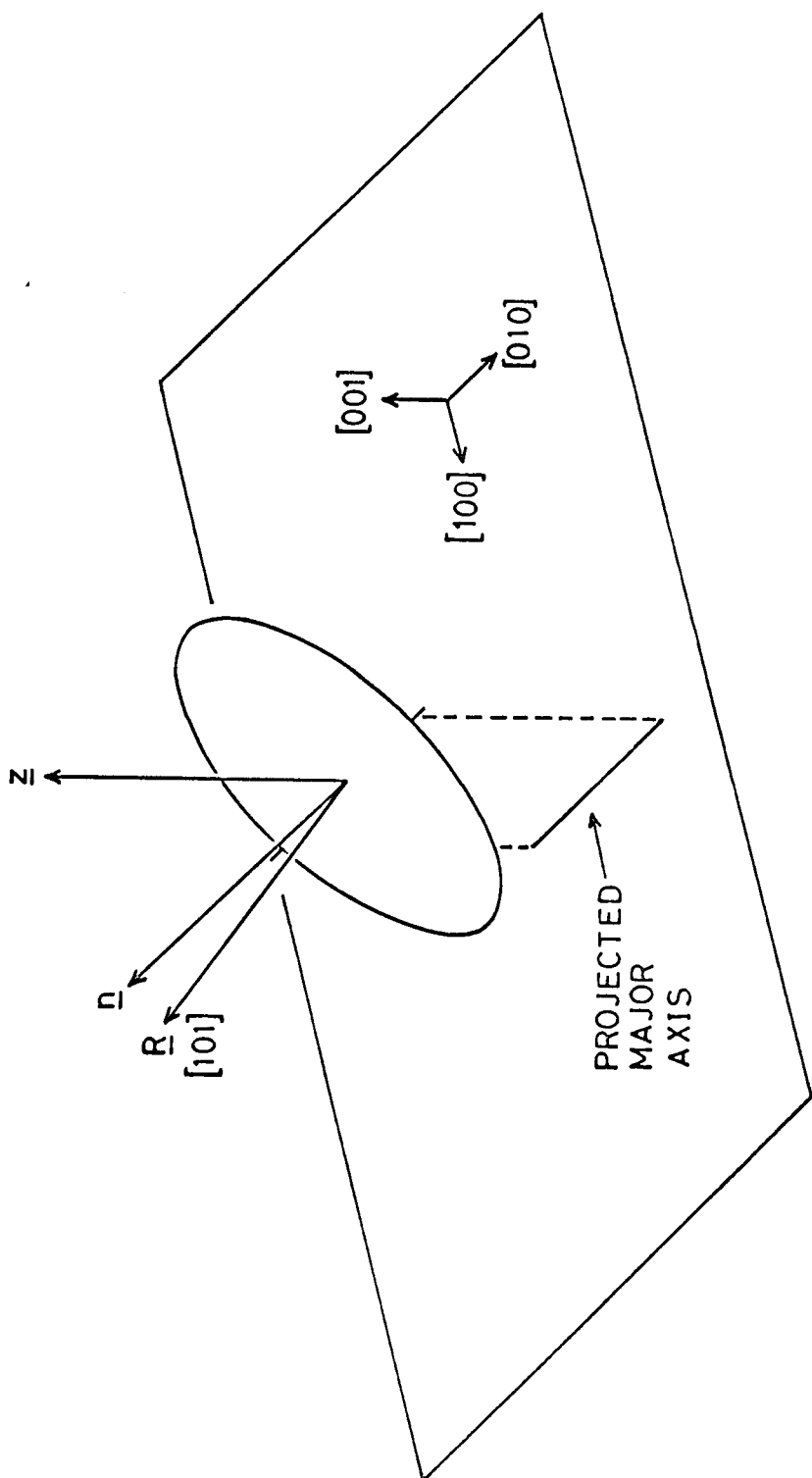


Fig. 5.28. Microdensitometric trace across the centre of one of the planar loops in externally irradiated (γ , 1000 MRad) KI illustrated in fig. 5.20a along the projection of the displacement vector R onto the (001) foil plane. The image width $\sim 0.4\xi_g$ is consistent with $R \sim a/\sqrt{2}$. The loop is also large enough and inclined sufficiently for displacement fault fringes to be visible if R differs appreciably from $a/\sqrt{2}$.

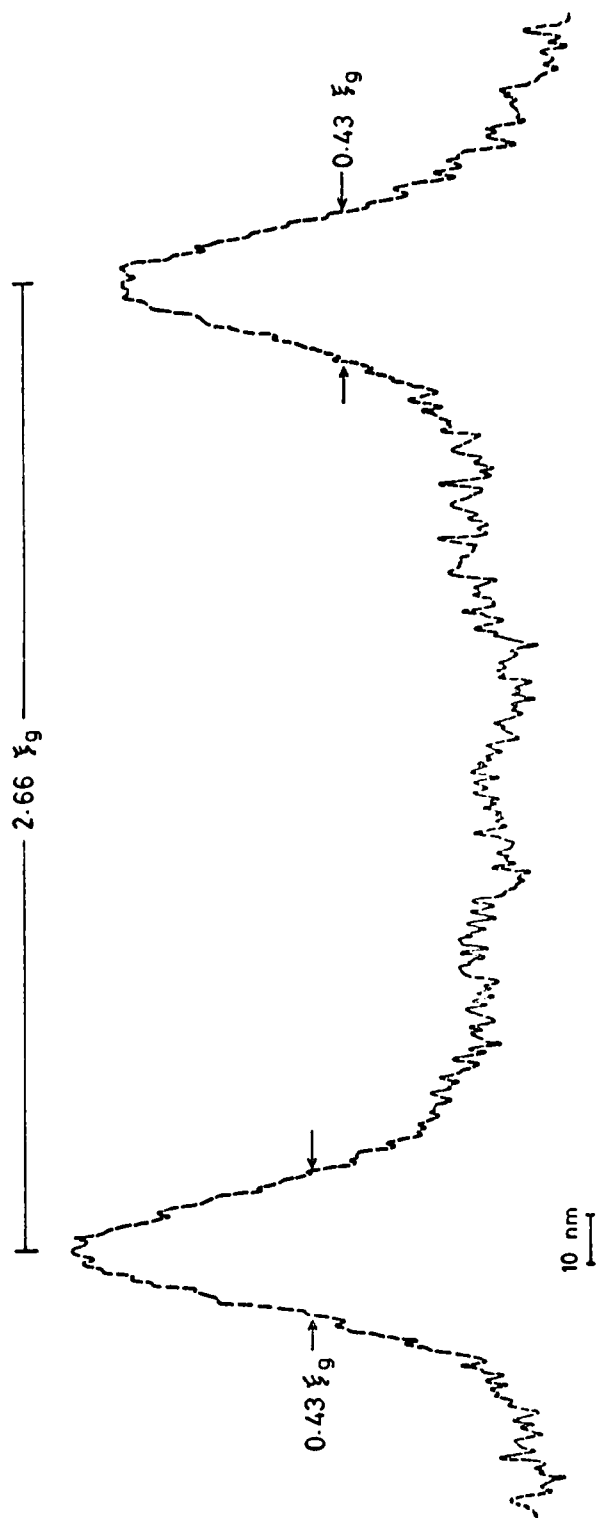
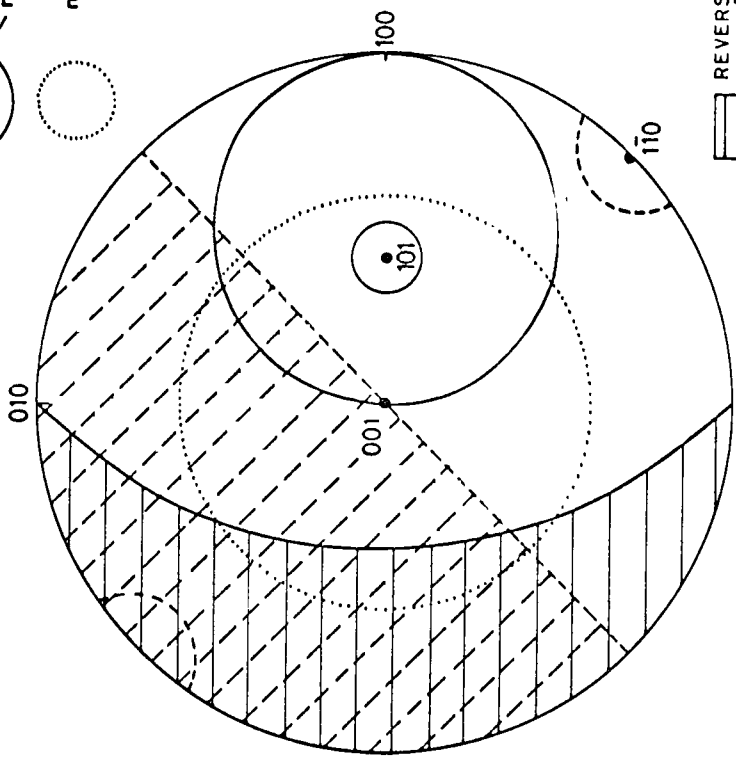
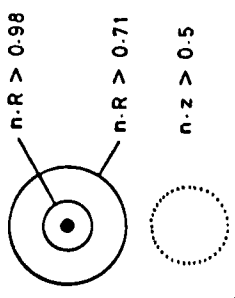
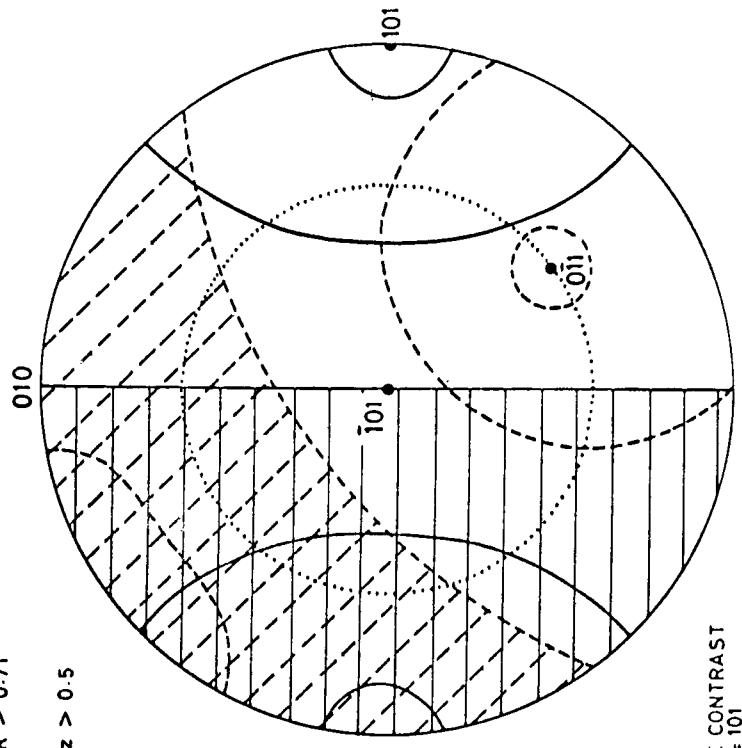


Fig. 5.29. Regions of normal and reverse inside/outside contrast behaviour for loops with $\langle 101 \rangle$ type displacement vectors $\underline{R}$ for foil orientations $\underline{z}$ near (a) $|001|$ and (b) $|\bar{1}01|$. If the foil normal $\underline{n}$ is within 75° of $\underline{R}$, all loops with appreciable projected area ($\underline{n} \cdot \underline{z} > 0.5$) exhibit normal contrast behaviour for $\underline{z} = |001|$. The same is not true for $\underline{z} = |\bar{1}01|$ unless $\underline{n}$ lies considerably closer to $\underline{R}$. A recent purported correction to this scheme (Van der Walt 1972) is incorrect.



