

SOME COMPUTATIONS ON THE BAND STRUCTURE
OF METALS.

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ABSTRACT.

The work is in two parts, the first part is concerned with the theory of symmetry adapted functions for all the cubic space groups and the second part is concerned with an application of this theory to band structure calculations, using the cellular method, for metals of one particular space group ($Fm\bar{3}m$) and the physical interpretation of the bands computed.

PART 1.

In the first chapter a brief introduction is given to the concepts and notation which are used extensively in the following chapters. In these chapters lattice harmonics are given for all the irreducible representations of the simple cubic ($Pm\bar{3}m$), face-centred cubic ($Fm\bar{3}m$) and body-centred cubic ($Im\bar{3}m$) space groups for $l \leq 12$. A general discussion of the treatment of asynmorphic space groups is given and one example is considered by way of illustration of the general method. The irreducible representations and lattice harmonics are discussed but the complete results which have been obtained for all the cubic and tetragonal groups have not been reproduced here for lack of space. All the expansions are given in polar coordinates and care has been taken that different bases corresponding to the same representation span identical rather equivalent representations, which are given in full. Moreover, all the different expansions listed in the tables

are fully orthogonal.

PART 2.

Part 2 is concerned with the use of some of the lattice harmonics deduced in Part 1 in a cellular calculation on several face centred cubic metals. A programme has been written for a Ferranti "Mercury" computer which can be used for any face-centred cubic metal provided the lattice spacing and the potential due to a free ion of the metal are available. The programme, which is fully automatic, calculates energies and wave functions at the points of symmetry and along the lines of symmetry in the Brillouin zone and from this the band structure of the metal is reconstructed. Chapters I - IV describe the details of the theory and of the programme, and some of the difficulties and errors are considered. The results of the computations are presented in Chapter V. From these band structures the density of states and Fermi surface are computed and in Chapter VI the observable quantities deducible from them are considered; these include the temperature coefficient of the electronic specific heat, the Pauli spin paramagnetic susceptibility, the de Haas-van Alphen effect, the high pressure behaviour of the electrical resistance of calcium, the magnetoresistance, the Knight shift and the effective mass. In chapter VII a self-consistent potential field for calcium is considered; this is a Hartree self-consistent

field among the conduction electrons with an approximate consideration of the inner 3s and 3p electrons.

A good review, by Callaway (1964), of the present state of band theory has just been published since the writing of this thesis.

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N.B. Where cross references are given in Part 1 to another Chapter, Section, Figure or Table these are also in Part 1 unless it is stated to the contrary; similarly in Part 2.

SYMMETRY ADAPTED FUNCTIONS FOR THE CUBIC
SPACE GROUPS.

CHAPTER I. INTRODUCTORY CHAPTER.

1.1 Preamble.

This work is concerned with using the knowledge of the symmetry properties of a physical or chemical system to simplify calculations of some of the measurable properties of that system. The particular application we shall be concerned with in part II is the case of the motion of electrons in the periodic potentials known to be present in metals. Part I is of completely general application to any case in which one requires a function possessing the symmetry of any subgroup of one of the cubic space groups. The work has been done in its somewhat lengthy entirety in the hope that the results will prove useful to people engaged on calculations of all kinds in cubic solids and possibly in complex cubic molecules, though of course usually the symmetry of a molecule is that of a point group. Functions possessing the symmetry of the irreducible representations of the five cubic point groups are already tabulated in several places up to $l = 6$, and they are given up to $l = 12$ by Altmann & Bradley (1963). Here, following that paper, spherical polar co-ordinates are used rather than cartesian co-ordinates for expressing the symmetry adapted functions. The reason is that in a calculation using a high order expansion of some function it is easier to calculate the spherical harmonics in terms of θ, ϕ , because

of the recurrence relations between the $P_l^m(\cos\theta)$ than to find the corresponding functions in terms of x, y, z .

These symmetry adapted functions are thus largely for application to problems in solid state theory and so perhaps it is as well to consider briefly the relationship between the mathematical theory behind the derivation of the space groups and the actual structure of a solid in terms of atoms and ions. In practice the space group of a particular solid is found by first of all using X-rays to find out how the atoms are arranged in the unit cell of the solid. Having found the structure it is only necessary to refer to the published sets of tables giving all possible positions of atoms in the unit cell for each space group to assign the solid to the appropriate space group. The standard reference is published by the International Union of Crystallography (1952).

1.2 Point Group, Bravais Lattice & Crystal System.

As is well known the point groups are sets of symmetry operators acting at a point and obeying the mathematical requirements of a group. Such operations are the identity, inversion, reflexion in a plane, and rotation about axes of order 1, 2, 3, 4, or 6. The 32 point groups can be classified into 7 crystal systems (or "syngonies") according to the order of the principal axis. There are five crystal systems for point groups with a principal axis of order 1, 2, 3, 4, or 6, -- the triclinic, monoclinic, trigonal, tetragonal and hexagonal

systems; and two more systems are also possible, the orthorhombic with 3 mutually perpendicular 2-fold rotation axes, and the cubic system with four 3-fold rotation axes directed towards the vertices of a regular tetrahedron. One can also consider another collection of groups, this time consisting only of translational symmetry operations; these are the 14 Bravais Lattices. Because these Bravais Lattices satisfy the mathematical requirements of a lattice (namely, the environment of any lattice point is exactly similar to that of any other point) they too can be divided among the 7 crystal systems according to their symmetry.

1.3 Space Group.

A space group arises by associating with each point of a Bravais lattice one of the point groups belonging to the same crystal system. In this way it is possible to obtain $\{n_1 p_1$ space groups where n_1 is the number of point groups in a certain crystal system and p_1 is the number of Bravais lattices in that system, the suffix 1 ranging over the 7 crystal systems. Since there are 5 cubic Bravais lattices and 5 cubic point groups there are 15 cubic space groups which can be derived in this way. This type of space group is said to be symmorphic, and it is a ^{semi-}direct product group of a point group and the translation group of the Bravais lattice. It should be noticed that it is possible to associate a trigonal point group with the hexagonal Bravais lattice so that for the

trigonal system $p_1 = 2$ ⁴ even though there is only one trigonal Bravais Lattice. Even so it does in fact happen that there can sometimes be two different orientations of a point group possible on the Bravais Lattice; this leads to a few extra symmorphic space groups which occur irregularly as shown in column 6 of Table 1.1. There are in fact 73 different symmorphic space groups.

A second type of space group can arise by starting with a symmorphic space group and replacing some of the reflexion planes by glide reflexion planes and some of the rotation axes by screw rotation axes; these are commonly called glide planes and screw axes respectively. If we denote a general space group operator by $(\underline{R}/\underline{t})$ a screw axis consists of a rotation $2\pi/n$ about an axis, so that with the translation $\underline{t}$ along this axis, $(\underline{R}/\underline{t})^n$ has a translation $n\underline{t}$ which must be equal to an integral number of lattice spacings in that direction. Similarly a glide plane is a plane with a translation in one of the crystal axis directions which is in that plane, again so that two successive translations of this type will be equal to an integral number of lattice spacings. It should be mentioned that when there are screw axes or glide planes present the operators need not all act at one point. They can however be made to act at a point, but then the translations may lose their sense of being along the axis of the "screw" rotation or in the plane of the "glide" plane and be in some strange direction. The number

of space groups of this type is finite because the mathematical defining properties of a group must be satisfied and they are distributed among the crystal systems as shown in the last column of Table 1.1. There are altogether 157 asymmetric space groups, and an analysis of them is given in Table 1.1.

TABLE 1.1 THE CLASSIFICATION OF THE 230 SPACE GROUPS.

crystal system	s	n_1	p_1	$n_1 p_1$	col 6	col 7	col 8	col 9
triclinic	1	2	1	2	-	2	-	2
monoclinic	2	3	2	6	-	6	7	13
orthorhombic	-	3	4	12	1	13	46	59
tetragonal	4	7	2	14	2	16	52	68
trigonal	3	5	2*	10	3	13	12	25
hexagonal	6	7	1	7	1	8	19	27
cubic	-	5	3	15	-	15	21	36
total	-	15**	32	66	7	73	157	230

* $n_1 = 2$, but only 1 trigonal Bravais Lattice.

** note that the hexagonal lattice is counted here twice.

col 7 is the total number of symmetric space groups in the given system, col 8 the total number of asymmetric space groups in the system, and col 9 the total number of space groups of either kind in the system.

s = order of the principal axes in the cases where it exists.

1.4 Seitz Space Group Operators.

It is customary to represent a general space group operation by the symbol $(\underline{R}/\underline{t})$ with the meaning that $\underline{R}$ is one of the point-group operations, and $\underline{t}$ is the translation vector associated with it. $\underline{R}$ can then be represented by a 3 by 3 matrix acting either on the points (x,y,z) of space or on the x, y, z axes of space. In symmorphic space groups all the elements have $\underline{t} = 0$. In asymmorphic space groups the screw axes and glide planes have non-zero $\underline{t}$. There is a simple but important relation for the multiplication of these operators:

$(\underline{R}_2/\underline{t}_2)(\underline{R}_1/\underline{t}_1) = (\underline{R}_2\underline{R}_1/\underline{t}_2 + \underline{R}_2\underline{t}_1)$, where the active operators $\underline{R}$ are used.

Proof.

$(\underline{R}_1/\underline{t}_1)$ operating on the vector $\underline{x}$ produces $\underline{x}'$.

so that $\underline{x}' = \underline{R}_1\underline{x} + \underline{t}_1$,

and $\underline{x}'' = \underline{R}_2\underline{x}' + \underline{t}_2$

$$= \underline{R}_2(\underline{R}_1\underline{x} + \underline{t}_1) + \underline{t}_2$$

$$= \underline{R}_2\underline{R}_1\underline{x} + (\underline{R}_2\underline{t}_1 + \underline{t}_2)$$

$$= \underline{R}\underline{x} + \underline{t}.$$

therefore $(\underline{R}_2/\underline{t}_2)(\underline{R}_1/\underline{t}_1) = (\underline{R}_2\underline{R}_1/\underline{t}_2 + \underline{R}_2\underline{t}_1)$.

The Seitz Space-group Operators for all the 230 space groups are listed, with a few errors, by Lyubarskii (1960).

(P.T.O.)

1.5 Classification and Labelling of Space Groups.

Before going on to the more detailed consideration of the cubic space groups there are just one or two remarks which should be made about space groups in general. The fact that the introduction of screw axes and glide planes leads to 157 asynorphic space groups was independently discovered by three workers towards the end of the nineteenth century, Fedorov, a Russian, Schoenflies, a German, and Barlow, a Londoner. At this stage it is as well to mention the "black and white" or "magnetic" space groups or Shubnikov groups which are obtained by considering a space with a spin variable as well as the x, y, z co-ordinates. That is, we are concerned with the symmetry properties of crystals in which the atoms' spins are to be included in the considerations. Alternatively, one can imagine each space-group operator to be associated with a further operator which can either turn white into black or black into white. These black and white space groups have been derived logically from the 230 (Fedorov) space groups by Shubnikov and his followers (1957). There are 1191 "black and white" space groups, which together with 230 "all black" and 230 "all white" space groups make up a total of 1651 Shubnikov groups. These are only mentioned here for completeness and will not be mentioned again.

Space groups are classified according to the seven crystal systems, then according to the 73 symorphic space

groups. All space groups containing screw axes or glide planes are classed with the symmorphic space group which would be obtained by putting $\underline{t} = 0$ in all the operators of the group. A space group is said to be 'isogonal', or by some crystallographers 'isomorphous', to the point group obtained by taking the group of all the $\underline{R}$'s present in the operations of the space group. Each space group is given the label of its isogonal point group and then some distinguishing label is attached to this; this is just an index number in the Schoenflies notation, the space groups being numbered straight through all the p_1 sets of space groups isogonal to the given point group (p_1 = number of Bravais lattices compatible with point groups of that system.) There are, for example, ten space groups isogonal to O_h ($m\bar{3}m$) and these are distributed among the three cubic Bravais lattices 4 primitive, 4 face-centred, and 2 body-centred, and are numbered $O_h^1, O_h^2, \dots, O_h^{10}$. This has the disadvantage that it is not possible to tell at a glance on which Bravais lattice the space group is based; e.g. O_h^8 is face-centred and O_h^9 is body-centred. Moreover there is no indication of whether the space group is symmorphic or asymmorphic. Both these disadvantages are overcome by using the international notation. Starting with the international point group symbol, e.g. $m\bar{3}m$, this is prefixed by the letter describing the Bravais lattice, e.g. P, F, I, for primitive, face-centred, and body-centred cubic respectively.

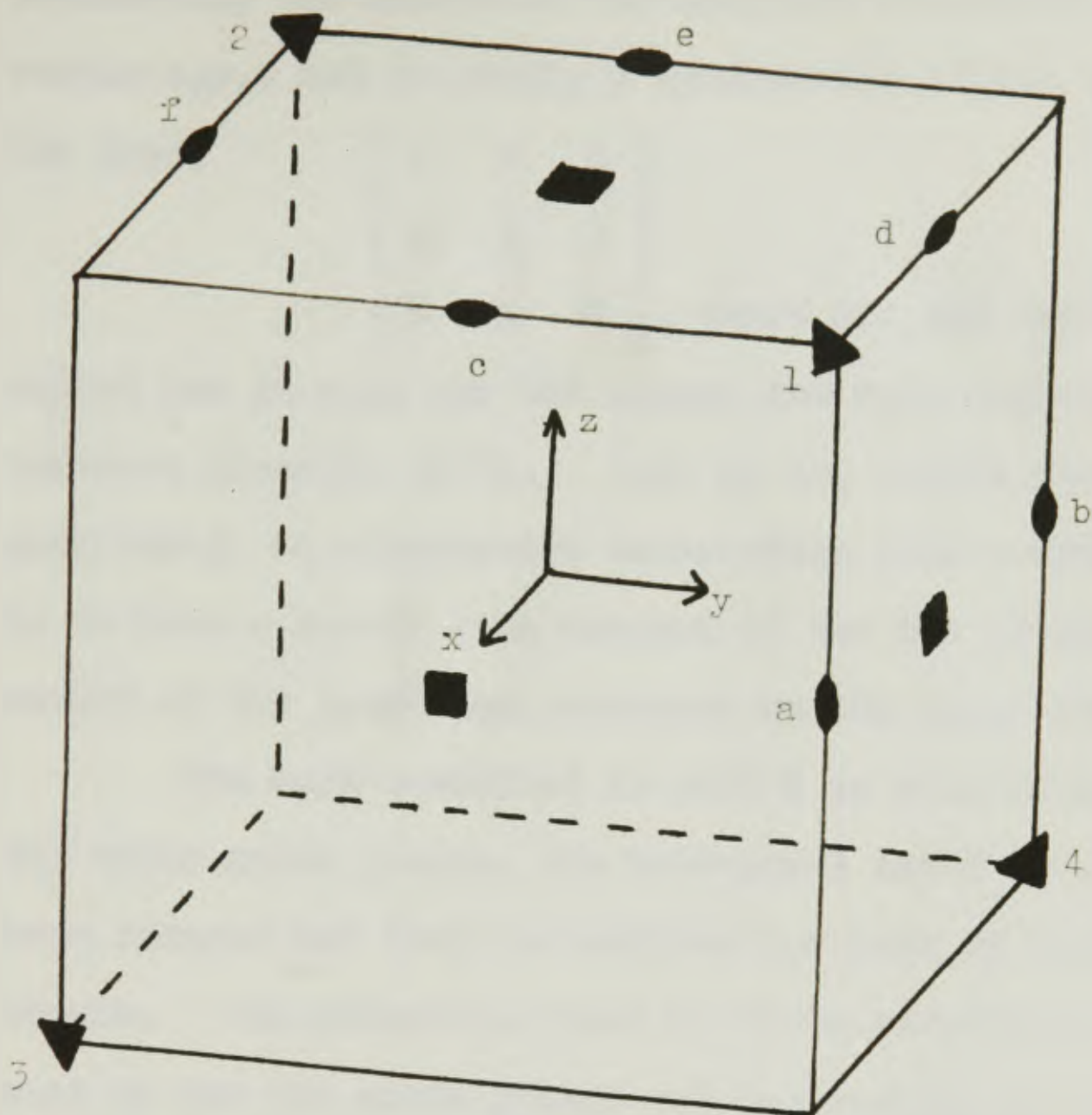
thus we get the symbols $Rm\bar{3}m$, $Fm\bar{3}m$ and $Im\bar{3}m$. These denote the three symmorphic space groups isogonal to the point group $m\bar{3}m (O_h)$. For asymmorphic space groups then, for any reflexion plane which has been replaced by a glide plane the appropriate part of the point group symbol is replaced by a letter (a, c, or d) denoting a glide plane; a, c, are used for glides in the x, z, directions and d for glides in a diagonal direction, the (1,1,1) or (1,1,0) direction as the case may be. Thus $Rd\bar{3}c (O_h^8)$ is face-centred and asymmorphic and $Im\bar{3}m (O_h^9)$ is body-centred and symmorphic. The 36 cubic space groups are listed in Appendix II in the international notation; also the arbitrary international space group number is given.