(a)



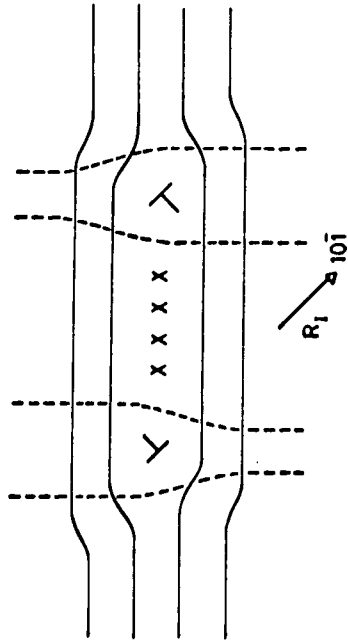
(b)

REVERSE CONTRAST
 $R \approx 101$
 REVERSE CONTRAST
 $R = 110, 011$

Fig. 5.30. Four possible loop configurations, two of interstitial and two of vacancy character, with the same general $|101|$ displacement vector projection along $|100|$ on the (001) foil plane for $z = |001|$. The angle indicated between $\underline{n}$ and $\underline{R}$ (illustrated here as $+45^\circ$) may vary from -45° to $+90^\circ$ with normal contrast behaviour preserved.

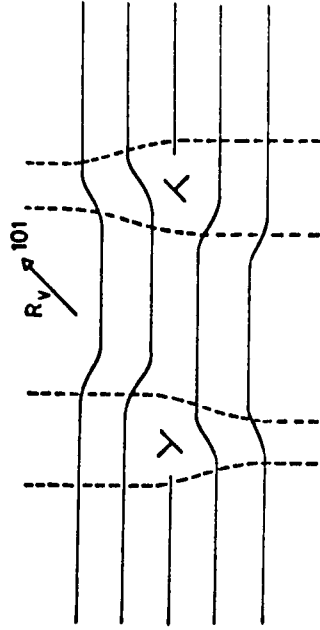
(a)

INTERSTITIAL LOOP



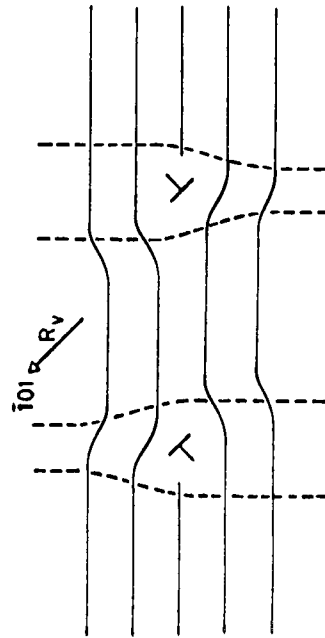
(b)

VACANCY LOOP



(c)

VACANCY LOOP



(d)

INTERSTITIAL LOOP

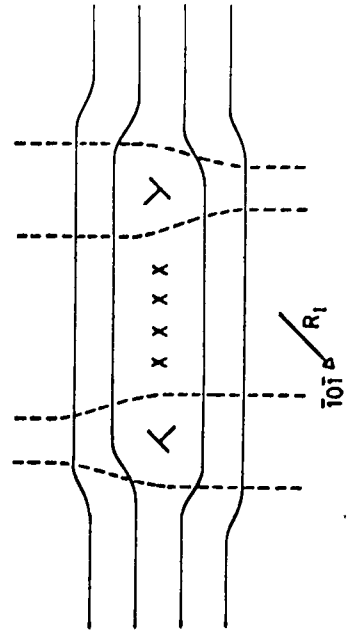
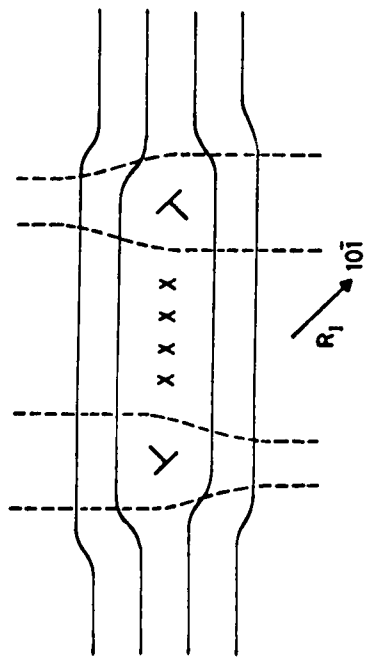


Fig. 5.31. Scheme for ascertaining the character of planar loops in an (001) foil. Images in $\underline{g}_1 = 200$ and $\underline{g}_2 = 200$ for $\underline{z} \sim |001|$ differentiate between cases (a, b) and (c, d) in fig. 5.30. The foil is then tilted by 18.4° to $\underline{z} \sim |013|$, where images in $\underline{g}_3 = 131$ and $\underline{g}_4 = 131$ distinguish between cases (a, c) and (b, d) by selective $\underline{g} \cdot \underline{R} = 0$ disappearance. These two criteria then enable a precise determination of the absolute direction of $\underline{R}$, and thus the loop character.

INTERSTITIAL LOOP



VACANCY LOOP

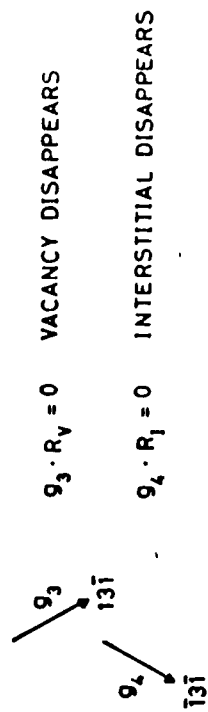
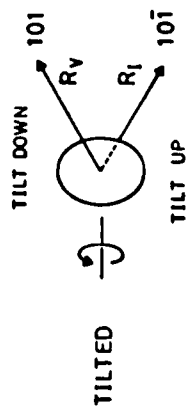
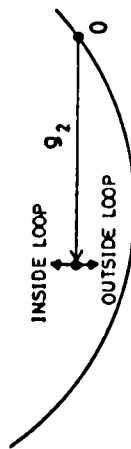
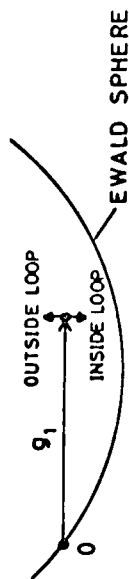
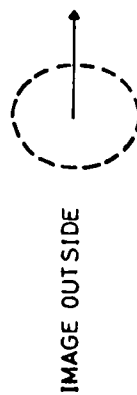
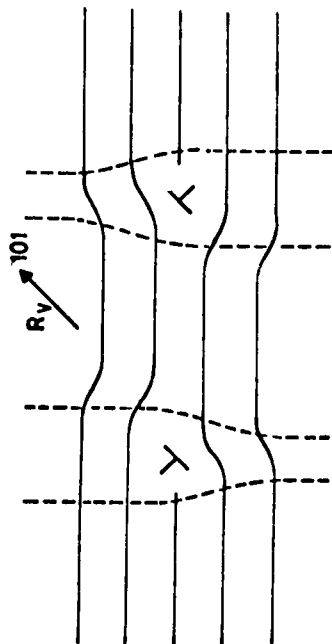
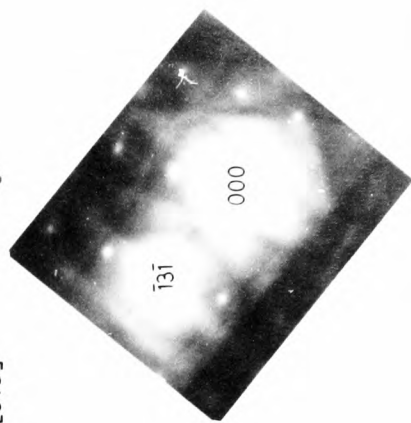
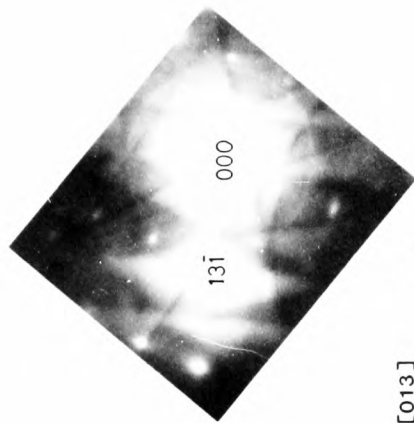
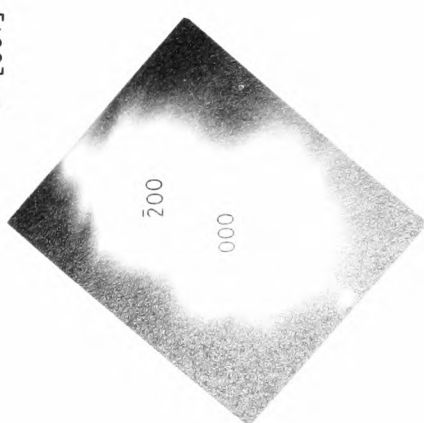
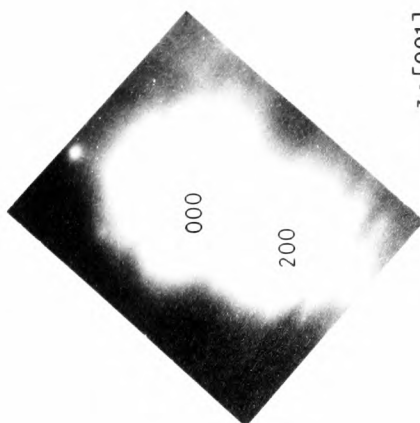
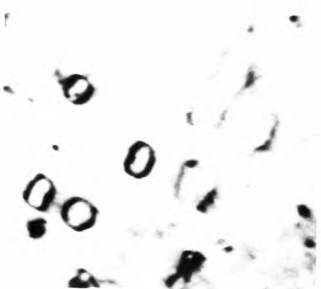
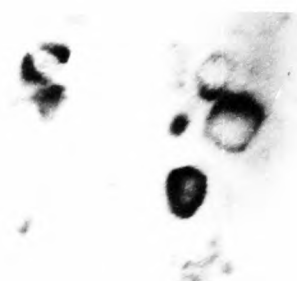
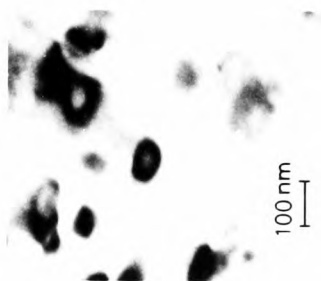


Fig. 5.32. A character analysis, following the scheme outlined in fig. 5.31, for loops produced by in situ irradiation of an (001) KI foil. Two sets of loops were analysed, and both are seen to be interstitial in character.



$z = [013]$



$z = [001]$

Fig. 5.33. Compression jig for use in alkali halide deformation tests. The jig is designed to mount onto an Instron model TM/M/L testing machine and is arranged so that with the crystal under load, top and bottom cages are free to move without friction between them. Compression anvils are hardened steel coated with PTFE lubricant.

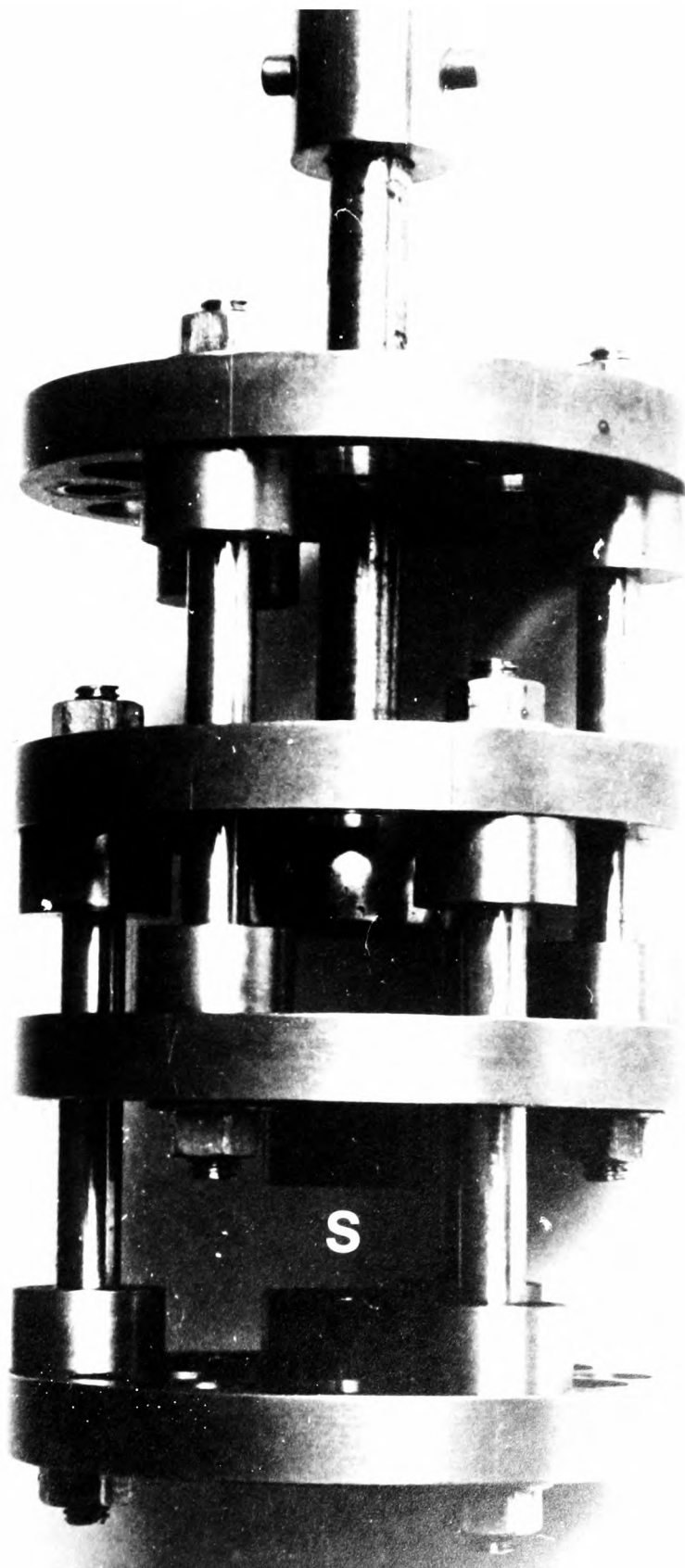


Fig. 5.34. Stress birefringence patterns from three {001} faces of a KCl single crystal deformed in [001] compression to 6% shear strain at room temperature and examined in polarised light. One $\langle 1\bar{1}0 \rangle$ {110} slip system predominantly activates with strong exclusion of the other three equally stressed systems.

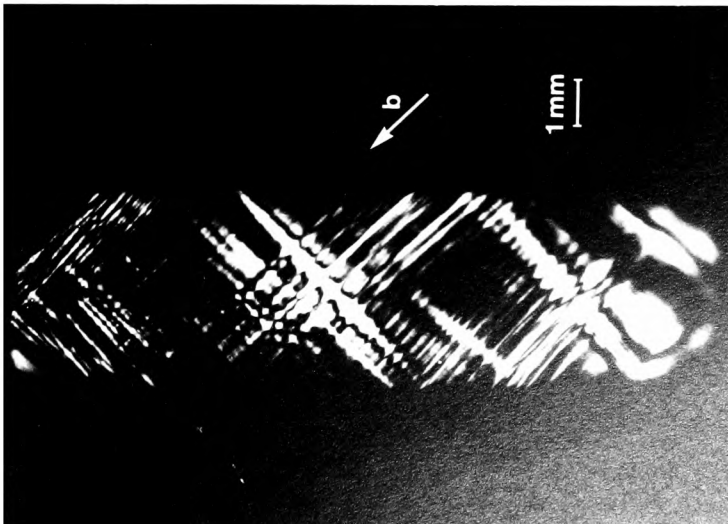
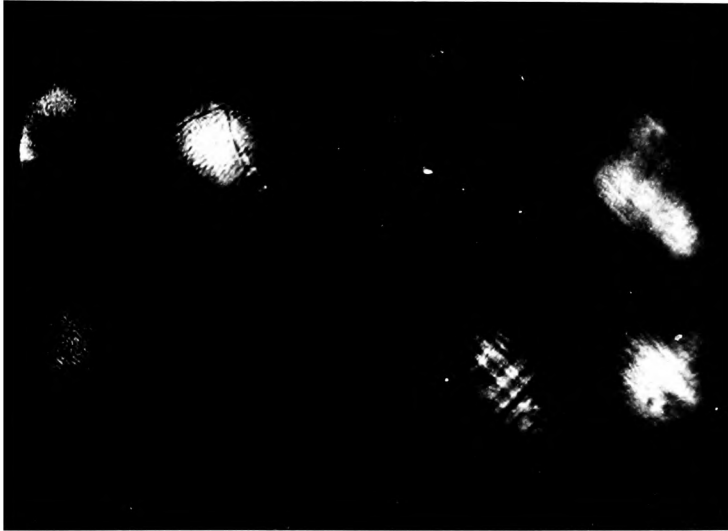


Fig. 5.35. Shear stress-shear strain curves illustrating deformation behaviour of NaCl, KCl, KI and NaBr single crystals in $|001|$ compression at room temperature. Three stage work-hardening behaviour is evident for each species. Initial yield stresses differ because of differing elastic constants and divalent impurity levels. The strain rate $\dot{\epsilon}$ was $\sim 5 \times 10^{-5} \text{ sec}^{-1}$.

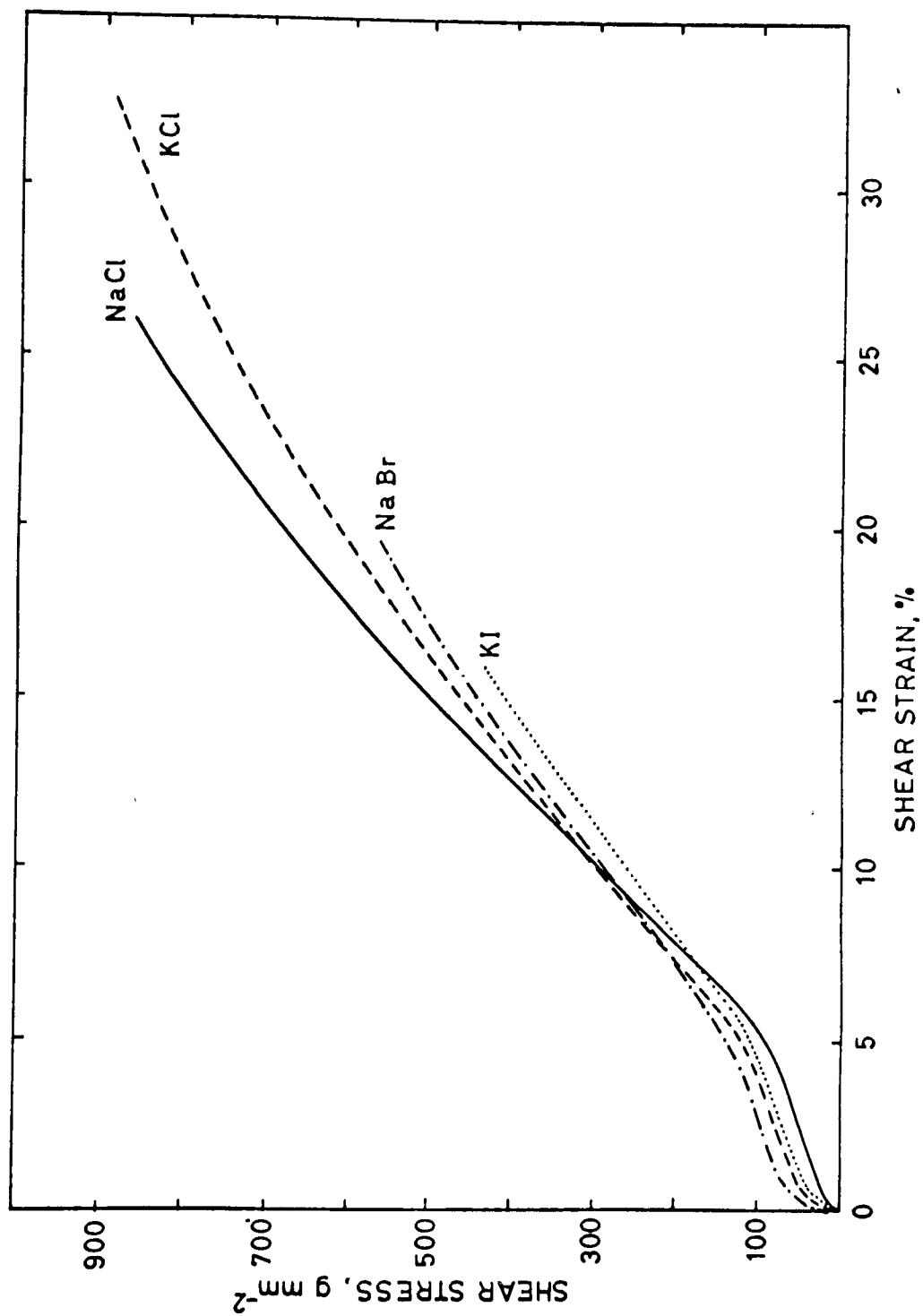


Fig. 5.36. Typical dislocation configurations in deformed alkali halides.

(a) Glide dislocations in a (101) foil of KCl deformed to stage II in $[001]$ compression and sectioned parallel to the primary slip plane. A common feature in deformed crystals are small dislocation loops (circled).

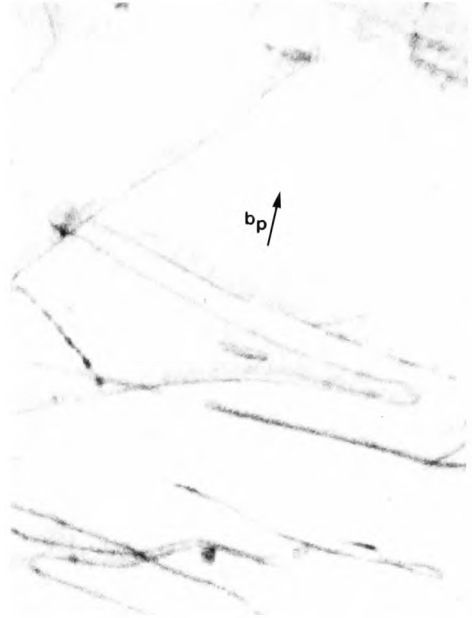
(b) Network formation in a (101) foil of KI deformed to stage II in $[001]$ compression and sectioned parallel to the primary slip plane. These networks arise from interaction of primary and oblique slip and involve reaction product dislocations formed from reactions of type (5.14).