1.6 Notation of the Symmetry Elements of the Cube.

Here we follow the notation of Altmann & Bradley (1963). The symmetry operations of the point group $m\bar{3}m (O_h)$ are shown in Figure 1.1, E is the identity operator and I the inversion operator, C_{2m} , C_{2p} , are two-fold rotations about the axes shown, C_{3f}^+ , C_{4m}^+ , are three-fold and four-fold rotations about the axes shown. The elements listed in the right hand column are the product of the inversion and the corresponding element in the left hand column. Other cubic point groups are sub-groups of this group.

The relation of these elements to those used by other authors will be clarified by the table in Appendix I. The correspondence with that used by other authors can readily be

FIGURE 1.1: THE SYMMETRY ELEMENTS OF THE CUBE.



ELEMENTS.

$E,$

$I,$

$C_{2m},$

$\sigma_m,$

$m = x, y, z,$

$C_{3i}^{\pm},$

$S_{6i}^{\mp},$

$i = 1, 2, 3, 4,$

$C_{2p},$

$\sigma_{dp},$

$p = a, b, c, d, e, f,$

$C_{4m}^{\pm},$

$S_{4m}^{\mp},$

$m = x, y, z.$

obtained via the Jones' faithful representation which records immediately the effect of the operator concerned on the vector x, y, z and is really a contraction of the matrices of

the type:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix}$$

, where all the matrix elements except one in each row and column are zero and each of the non-zero elements is ± 1 . This is the active sense of the operators; an alternative description (the passive sense) is to have a matrix (the inverse of the one given) for the effect of the operation concerned on the x, y, z axes.

The work described in part I is only concerned with the cubic space groups, the tetragonal space groups have also been reduced but they are omitted for lack of space in this thesis. The principles used in their reduction are just the same as for the cubic groups and the working is a little easier.

APPENDIX I: THE OPERATIONS OF THE POINT GROUP $m\bar{3}m$ (O_h).

This work		Jones		Herring	
E	I	xyz	$\bar{x}\bar{y}\bar{z}$	ϵ	i
C_{2x}	σ_x	$x\bar{y}\bar{z}$	$\bar{x}yz$	δ_{2x}	ρ_{2x}
C_{2y}	σ_y	$\bar{x}y\bar{z}$	$x\bar{y}z$	δ_{2y}	ρ_{2y}
C_{2z}	σ_z	$\bar{x}\bar{y}z$	$xy\bar{z}$	δ_{2z}	ρ_{2z}
C_{4x^-}	S_{4x^+}	xzy	$\bar{x}\bar{z}y$	δ_{4x^-}	σ_{4x^-}
C_{4y^-}	S_{4y^+}	$\bar{z}yx$	$z\bar{y}\bar{x}$	δ_{4y^-}	σ_{4y^-}
C_{4z^-}	S_{4z^+}	$y\bar{x}z$	$\bar{y}\bar{x}\bar{z}$	δ_{4z^-}	σ_{4z^-}
C_{4x^+}	S_{4x^-}	xzy	$\bar{x}z\bar{y}$	δ_{4x^+}	σ_{4x^+}
C_{4y^+}	S_{4y^-}	$\bar{z}yx$	$\bar{z}\bar{y}x$	δ_{4y^+}	σ_{4y^+}
C_{4z^+}	S_{4z^-}	$y\bar{x}z$	$y\bar{x}\bar{z}$	δ_{4z^+}	σ_{4z^+}
C_{31^-}	S_{61^+}	$y\bar{z}x$	$\bar{y}\bar{z}\bar{x}$	$\delta_{3x\bar{y}z}$	$\sigma_{6x\bar{y}z}$
C_{32^-}	S_{62^+}	$y\bar{z}\bar{x}$	$\bar{y}zx$	$\delta_{3\bar{x}yz}$	$\sigma_{6\bar{x}yz}$
C_{33^-}	S_{63^+}	$\bar{y}z\bar{x}$	$y\bar{z}x$	$\delta_{3\bar{x}\bar{y}z}$	$\sigma_{6\bar{x}\bar{y}z}$
C_{34^-}	S_{64^+}	$\bar{y}zx$	$y\bar{z}\bar{x}$	$\delta_{3x\bar{y}\bar{z}}$	$\sigma_{6x\bar{y}\bar{z}}$
C_{31^+}	S_{61^-}	zxy	$\bar{z}\bar{x}\bar{y}$	$\delta_{3x\bar{y}z}^+$	$\sigma_{6x\bar{y}z}^+$
C_{32^+}	S_{62^-}	$\bar{z}xy$	$z\bar{x}\bar{y}$	$\delta_{3\bar{x}yz}^+$	$\sigma_{6\bar{x}yz}^+$
C_{33^+}	S_{63^-}	$\bar{z}\bar{x}\bar{y}$	zxy	$\delta_{3\bar{x}\bar{y}z}^+$	$\sigma_{6\bar{x}\bar{y}z}^+$
C_{34^+}	S_{64^-}	$z\bar{x}\bar{y}$	$\bar{z}xy$	$\delta_{3x\bar{y}\bar{z}}^+$	$\sigma_{6x\bar{y}\bar{z}}^+$
C_{2a}	σ_{da}	$y\bar{x}\bar{z}$	$\bar{y}\bar{x}z$	δ_{2xy}	ρ_{xy}
C_{2b}	σ_{db}	$\bar{y}\bar{x}z$	$y\bar{x}\bar{z}$	$\delta_{2\bar{x}y}$	$\rho_{\bar{x}y}$
C_{2c}	σ_{dc}	$\bar{z}yx$	$\bar{z}\bar{y}\bar{x}$	δ_{2zx}	ρ_{zx}
C_{2d}	σ_{dd}	$\bar{x}zy$	$x\bar{z}\bar{y}$	δ_{2yz}	ρ_{yz}
C_{2e}	σ_{de}	$\bar{z}\bar{y}\bar{x}$	zyx	$\delta_{2\bar{z}x}$	$\rho_{\bar{z}x}$
C_{2f}	σ_{df}	$\bar{x}\bar{z}\bar{y}$	xzy	$\delta_{2\bar{y}z}$	$\rho_{\bar{y}z}$

APPENDIX II: THE CUBIC SPACE GROUPS.

P		F		I	
P23	195	F23	196	I23	197
P2 ₁ 3	198			I2 ₁ 3	199
Pm3	200	Fm3	202	Im3	204
Pa3	205			Ia3	206
Pn3	201	Fd3	203		
P43m	215	F43m	216	I43m	217
P43c	218	F43c	219	I43d	220
P432	207	F432	209	I432	211
P4 ₁ 32	213	F4 ₁ 32	210	I4 ₁ 32	214
P4 ₂ 32	208				
P4 ₃ 32	212				
Pn3m	221	Fm3m	225	Im3m	229
Pn3c	223	Fm3c	226		
Pn3n	224	Fd3m	227		
Pn3c	222	Fd3c	228	Ia3d	230

CHAPTER II. LATTICE HARMONICS FOR THE SPACE

GROUPS $Pm\bar{3}m$, $Fm\bar{3}m$, $Im\bar{3}m$.

2.1 Introduction.

In many physical problems it is necessary to use linear combinations of spherical harmonics that belong to the irreducible representations of the space group of a crystal. They were first obtained by von der Lage & Bethe (1947), who considered only the cubic lattice. Rather than starting from spherical harmonics defined in polar coordinates they gave a method to obtain directly homogeneous polynomials in the cartesian coordinates x, y, z , with the required symmetry properties. von der Lage & Bethe called these polynomials cubic harmonics. Their work was extended for other space by Bell (1954), who introduced the name lattice harmonics for the linear combinations which she obtained. In the terminology of Melvin (1956) they are functions that are symmetry adapted with respect to the irreducible representations of a space group.