(c) Widely-spaced dipoles in a (101) foil of NaCl deformed to stage II in $[011]$ compression and sectioned parallel to the primary slip plane. These dipoles are thought to result from extensive cross slip, the result of applying appreciable resolved shear stress on the (010) cross slip planes.

(d) Narrow edge dipoles in a (101) foil of NaBr deformed in $[001]$ compression and sectioned parallel to the primary slip plane. Since there is no macroscopic shear stress resolved on the cross slip plane, it is probable these dipoles (a common feature in all alkali halide deformations) arise from a multiple cross glide multiplication mechanism.



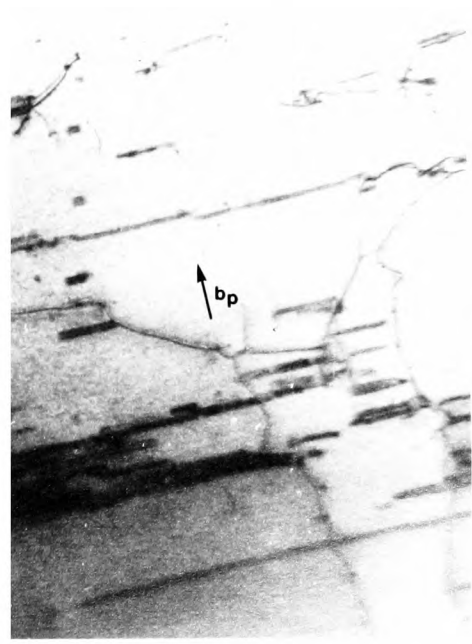
B



C



A



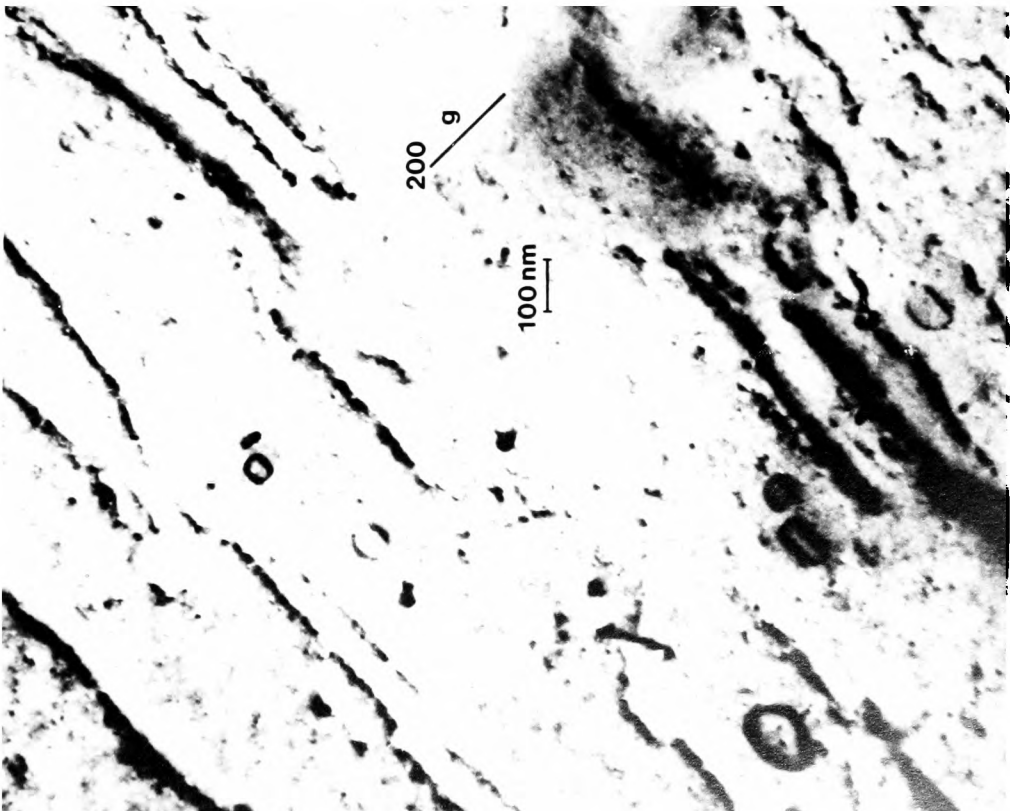
D

500 nm

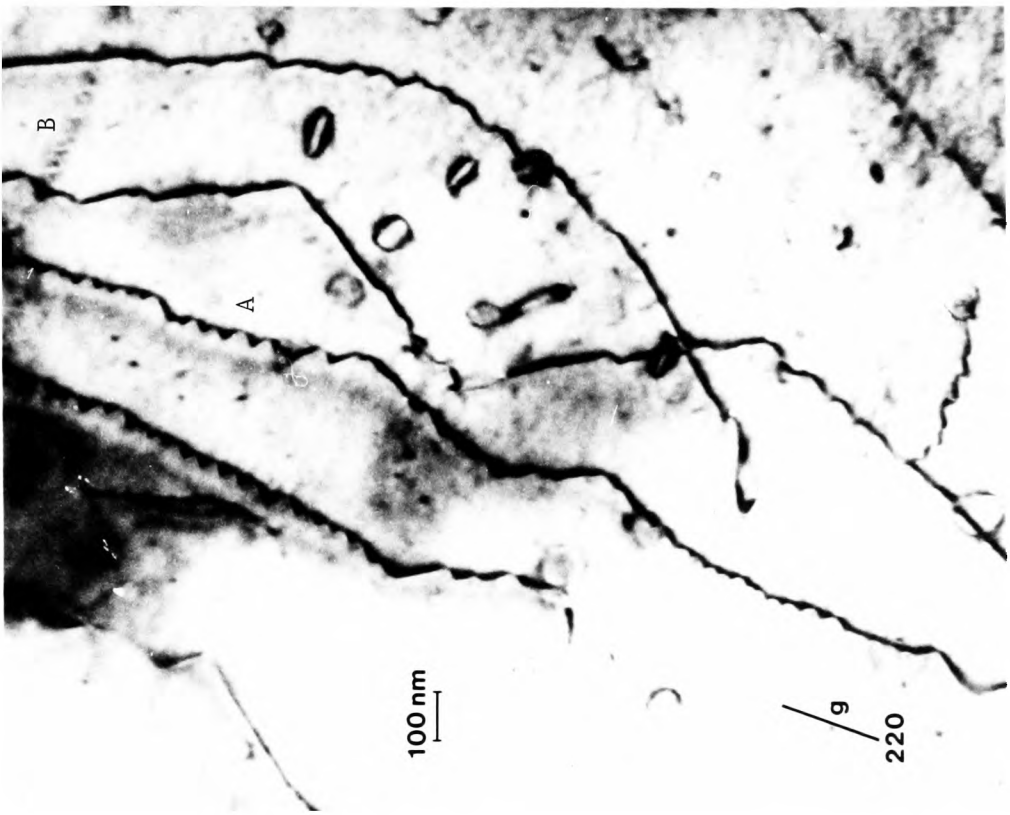
Fig. 5.37. Effect of irradiation on existing dislocations in KI.

(a) (001) KI foil, prepared from a section previously deformed, and irradiated in the microscope at room temperature. Edge dislocations are observed to disintegrate within the first second or so of irradiation, and appear heavily decorated with small defect clusters. A lower density of planar loop clusters obtains in the vicinity of these dislocations than in undeformed regions.

(b) (001) KI foil prepared from a section previously deformed by bending then irradiated externally with 400 keV electrons to a dose ~ 1000 MRad (2×10^{18} F cm⁻³) at room temperature. Dislocations near screw orientation at A are seen to have climbed into helices, sometimes degenerating into strings of loops at B. Analysis of the climb indicates that defects have condensed from a radius ~ 150 nm which is consistent with interstitial condensation.



A



B

Fig 5.38. Analysis of climb.

(a) Interstitial climb according to an FS/RH convention for defining b.

(b, c) The sense of the resulting helix depends not only on the species condensing (interstitial illustrated) but also on the sign of b.

(d) The sense of the helix may be determined in principle by tilting in a known direction and examining its projection.

(e) The sign of b may be determined for a given sense of helix by the cusped appearance of the untilted helix arising from inside/outside contrast, and thus the character of the helix determined.

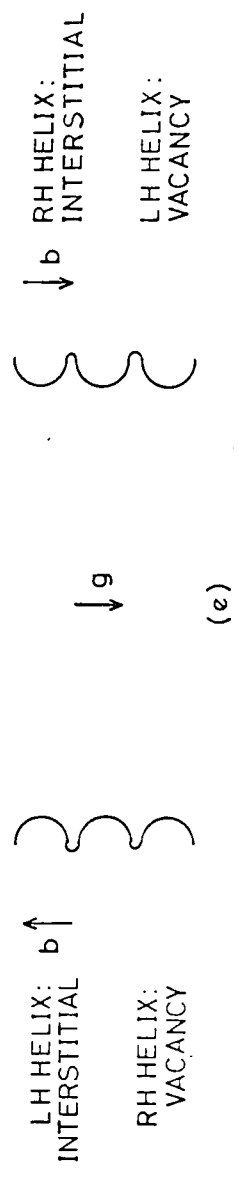
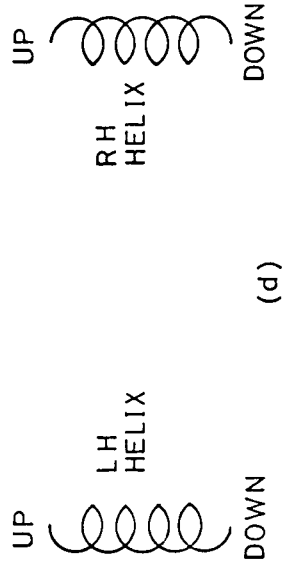
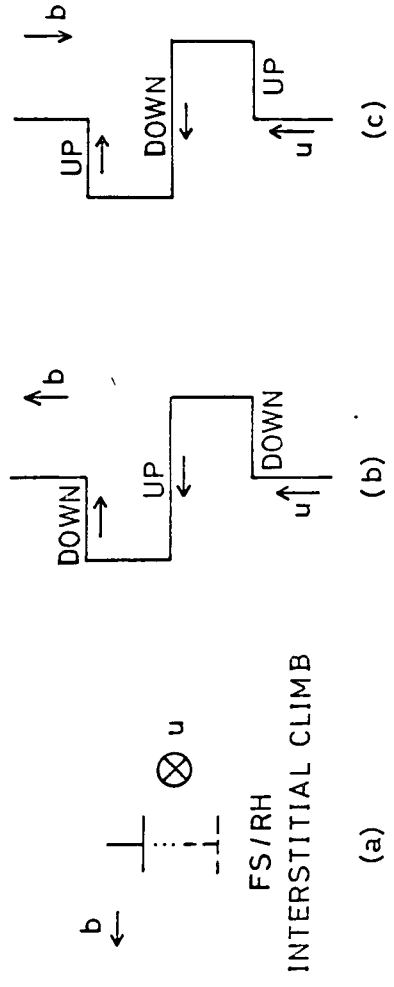


Fig. 5.39. Interaction of glide dislocations and planar loop clusters in KI previously irradiated to 1000 MRad dose at room temperature, then sectioned and deformed by bending before thinning to an (001) foil. Two sorts of interaction are illustrated at A and B.