A similar problem arises when dealing with the point groups and Altmann (1957) gave a group-theoretical method to obtain symmetry-adapted spherical harmonics for them, working directly in polar coordinates. As regards the space groups, Altmann (1958) showed how his method could be extended for them, and considered the central point of the Brillouin Zone of the close-packed Hexagonal lattice. For

the cubic point groups the lattice harmonics are given for $1 \leq l \leq 12$, Altmann & Bradley (1963). The three cubic space groups which are considered in this chapter are assumed by a very large number of metal crystals: the results obtained were required for the work described in part 2. In the next chapter the rest of the cubic space groups will be considered.

2.2 General Theory.

The method used to obtain symmetry adapted functions is well known (see e.g. Altmann (1962)). Consider a group G of operations R , and assume given an irreducible representation of matrices $D^i(R)$. Then

$$\sum_{R \in G} D^i(R)^*_{ss} R$$

is a projection operator which applied to any function ϕ will adapt it into a function belonging to the s -th column of the i -th irreducible representation of G . In our case the function ϕ will always be a spherical harmonic.

Before we consider the way in which the above-mentioned methods for the point groups can be extended for the space-group operators, it is very important to pay attention to the following point. A symmetry operation can be interpreted either as an axes transformation (passive interpretation) or as a point transformation (active interpretation). The passive interpretation was the one used for the point groups by Altmann (1957) and Altmann & Bradley (1963), but the Seitz

space-group operators are active. If this interpretation were changed, the multiplication rule given in chapter I, §1.4, which is in general use in the literature would require alteration. Therefore we shall use the active interpretation throughout. The correspondence with the work on the point groups is immediate: the active operator $\underline{R}$ corresponds to the passive operator $\underline{R}^{-1}$. This rule also allows us to transform the matrix representations of the passive operators into those for the active ones.

The theory of the space groups given by Seitz (1936) and Bouckaert, Smoluchowski & Wigner (1936) (see also Koster (1957), Johnston (1960) and Altmann (1963)) shows that the bases of the irreducible representations of space groups are Bloch functions, $\psi_{\underline{k}}(\underline{r})$, such that if $(\underline{E}/\underline{t})$ is a translation of the translation subgroup Γ of the group,

$$(\underline{E}/\underline{t})\psi_{\underline{k}}(\underline{r}) = \psi_{\underline{k}}(\underline{r}-\underline{t}) = \exp(-i\underline{k}\cdot\underline{t})\psi_{\underline{k}}(\underline{r}) \quad (i)$$

Here the vector $\underline{k}$ is a label of the representation. An irreducible representation of a space group is fully determined by means of the group of the $\underline{k}$ vector, $G_{\underline{k}}$, (the subgroup of the operations of the space group that leave $\underline{k}$ invariant or transform it into an equivalent one) and one of its representations. The reduction of the space group is therefore achieved by the reduction of $G_{\underline{k}}$.

The space groups we deal with in this chapter are symmorphic. In this case all the operations of the space

group can be written as products $(\underline{R}/\underline{t})(\underline{R}/\underline{0})$, where $(\underline{R}/\underline{t}) \in \Gamma$. In the notation of Altmann (1963) $\underline{G}^{\underline{k}}$ can be expressed as a semi-direct product: $\underline{G}^{\underline{k}} = \underline{\Gamma} \ltimes \underline{U}^{\underline{k}}$, where $\underline{U}^{\underline{k}}$ the co-group of $\underline{k}$ is the subgroup of operations of the point group that belong to $\underline{G}^{\underline{k}}$. In this manner the reduction of the space group is achieved by reducing the point group $\underline{G}^{\underline{k}}$.

The operator $\sum_{\underline{R} \in \underline{G}} D^{\underline{k}}(\underline{R})^* \underline{R}$ applied on a spherical harmonic will now take the form

$$\sum_{\underline{R} \in \underline{G}} D(\underline{R}/\underline{t})^* (\underline{R}/\underline{t}) \sum_{\underline{G}^{\underline{k}}} D(\underline{R}/\underline{0})^* (\underline{R}/\underline{0}) Y_1^m$$

the summation being over the point-group operations. The result of this summation will be a spherical harmonic of order 1, symmetry-adapted to $\underline{U}^{\underline{k}}$, which we call $X_{1\nu}$. This is a linear combination of several Y_1^m with constant 1 and varying m : the index ν is an arbitrary label to distinguish the various harmonics of the same order that belong to the same representation. We shall always take $X_{1\nu} = X_{1\nu}(\varphi, \theta)$ as a function of the polar coordinates around the origin of coordinates for the lattice, $\underline{r} = 0$. Let us define $\underline{t}X_{1\nu}$ as a function identical with $X_{1\nu}$ except that it is centred around the point at the end of the vector $\underline{t}$ of the lattice ($\underline{r} = \underline{t}$). That is $(\underline{R}/\underline{t}) X_{1\nu} = \underline{t}X_{1\nu}$, so that, taking $D(\underline{R}/\underline{t}) = \exp(-i\mathbf{k} \cdot \underline{t})$ (see (i)), we have $\sum_{\underline{t}} e^{i\mathbf{k} \cdot \underline{t}} \underline{t}X_{1\nu}$, all $\underline{t} \in \Gamma$.

This multi-centred expansion is a lattice harmonic. It should be noticed that it is fully given if we know $X_{1\nu}$ in the unit cell at the origin. The expansion throughout

the lattice follows at once, if required, from the Bloch condition, as is apparent from above. Therefore it will be enough to give, for symmorphic groups, the expansions $X_{\mathbf{l}\nu}$; and the discussion of asymmorphic groups will be left until the following chapter.

2.2 The Method for the Cubic Groups.

It follows from the previous section that the problem of obtaining lattice harmonics for the cubic lattices is in principle solved: we must obtain harmonics adapted to the various $\underline{G}^{\mathbf{k}}$ groups that appear in the lattice. $\underline{G}^{\mathbf{k}}$ is a point group and clearly also a subgroup of the full cubic group $m\bar{3}m (O_h)$. Although $\underline{G}^{\mathbf{k}}$ may be a point group given in the tables of Altmann & Bradley (1963), it will often appear in our present work in an orientation that differs from the standard one and this causes a drastic change in the harmonics. Rather than repeating their work for these new orientations, the following method yields the results more quickly and in a more convenient form.

Consider the group of operators $\underline{G}^{\mathbf{k}}$, a subgroup of $m\bar{3}m$, and take an irreducible representation of $m\bar{3}m$ from the tables, with basis symbolically written as a row-vector $\langle \phi |$. The matrices of this representation that correspond to the operators of $\underline{G}^{\mathbf{k}}$ form a representation of $\underline{G}^{\mathbf{k}}$ which is called a subduced representation. This is, in general, reducible. We reduce it under a unitary transformation with a matrix U and we obtain the subduced irreducible representations of

of $\bar{G}^k$ that are required. At the same time the new bases are given, as is well known, by $\langle \psi | = \langle \phi | \underline{M}$. We therefore have the new symmetry adapted harmonics as well as the representations that they span.

In order to solve the problem as stated we must find the matrix $\underline{M}$ that reduces the subduced representation. Although most methods given in the literature for this purpose require a knowledge of the irreducible representations which appear under reduction, which would defeat our purpose, there is a method free from this drawback (Altmann (1962), p.123). The method is as follows. Consider a matrix representation which is to be reduced: take all the matrices of any class and sum them. Find the matrix $\underline{M}$ that diagonalises the matrix obtained, and this is the matrix which reduces the representation.

It should be noticed that two bases of the same representation may subduce into equivalent rather than identical representations. If this is the case a similarity transformation is required to make all the bases obtained span the same representation.

2.4 Normalisation.

As follows from above the symmetry-adapted spherical harmonics will be given as linear combinations of those for the cubic groups. The latter are given in tables 8 - 11 of Altmann & Bradley (1963). However in that paper unnormalized

spherical harmonics $y_l^m = P_l^m(\cos\theta)\exp(im\phi)$ were used, so as to give the necessary coefficients in the X_{1v} exact to any number of figures. In practical applications normalized spherical harmonics

$$Y_l^m(\theta, \phi) = \sqrt{\left(\frac{2l+1}{4\pi} \frac{(1-|m|)!}{(1+|m|)!}\right)} P_l^m(\cos\theta) e^{im\phi}$$

are required and expansions X_{1v} in terms of them were obtained on a Ferranti Mercury computer and are given in Table 2.1. The coefficients are correct to at least seven significant figures. Various checks and repeated calculation have been used to ensure that these tables are free from error.

2.5 Results.

We must first identify the co-groups $\underline{G}^k$ for all the k -vectors of symmetry in the cubic lattices. The latter are shown in Figures 2.1, 2.2, 2.3, in the standard notation of Bouckaert et al. (1956). For each k the symmetry operations of $\underline{G}^k$ are obtained in the notation of Figure 1.1 of chapter I. The character tables of the corresponding groups are given in Table 2.2, where the actual symmetry operations for each group can be identified from the heading. The two- and three-dimensional representations that appear under subduction are given in Table 2.3 and the symmetry-adapted harmonics in Table 2.4.

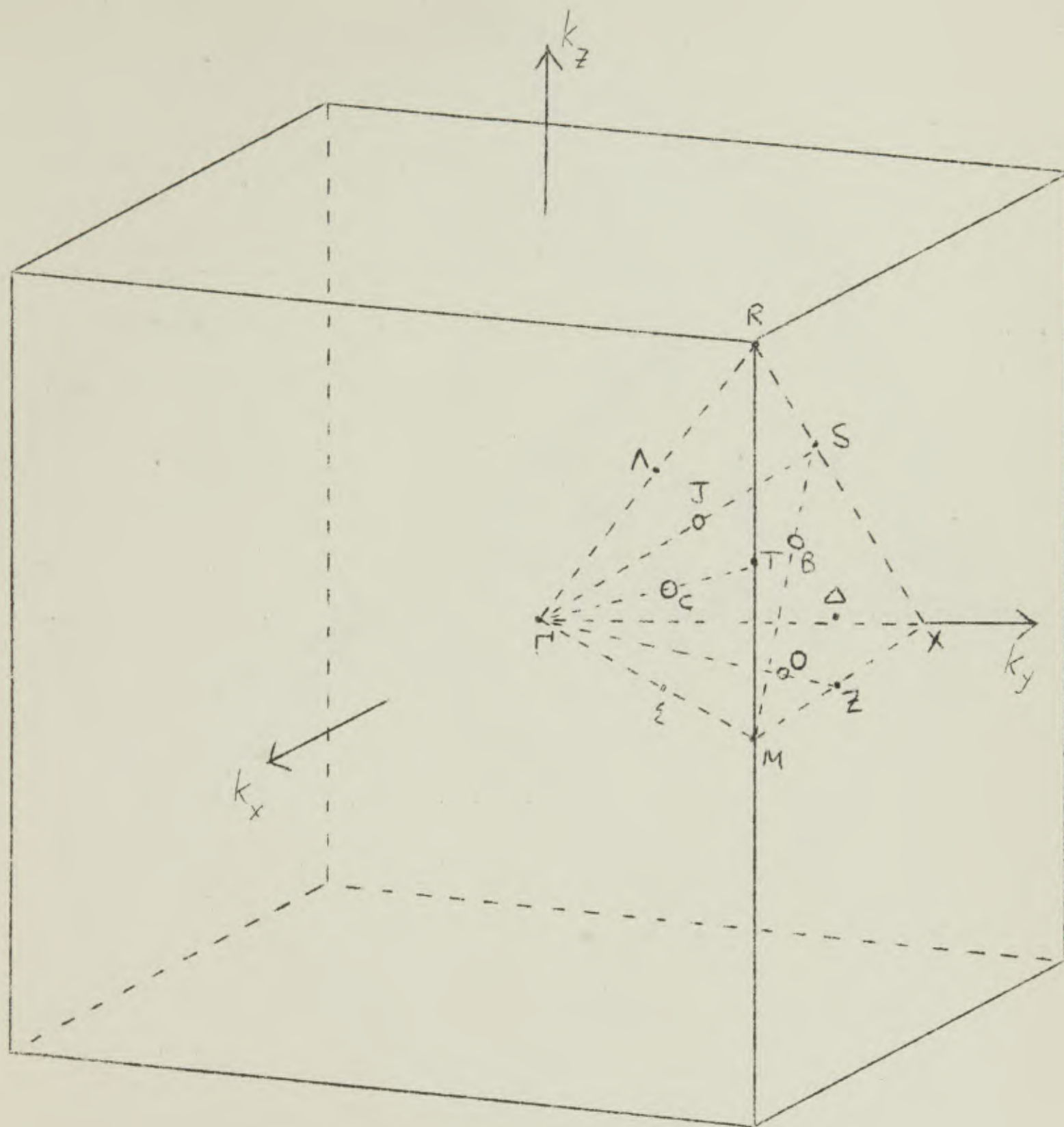


Figure 2.1. The first Brillouin Zone for the simple cubic lattice. The points marked with open circles belong to planes, but not lines, of symmetry. A is a general point.

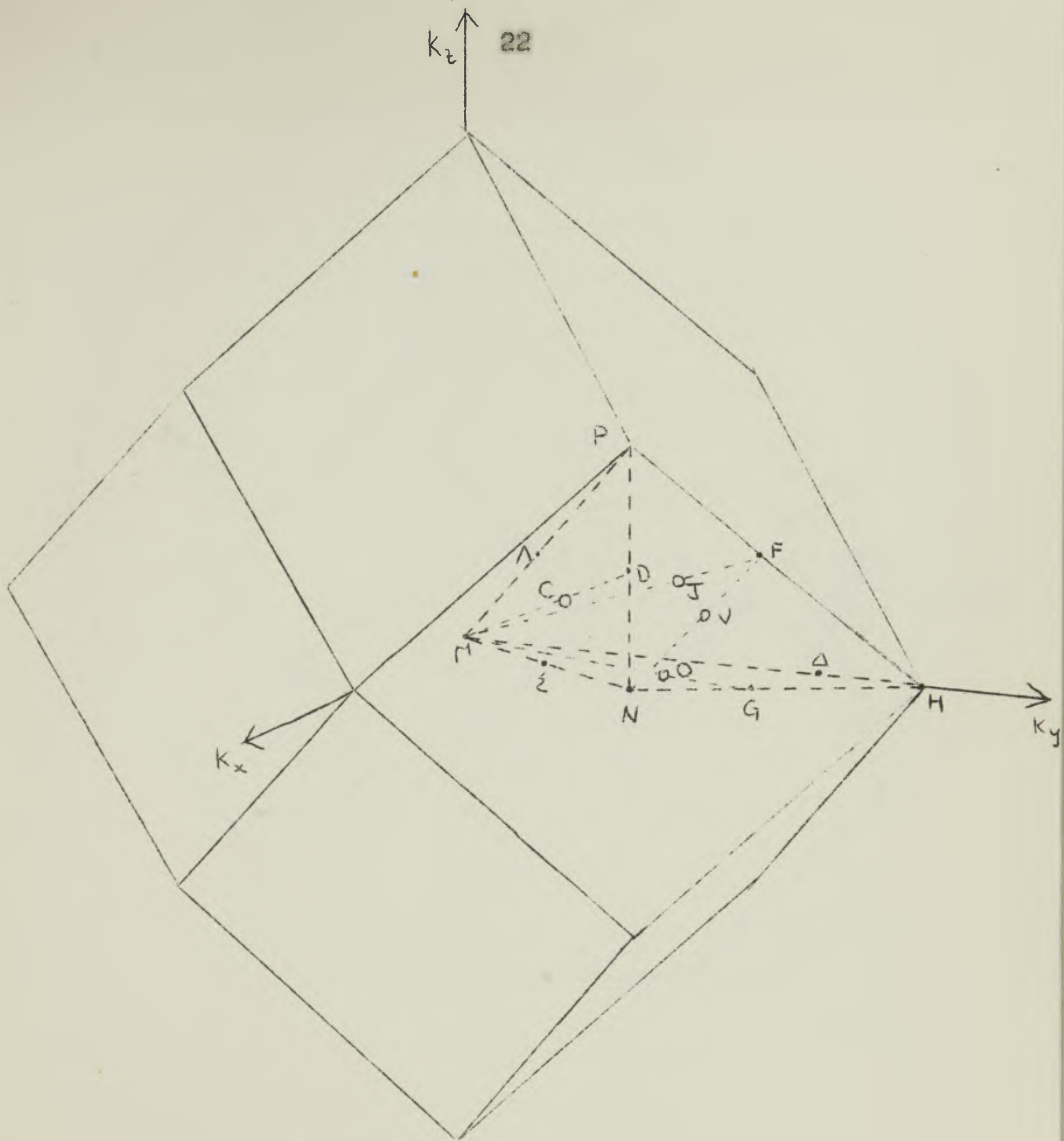


Figure 2.2. The first Brillouin Zone for the body-centred cubic lattice. The points marked with open circles belong to planes, but not lines, of symmetry. A is a general point.