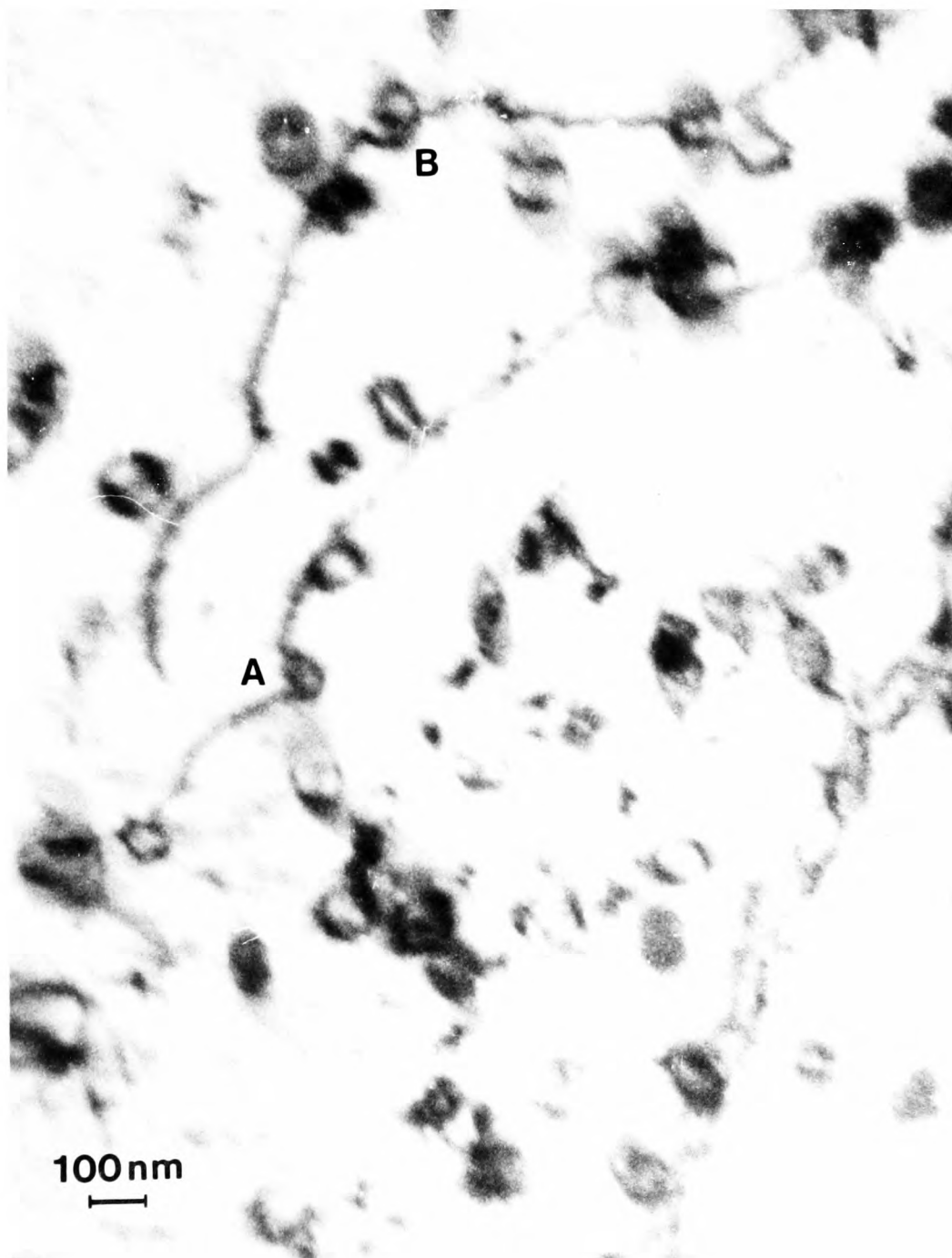


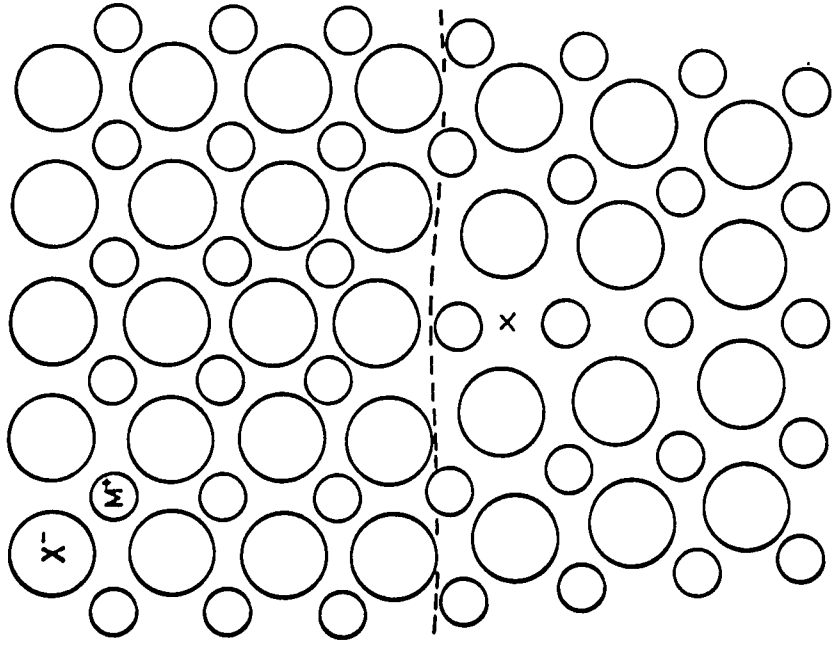
Fig. 5.40. Four models for interstitial climb of a perfect $a/2$ $\langle 110 \rangle$ edge dislocation ($\underline{u}$ normal to the (100) plane of the illustration) by interstitial defect condensation.

(a, b) Perfect interstitial climb by condensation of anion-cation interstitial pairs.

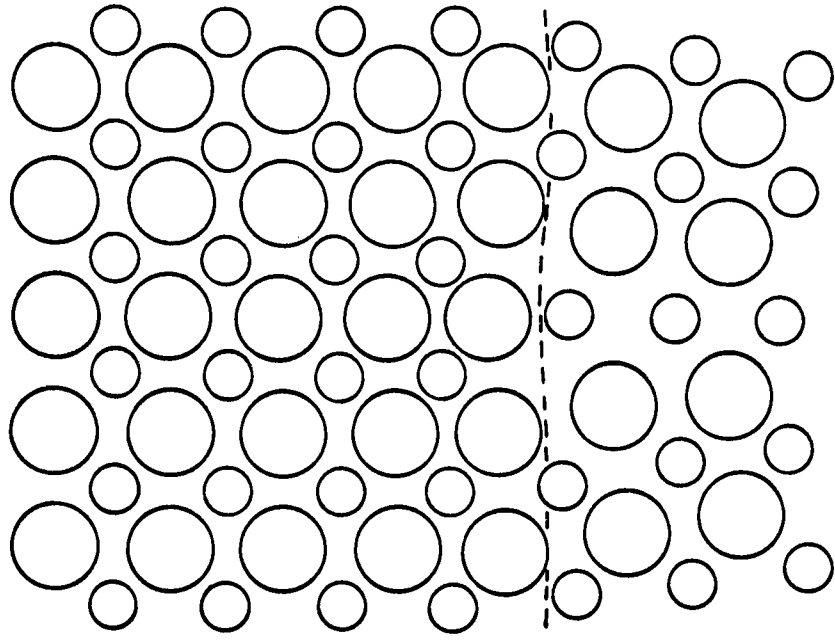
(c, d) H centre condensation for the two equilibrium dislocation positions along the slip plane illustrated in fig. 1.2. The $\langle 110 \rangle$ H centre orientation near the core is by no means certain, and a configuration nearer $\langle 100 \rangle$ can be envisaged straddling the slip plane.

(e, f) $|X_2^0|$ interstitial halogen molecule condensation at the core. The displacements expected on a hard sphere model are indicated in Table 5.6 and are substantial fractions of $a/\sqrt{2}$. This molecular configuration may be stabilised by hole delocalisation to form $|X_4^{2-}|$.

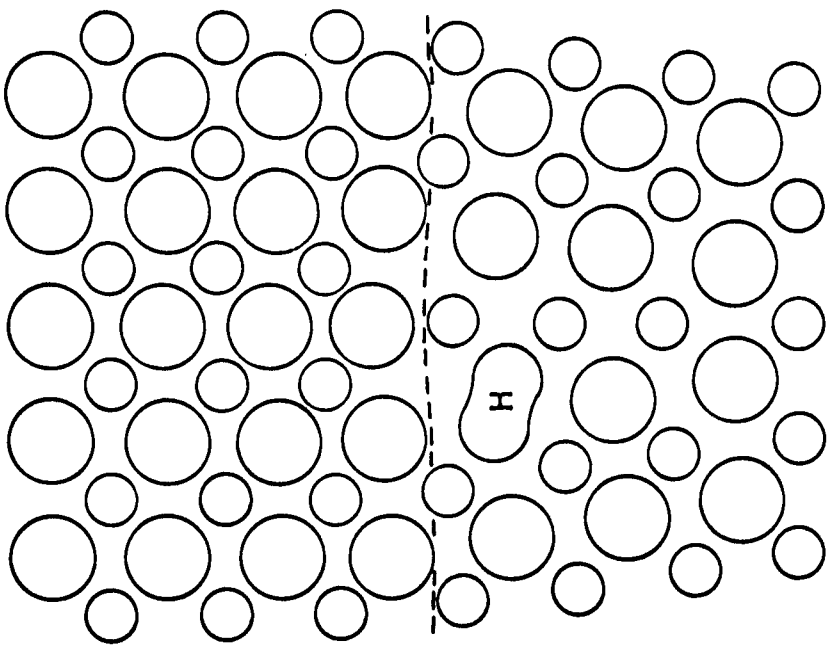
(g, h) Induced crowdion mechanism in which strains arising from the formation of an interstitial molecule induce displacement of an anion-cation pair to the dislocation core, the molecule occupying the resulting divacancy. A mechanism for arriving at the configuration in (h) from initial condensation of a halogen molecule at the core, as in (f), is indicated in fig. 5.44.