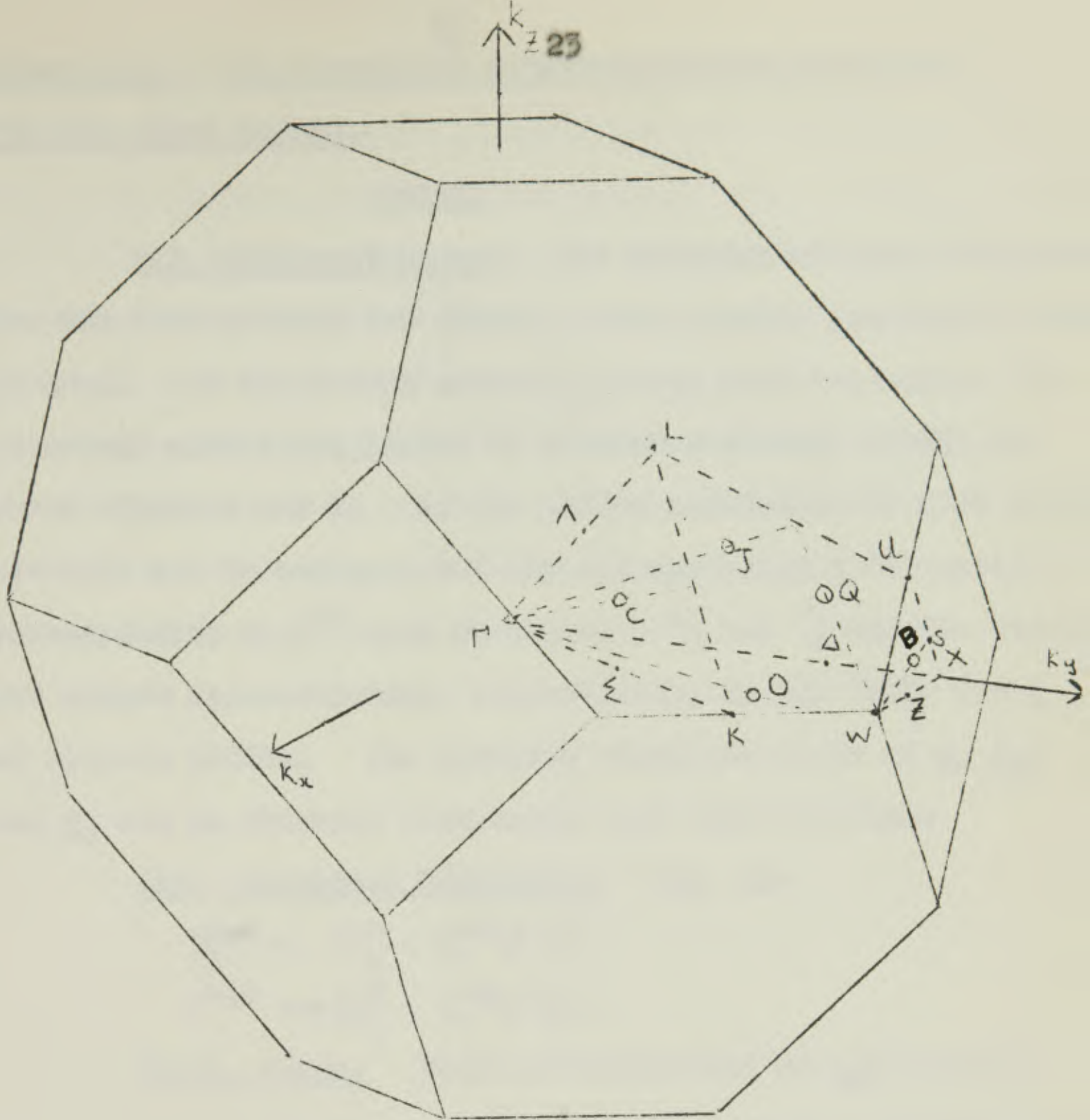


Figure 2.3. The first Brillouin Zone for the face-centred cubic lattice. The points marked with open circles belong to planes, but not lines of symmetry. A is a general point.

TABLE 2.1. THE NORMALIZED SYMMETRY-ADAPTED HARMONICS
FOR THE CUBIC GROUPS.

Notes.

(i) Representations. The symmetry-adapted harmonics are the same whether the active or the passive interpretation is used. In the latter case the matrix representatives are identical with those listed by Altmann & Bradley (1963) in their tables 6 and 7. If the active convention is used these matrices can be employed but for the operation $\underline{R}$ the matrix corresponding to $\underline{R}^{-1}$ must be taken. $^1\underline{E}$ and $^2\underline{E}$ are the first and second representation, respectively, in the table for $\underline{T}$ of Altmann (1962). The complete representations of $\underline{O}$, $\underline{O}_h$, and $\underline{T}_d$ can be obtained from Tables 2.2 and 2.3 below.

(ii) Spherical harmonics. They are

$$Y_1^{m,c} = (Y_1^m + Y_1^{-m})/\sqrt{2}$$

$$Y_1^{m,s} = -i(Y_1^m - Y_1^{-m})/\sqrt{2}.$$

(iii) Bases. They are understood as row vectors.

Their transformation properties are obtained by postmultiplying them with the matrix representative: the first function belongs to the first column of the representation, the second to the second, etc.

(iv) Notation of the Tables. A harmonic such as $aY_1^{m,c} + bY_1^{n,c} + cY_1^{p,c}$ is given as follows: the values of l and the superscript c (or s) appear under the headings l and δ -dep., respectively. The rest of the expansion appears on the same line in the form $a(m) + b(n) + c(p)$. Degenerate

representations are given in several lines and the must be understood as a row vector, the successive lines corresponding to the successive columns of the vector. In the three-dimensional representations the first two partners are given in one: the first letter under ' ϕ -dep.' and the upper sign in the expansion correspond to the first partner.

(v) Orthogonality. The expansions X_{lv} given here are orthogonal for different l or different v . Also in a multi-dimensional basis all the partners in the same basis are orthogonal, (see Altmann & Bradley (1968)).

TABLE 2.1(a). HARMONICS FOR THE ONE-DIMENSIONAL
REPRESENTATIONS.

T	T_h	T_d	O	O_h	l	ρ -deg	spherical harmonic.
A	A_g	A_1	A_1	A_{1g}	0	c	1(0)
A	A_u	A_1	A_2	A_{2u}	3	s	1(2)
A	A_g	A_1	A_1	A_{1g}	4	c	0.76376261(0) + 0.64549722(4)
A	A_g	A_1	A_1	A_{1g}	6	c	0.35355339(0) - 0.93541435(4)
A	A_g	A_2	A_2	A_{2g}	6	c	0.82915619(2) - 0.55901699(6)
A	A_u	A_1	A_2	A_{2u}	7	s	0.73598007(2) + 0.67700320(6)
A	A_g	A_1	A_1	A_{1g}	8	c	0.71807033(0) + 0.38188131(4) + 0.58184333(8)
A	A_u	A_1	A_2	A_{2u}	9	s	0.43301270(2) - 0.90138782(6)
A	A_u	A_2	A_1	A_{1u}	9	s	0.84162541(4) - 0.54006172(8)
A	A_g	A_1	A_1	A_{1g}	10	c	0.41142537(0) - 0.58630197(4) - 0.59783892(8)
A	A_g	A_2	A_2	A_{2g}	10	c	0.80201569(2) + 0.15728822(6) - 0.57622153(10)
A	A_u	A_1	A_2	A_{2u}	11	s	0.56536331(2) - 0.45927933(6) - 0.58851862(10)
A	A_g	A_1	A_1	A_{1g}	12	c	0.69550266(0) + 0.31412557(4) + 0.34844954(8) + 0.54422798(12)
A	A_g	A_1	A_1	A_{1g}	12	c	0.55897937(4) - 0.80626751(8) + 0.19358400(12)
A	A_g	A_2	A_2	A_{2g}	12	c	0.21040635(2) - 0.82679728(6) + 0.62166600(10)

TABLE 2.1(b). HARMONICS FOR THE COMPLEX REPRESENTATIONS

OF T AND T_h .

The harmonics of 2E , 2E_g and 2E_u are the complex conjugates of the expansions listed in this Table.

T	T_h	l	δ -deg	spherical harmonic
1E	1E_g	2	c	$0.70710678(0) + 0.70710678(2)i$
1E	1E_g	4	c	$0.45643546(0) - 0.54006172(4)$ $- 0.70710678(2)i$
1E	1E_u	5	s	$0.70710678(2) + 0.70710678(4)i$
1E	1E_g	6	c	$0.66143783(0) + 0.25(4)$ $+ [0.39528471(2) + 0.58630196(6)]i$
1E	1E_u	7	s	$0.47871355(2) - 0.52041650(6)$ $- 0.70710678(4)i$
1E	1E_g	8	c	$0.49212549(0) - 0.27860540(4) - 0.42448973(8)$ $- [0.46010167(2) + 0.53694176(6)]i$
1E	1E_g	8	c	$0.59115342(4) - 0.38799180(8)$ $- [0.53694176(2) - 0.46010167(6)]i$
1E	1E_u	9	s	$0.38188131(4) + 0.59511903(8)$ $- [0.63737744(2) + 0.30618622(6)]i$
1E	1E_g	10	c	$0.64448784(0) + 0.18714046(4) + 0.22274170(8)$ $+ [0.31464779(2) + 0.34379898(6)$ $+ 0.53178852(10)]i$
1E	1E_g	10	c	$0.54139029(4) - 0.45465883(8) + [0.28174844(2)$ $- 0.60780957(6) + 0.22624178(10)]i$

$\underline{T}$ $\underline{T}_n$ 1 ϕ -dep

spherical harmonic

$$1_E 1_{E_u} \quad 11 \quad o \quad 0.52786914(2) - 0.28945395(6) - 0.37090508(10) \\ - [0.35023357(4) + 0.61427717(8)]_1$$

$$1_E 1_{E_u} \quad 11 \quad o \quad 0.55744745(6) - 0.43503142(10) + \\ - [0.61427717(4) - 0.35023357(8)]_1$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.50807284(0) - 0.21500378(4) - 0.23849688(8) \\ - 0.37249777(12) - [0.36487352(2) \\ + 0.38689303(6) + 0.46602693(10)]_1$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.49820374(4) + 0.23953507(8) - 0.44092628(12) \\ - [0.58713874(2) - 0.09228708(6) \\ - 0.38308119(10)]_1$$

$$1_E 1_{E_g} \quad 12 \quad o \quad -1(0)$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.37143434(0) - 0.37143434(0)$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.50807284(0) - 0.21500378(4) - 0.23849688(8)$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 2(4)$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.50807284(0) - 0.21500378(4) - 0.23849688(8)$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.50807284(0) - 0.21500378(4) - 0.23849688(8) - 0.37249777(12)$$

$$1_E 1_{E_g} \quad 12 \quad o \quad -0.37249777(12) - [0.36487352(2) + 0.38689303(6) + 0.46602693(10)]_1$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.50807284(0) - 0.21500378(4) - 0.23849688(8)$$

$$1_E 1_{E_g} \quad 12 \quad o \quad -0.37249777(12) - [0.36487352(2) + 0.38689303(6) + 0.46602693(10)]_1$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.50807284(0) - 0.21500378(4) - 0.23849688(8)$$

$$1_E 1_{E_g} \quad 12 \quad o \quad -0.37249777(12) - [0.36487352(2) + 0.38689303(6) + 0.46602693(10)]_1$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.50807284(0) - 0.21500378(4) - 0.23849688(8) - 0.37249777(12)$$

$$1_E 1_{E_g} \quad 12 \quad o \quad 0.50807284(0) - 0.21500378(4) - 0.23849688(8) - 0.37249777(12) - [0.36487352(2) + 0.38689303(6) + 0.46602693(10)]_1$$

TABLE 2.1(c). HARMONICS FOR THE TWO-DIMENSIONAL
REPRESENTATIONS OF T_d , O AND O_h .

For the representations marked with an asterisk the partners must be interchanged and the sign of one of them reversed.

T_d	O	O_h	l	ϕ -deg	spherical harmonic
E	E	E_g	2	c	1(0).
				c	1(2)
E	E	E_g	4	c	0.64549722(0) - 0.76376262(4)
				c	-1(2).
E*	E	E_u	5	s	1(4)
				s	-1(2)
E	E	E_g	6	c	0.93541434(0) + 0.35355339(4)
				c	0.55901699(2) + 0.82915619(6)
E*	E	E_u	7	s	1(4)
				s	0.67700320(2) - 0.73598007(6)
E	E	E_g	8	c	0.69597054(0) - 0.39400753(4) - 0.60031913(8)
				c	-0.65068202(2) - 0.75935032(6)
E	E	E_g	8	c	0.83601718(4) - 0.54870326(8)
				c	-0.11588441(2) + 0.99326270(6)
E*	E	E_u	9	s	0.54006172(4) + 0.84162541(8)
				s	-0.90138782(2) - 0.43301270(6)
E	E	E_g	10	c	0.21628928(0) + 0.62804094(4) + 0.74751824(8)
				c	0.44497917(2) + 0.48620518(6) + 0.75206253(10)

spherical harmonic

E	E	E _g	10	c	$0.76564149(4) - 0.64326752(8)$
				c	$0.39845246(2) - 0.85957253(6) + 0.31995420(10)$
E*	E	EE _u	11	c	$0.49530506(4) + 0.86871911(8)$
				s	$0.74651970(2) - 0.40934970(6) - 0.52453900(10)$
E*	E	E _u	11	c	$0.86871911(4) - 0.49530506(8)$
				s	$-0.78834975(6) + 0.61522733(10)$
E	E	E _g	12	c	$0.71852351(0) - 0.30406127(4)$
					$-0.33728553(8) - 0.52679140(12)$
				c	$-0.51600908(2) + 0.54714937(6)$
					$+ 0.65906160(10)$
E	E	E	12	c	$0.70456648(4) + 0.33875374(8) - 0.62356392(12)$
				c	$-0.83033957(2) + 0.13051364(6) + 0.54175861(10)$

TABLE 2.1(a). HARMONICS FOR THE THREE-DIMENSIONAL

REPRESENTATIONS OF THE FIVE CUBIC GROUPS.

T	T_h	T_d	O	O_h	l	δ -deg	spherical harmonic
T	T_u	T_2	T_1	T_{1u}	1	c,s	1(1)
						c	1(0)
T	T_g	T_2	T_2	T_{2g}	2	s,c	1(1)
						s	1(2)
T	T_u	T_2	T_1	T_{1u}	3	c,s	$0.61237243(1) \mp 0.79056941(3)$
						c	-1(0)
T	T_u	T_1	T_2	T_{2u}	3	c,s	$\mp 0.79056941(1) - 0.61237243(3)$
						c	1(2)
T	T_g	T_2	T_2	T_{2g}	4	s,c	$0.35355339(1) \mp 0.93541435(3)$
						s	-1(2)
T	T_g	T_1	T_1	T_{1g}	4	s,c	$\mp 0.93541435(1) - 0.35355339(3)$
						s	1(4)
T	T_u	T_2	T_1	T_{1u}	5	c,s	$0.48412292(1) \mp 0.52291252(3)$
							$+ 0.70156376(5)$
						c	1(0)
T	T_u	T_1	T_2	T_{2u}	5	c,s	$\pm 0.66143785(1) - 0.30618622(3)$
							$\mp 0.68465320(5)$
						c	1(2)
T	T_u	T_2	T_1	T_{1u}	5	c,s	$0.57282196(1) \pm 0.79549513(3)$
							$+ 0.19764235(5)$
						c	1(4)