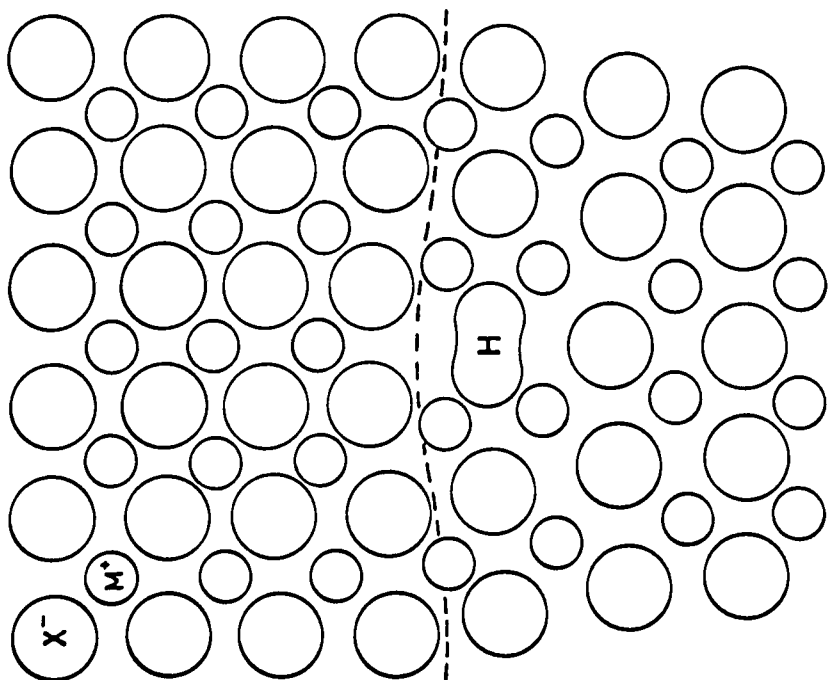
(a)



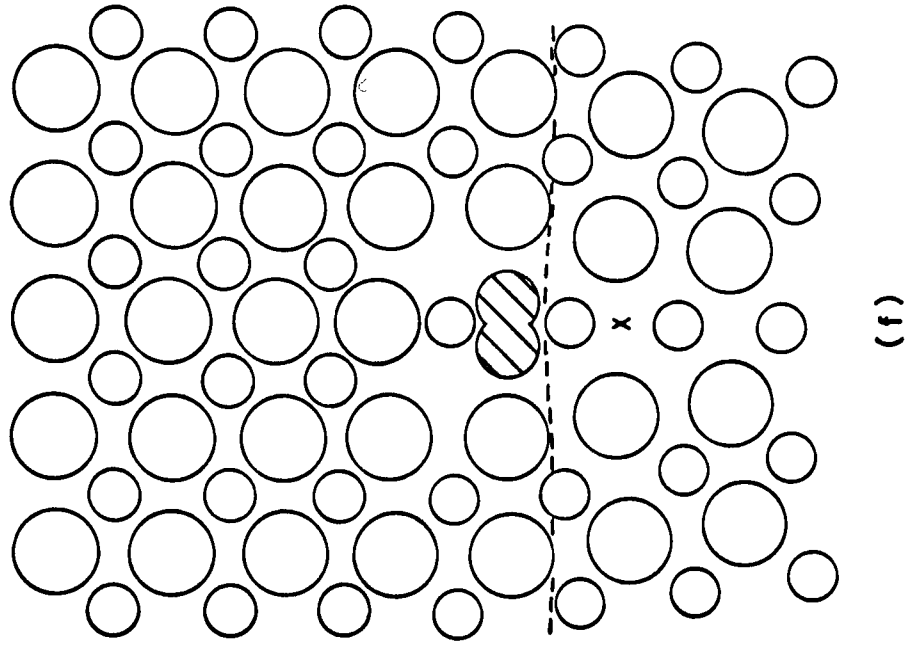
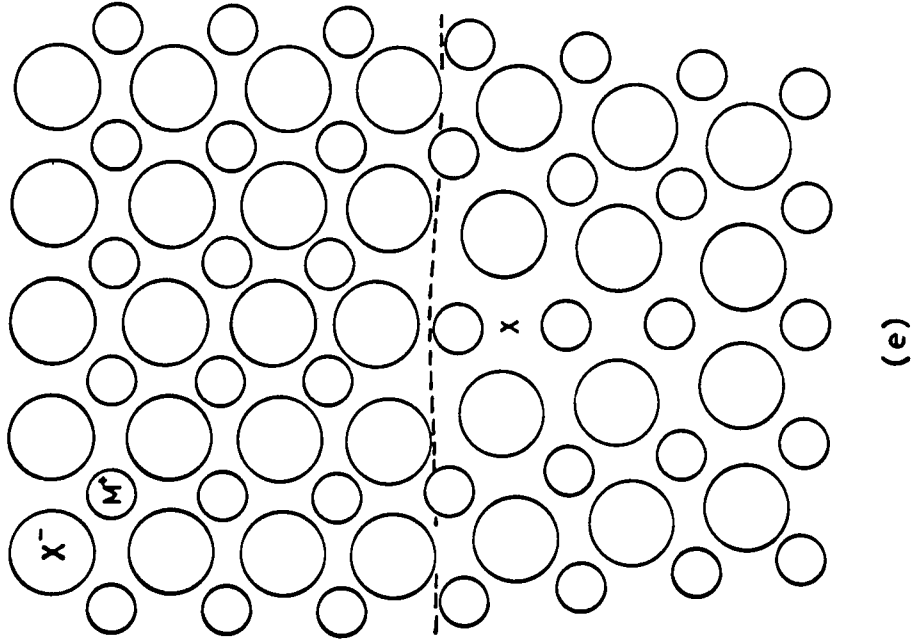
(b)

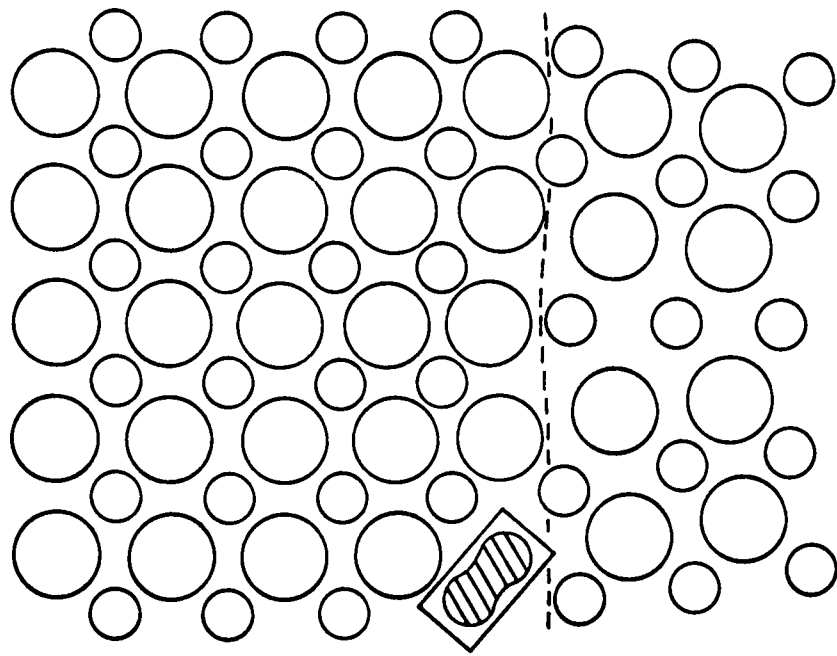


(d)

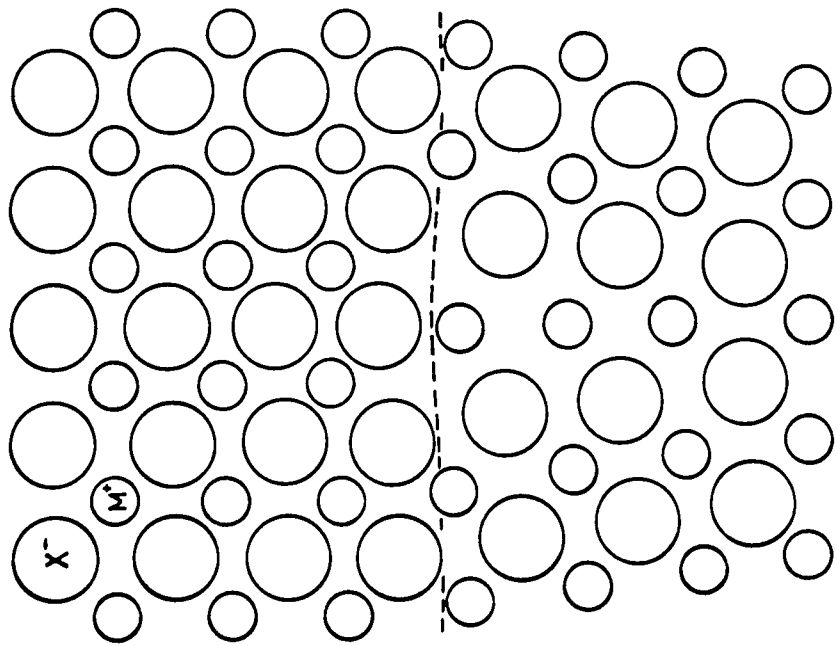


(c)





(h)



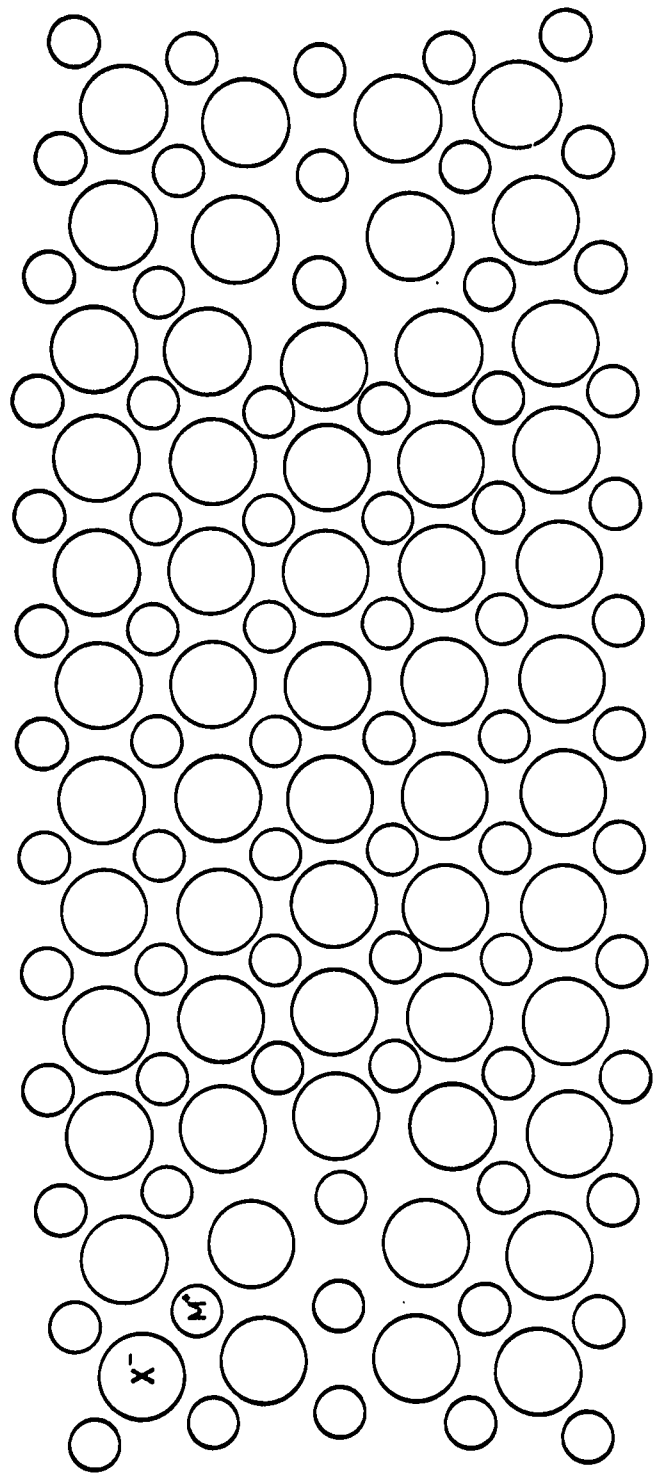
(g)

Fig. 5.41. Three models for planar loop clusters with $R \approx a/2 \langle 110 \rangle$ based on the climb mechanisms illustrated in fig. 5.40. For simplicity, pure edge loops are illustrated, viewed edge-on.

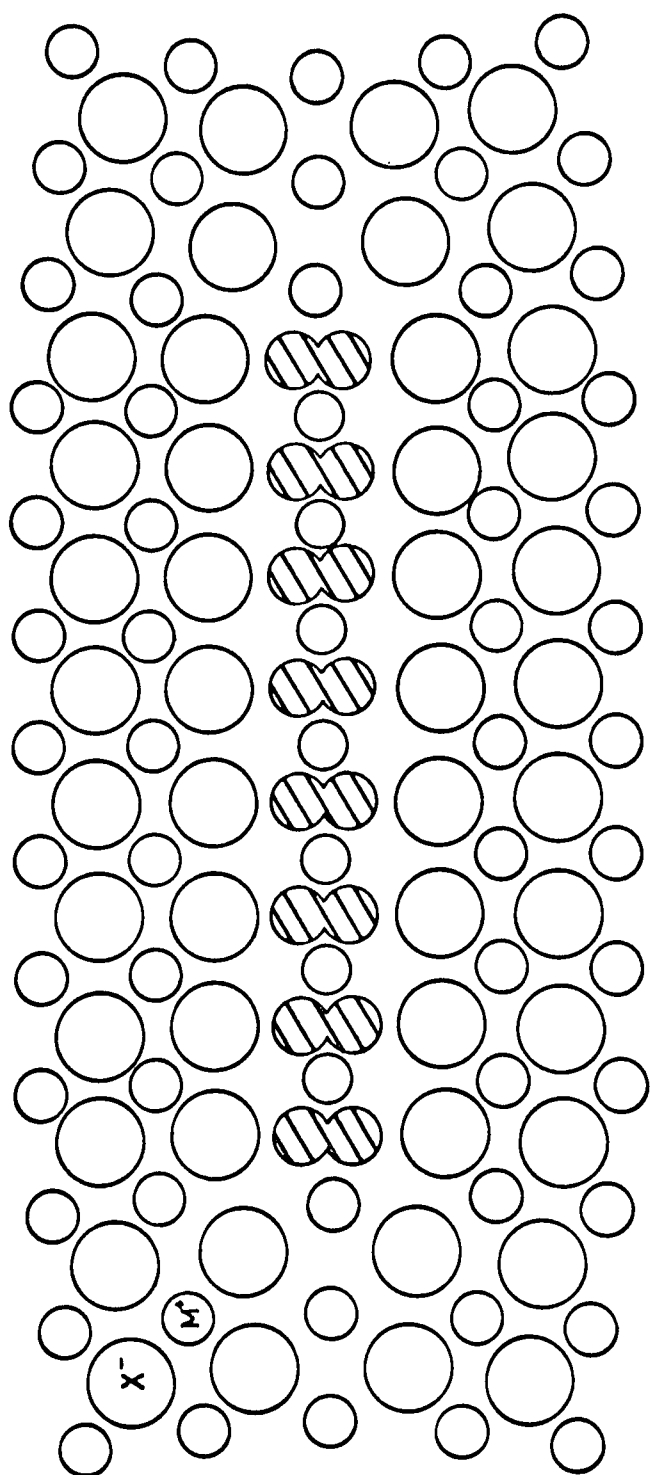
(a) Perfect dislocation loop.

(b) $|X_2^O|$ planar precipitate. Elastic dipole-dipole interactions between neighbouring molecules are able to explain loop orientation.

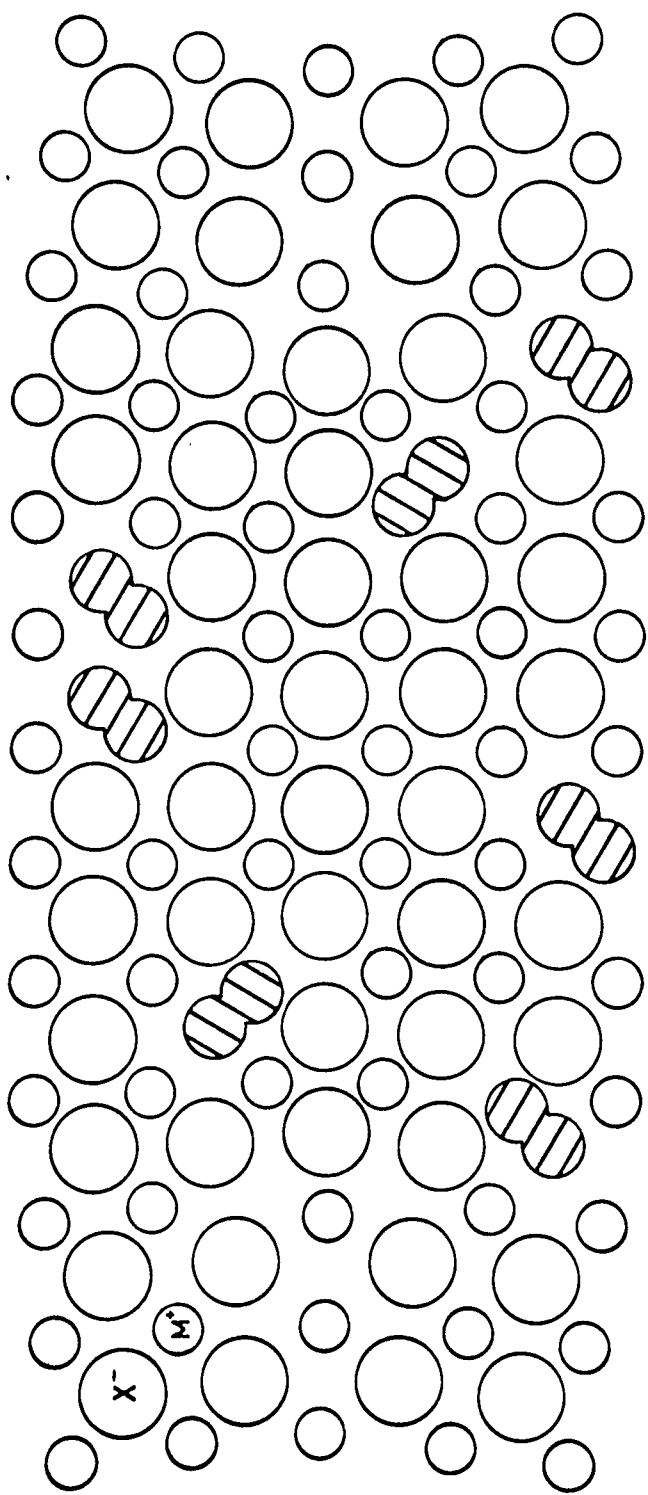
(c) Molecule-induced perfect loop. The halogen molecules responsible reside in the divacancies they induce and lie randomly distributed on either side of the dislocation core. A molecule-divacancy defect is essentially an $|H_V^+|$ centre and has a substantial electric dipole moment.



(a)

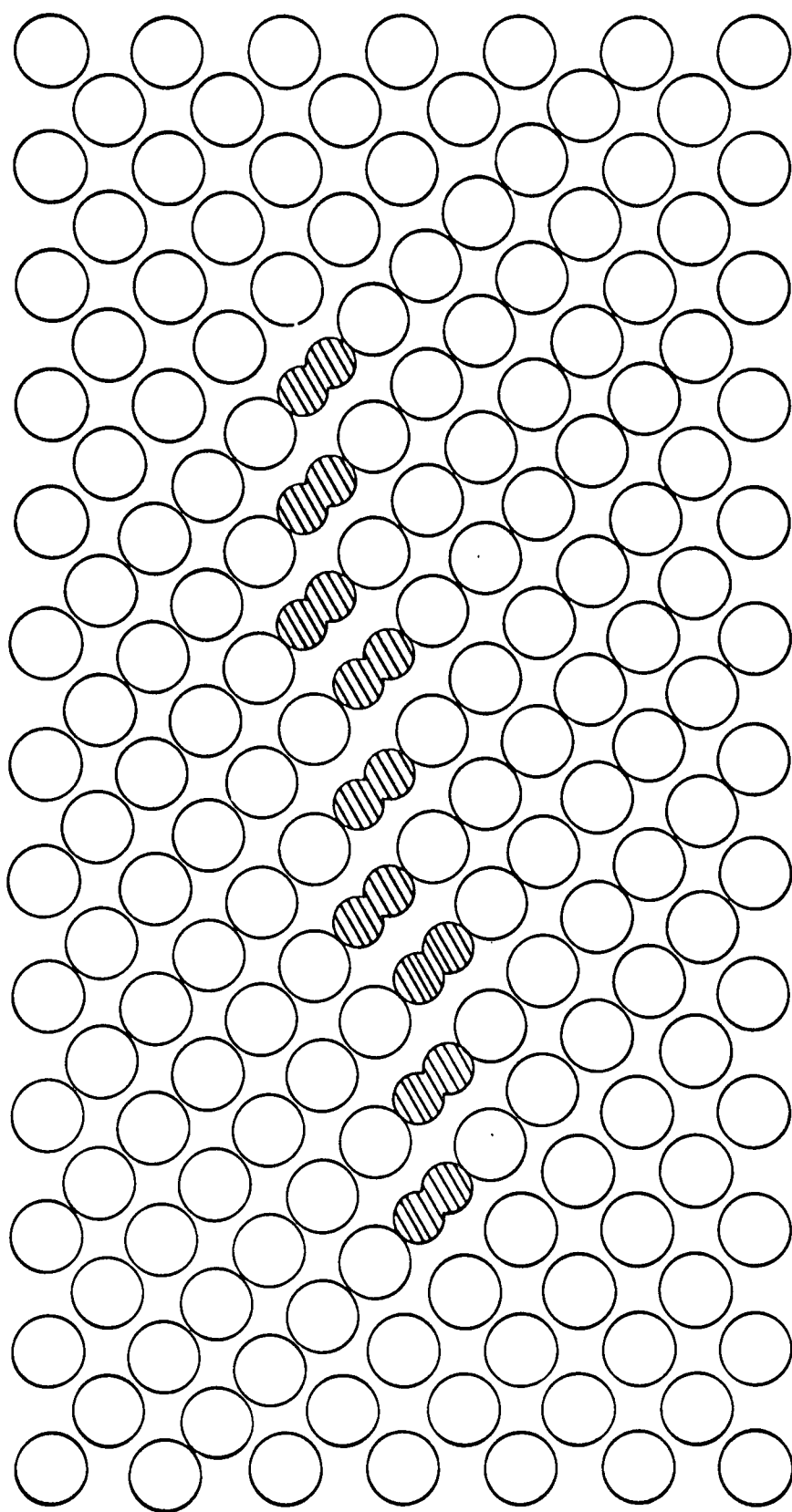


(a)



(c)

Fig. 5.42. Staggered halogen molecule precipitate viewed edge-on, producing a loop normal $\underline{n}$ between $|101|$ and $|001|$. In externally irradiated crystals, a loop normal $\sim 10^\circ$ from $|101|$, $\sim 35^\circ$ from $|001|$ is observed. For in situ irradiation in (001) foils, $\underline{n}$ is nearer $|001|$.



(100) HALIDE SUBLATTICE

- . Fig. 5.43. Behaviour of the elastic interaction between molecular dipoles. θ is the angle between the vector joining adjacent dipole centres and the dipole axis, the dipole axes assumed to be parallel. v is assumed to be 0.25. Maximum attractive interaction occurs at $\theta = 57^\circ$, strong repulsion occurs for $\theta < 39^\circ$.

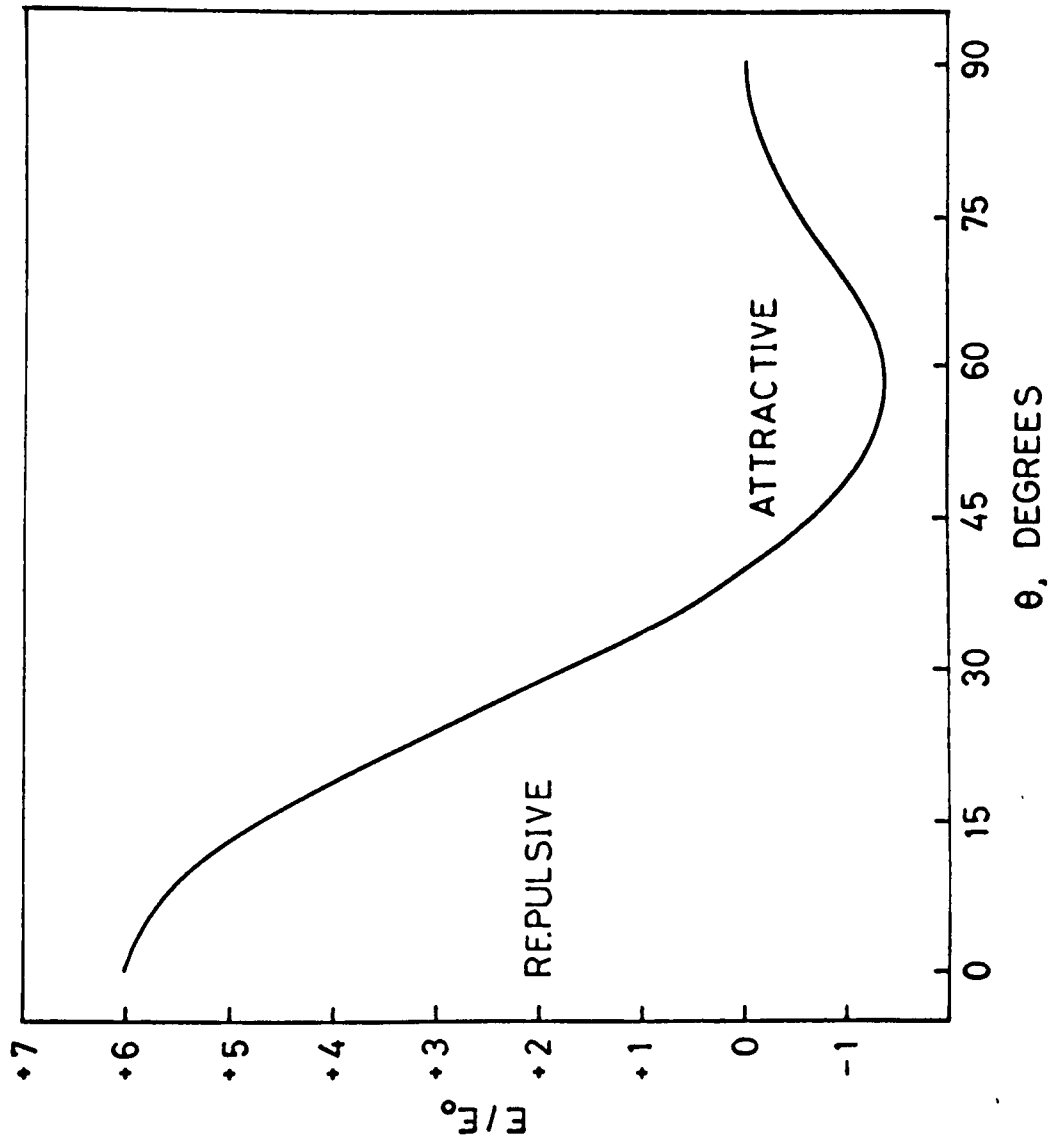


Fig. 5.44. Planar loop nucleation in very thin foils on the molecular precipitation models. A, B and C refer to eventual loop configurations as described in fig. 5.2 for KCl. Initial nucleation in orientation C is least favoured in the presence of surface image forces, orientation B most favoured.

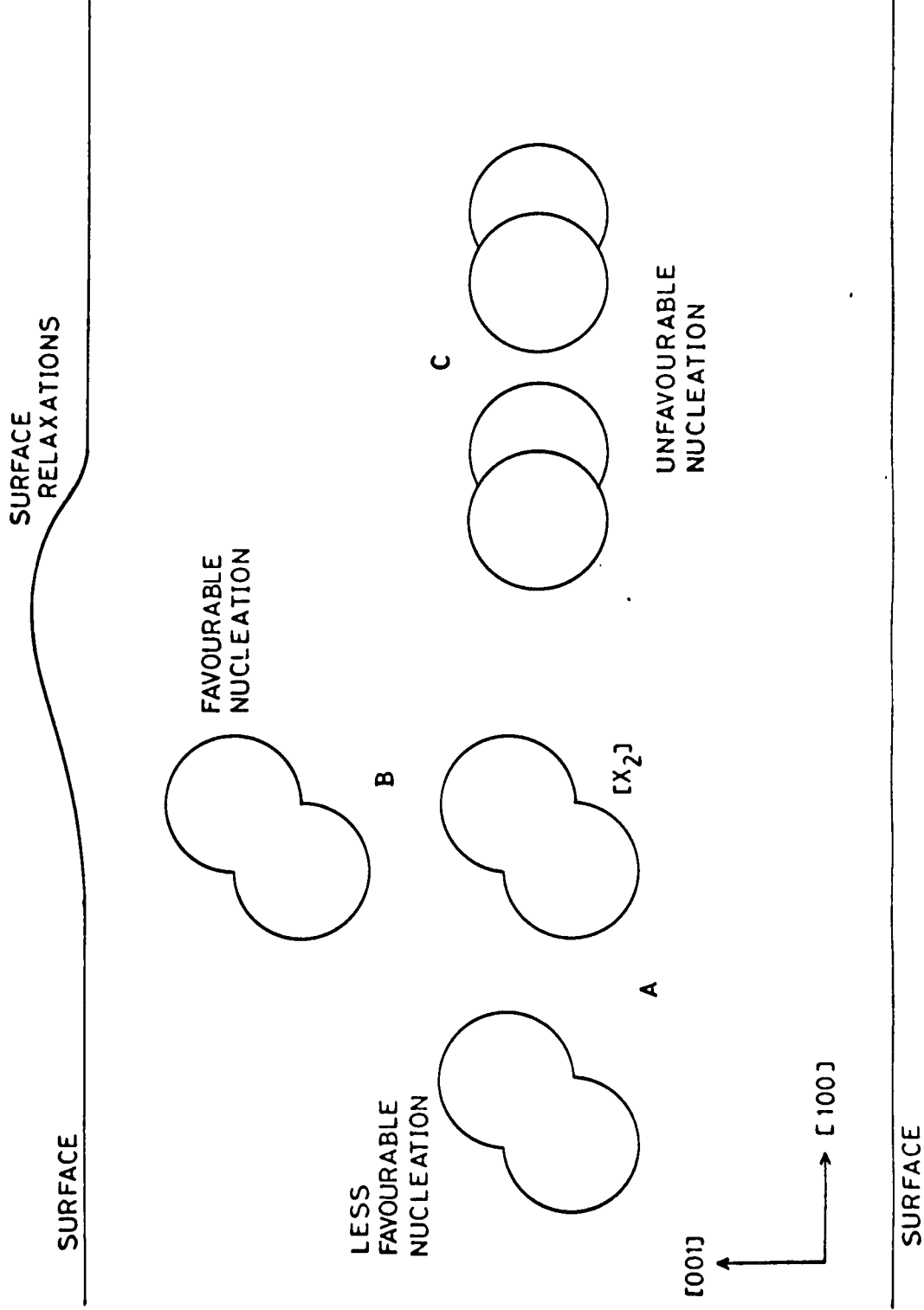
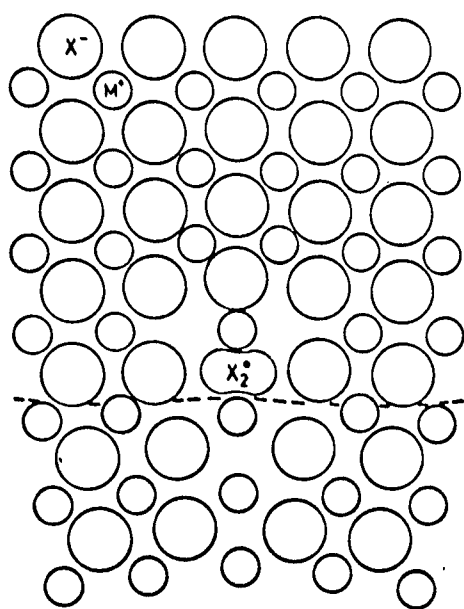
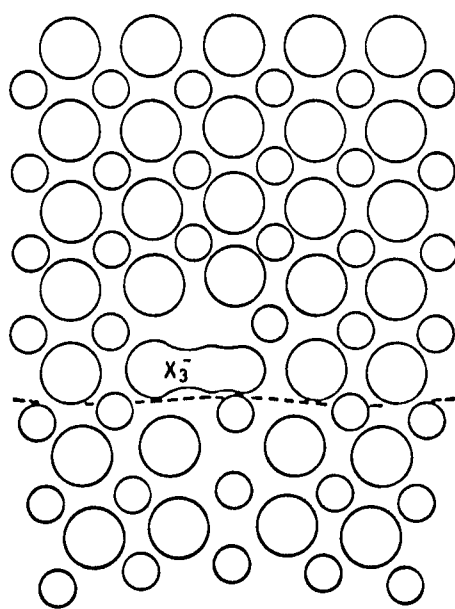


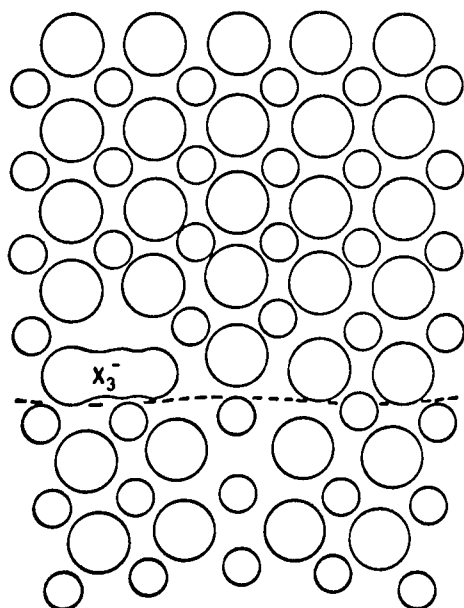
Fig. 5.45. Transport mechanism for converting $|X_2^0|$ precipitation at a dislocation core, fig. 5.40f to the molecule-divacancy configuration, fig. 5.40h. An $|X_3^-|$ molecular ion transports itself by hole motion along $\langle 110 \rangle$ just above the slip plane, accompanied at each stage by adjacent cation motion in the opposite direction, until the molecule finally relaxes into the resulting cation vacancy at some position well removed from the loop core.



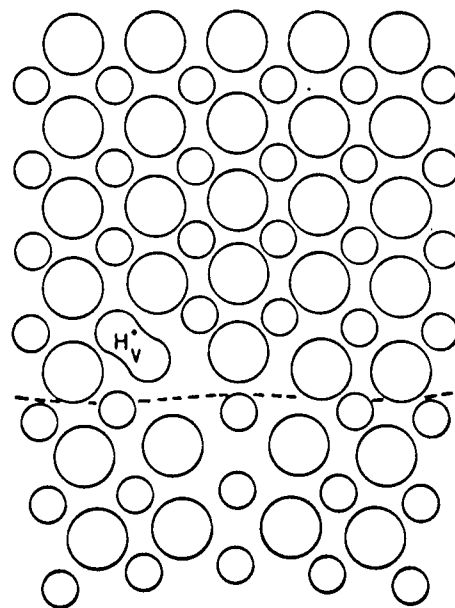
(a)



(b)



(c)



(d)

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