T	T_h	T_d	O	O_h	1	ϕ -dep	spherical harmonic
T	T_g	T_2	T_2	T_{2g}	6	s,c	$0.19764235(1) \mp 0.56250000(3)$ $+ 0.80282703(5)$ s 1(2)
T	T_g	T_1	T_1	T_{1g}	6	s,c	$\pm 0.45301270(1) - 0.68465320(3)$ $\mp 0.58630197(5)$ s 1(4)
T	T_g	T_2	T_2	T_{2g}	6	s,c	$0.87945295(1) \pm 0.46351240(3)$ $+ 0.10825318(5)$ s 1(6)
T	T_u	T_2	T_1	T_{1u}	7	c,s	$0.41339364(1) \mp 0.42961647(3)$ $+ 0.47495838(5) \mp 0.64725985(7)$ c -1(0)
T	T_u	T_1	T_2	T_{2u}	7	c,s	$\mp 0.57409916(1) + 0.41984465(3)$ $\mp 0.07528775(5) - 0.69912054(7)$ c 1(2)
T	T_u	T_2	T_1	T_{1u}	7	c,s	$0.53855275(1) \pm 0.10364452(3)$ $- 0.78125000(5) \mp 0.29810600(7)$ c -1(4)
T	T_u	T_1	T_2	T_{2u}	7	c,s	$\mp 0.45768183(1) - 0.79272818(3)$ $\mp 0.39836090(5) - 0.05846340(7)$ c 1(6)
T	T_g	T_2	T_2	T_{2g}	8	s,c	$0.13072813(1) \mp 0.38081430(3)$ $+ 0.59086470(5) \mp 0.69912054(7)$ s -1(2)

T	T_b	T_d	0	Q_b	1	δ -dep	spherical harmonic
T	T_g	T_1	T_1	T_{1g}	8	s,c	$\mp 0.27421764(1) + 0.60515364(3)$ $\mp 0.33802043(5) - 0.56558528(7)$ e 1(4)
T	T_g	T_2	T_2	T_{2g}	8	s,c	$0.45768183(1) \mp 0.47134697(3)$ $-0.70883101(5) \mp 0.25574495(7)$ s -1(5)
T	T_g	T_1	T_1	T_{1g}	8	s,c	$\mp 0.83560887(1) - 0.51633474(3)$ $\mp 0.18487749(5) - 0.03125000(7)$ s 1(3)
T	T_u	T_2	T_1	T_{1u}	9	c,s	$0.36685490(1) \mp 0.37548796(3)$ $+ 0.39636409(5) \mp 0.44314853(7)$ $+ 0.60904939(9)$ c 1(0)
T	T_u	T_1	T_2	T_{2u}	9	c,s	$\pm 0.51301422(1) - 0.42961647(3)$ $\pm 0.25194555(5) + 0.05633674(7)$ $\mp 0.69684697(9)$ c 1(2)
T	T_u	T_2	T_1	T_{1u}	9	c,s	$0.49435287(1) \mp 0.13799626(3)$ $- 0.39218439(5) \pm 0.67232906(7)$ $+ 0.36157614(9)$ c 1(4)
T	T_u	T_1	T_2	T_{2u}	9	c,s	$\mp 0.45768183(1) + 0.29810600(3)$ $\mp 0.60515365(5) - 0.55832917(7)$ $\mp 0.11158452(9)$ c 1(6)

T	T _h	T _d	O	O _h	1	0-dep	spherical harmonic
T	T _u	T ₂	T ₁	T _{1u}	9	c,s	0.38519666(1) - 0.75268075(3) + 0.50931269(5) ± 0.15944009(7) + 0.01657282(9) c 1(8)
T	T _g	T ₂	T ₂	T _{2g}	10	s,c	0.09472153(1) ± 0.27885263(3) + 0.44538102(5) ± 0.57386942(7) + 0.62002414(7) s 1(2)
T	T _g	T ₁	T ₁	T _{1g}	10	s,c	± 0.19515619(1) - 0.48613591(3) ± 0.49410588(5) - 0.09110862(7) ± 0.68785502(9) s 1(4)
T	T _g	T ₂	T ₂	T _{2g}	10	s,c	0.31049159(1) ± 0.53906250(3) - 0.01746928(5) ± 0.69255289(7) + 0.36479021(9) s 1(6)
T	T _g	T ₁	T ₁	T _{1g}	10	s,c	± 0.46456465(1) - 0.31560953(3) ± 0.70572436(5) - 0.42100605(7) ± 0.09631897(9) s 1(8)
T	T _g	T ₂	T ₂	T _{2g}	10	s,c	0.80044772(1) ± 0.54379714(3) + 0.24319347(5) ± 0.06594509(7) + 0.00873464(9) s 1(10)

$T \quad T_h \quad T_d \quad 0 \quad C_h \quad 1 \quad \delta\text{-dep} \quad \text{spherical harmonic}$

$$T \quad T_u \quad T_2 \quad T_1 \quad T_{1u} \quad 11 \quad c, s \quad 0.33321251(1) \mp 0.33846028(3) \\ + 0.35033967(5) \mp 0.37296506(7) \\ + 0.41975833(9) \mp 0.57997947(11)$$

$$c \quad -1(0)$$

$$T \quad T_u \quad T_1 \quad T_2 \quad T_{2u} \quad 11 \quad c, s \quad \mp 0.46765008(1) + 0.41655170(3) \\ \mp 0.31014124(5) + 0.13689999(7) \\ \pm 0.13594929(9) - 0.68875008(11)$$

$$c \quad 1(2)$$

$$T \quad T_u \quad T_2 \quad T_1 \quad T_{1u} \quad 11 \quad c, s \quad 0.45637974(1) \mp 0.23534954(3) \\ -0.13435456(5) \pm 0.49510852(7) \\ - 0.55722625(9) \mp 0.4032(075)(11)$$

$$c \quad -1(4)$$

$$T \quad T_u \quad T_1 \quad T_2 \quad T_{2u} \quad 11 \quad c, s \quad \mp 0.43552936(1) - 0.04764184(3) \\ \pm 0.52272828(5) - 0.32425699(7) \\ \mp 0.63603689(9) - 0.15847416(11)$$

$$c \quad 1(6)$$

$$T \quad T_u \quad T_2 \quad T_1 \quad T_{1u} \quad 11 \quad c, s \quad 0.40022386(1) \pm 0.39401846(3) \\ - 0.40784786(5) \mp 0.65553754(7) \\ - 0.29501240(9) \mp 0.03832308(11)$$

$$c \quad -1(8)$$

$$T \quad T_u \quad T_1 \quad T_2 \quad T_{2u} \quad 11 \quad c, s \quad \mp 0.33485131(1) - 0.70641321(3) \\ \mp 0.56871666(5) - 0.24930093(7) \\ \mp 0.05695964(9) - 0.00458048(11)$$

$$c \quad 1(10)$$

TABLE 2.2. CHARACTER TABLES OF THE CO-GROUPS OF THE
k-VECTOR FOR ALL THE k-VECTORS OF THE CUBIC LATTICES.

Notes.

(i) Points. The points in k space (k -vectors) should be identified from figures 2.1, 2.2, and 2.3.

(ii) Symmetry operations. They should be identified from Figure 1.1. The suffixes m , i , p take the following values, with reference to the symmetry operations of Figure 1.1:
 m : x, y , and z ; i : 1, 2, 3, and 4; p : a, b, c, d, e , and f .

A symbol such as $\sigma_d(b, e, f)$ stands for the three operations σ_{db} , σ_{de} , and σ_{df} .

(iii) Direct product groups. These are recognized in the tables because the names of two representations appear in the column under the name of the point. Also, the operations are listed in two rows linked with braces. For the two representations listed together the characters of the operations in the first row are those given in the table. The characters of the operations in the second row are, for the first representation listed, those in the table and, for the second, their negatives.

(iv) Nomenclature of the irreducible representations. It is the standard one for the point groups (see Altmann (1962), p.163) rather than the one used by Bouckaert et al (1936). A symbol such as ΣA_2 will be used to denote the A_2 representation of the point Σ .

Γ, H, R		$\left\{ \begin{array}{l} E \\ I \\ E \end{array} \right.$	$8C_{3i}^+$	$3C_{2m}$	$6C_{4m}^+$	$6C_{2p}$
			$8S_{6i}^+$	$3\sigma_m$	$6S_{4m}^+$	$6\sigma_{dp}$
			$8C_{3i}^+$	$3C_{2m}$	$6S_{4m}^+$	$6\sigma_{dp}$
O_h	T_d					
A_{1g}, A_{1u}	A_1	1	1	1	1	1
A_{2g}, A_{2u}	A_2	1	1	1	-1	-1
E_g, E_u	E	2	-1	2	0	0
T_{1g}, T_{1u}	T_1	3	0	-1	1	-1
T_{2g}, T_{2u}	T_2	3	0	-1	-1	1
Σ, K		$\left\{ \begin{array}{l} E \\ E \\ E \\ E \\ E \\ E \\ E \\ I \\ I \end{array} \right.$	C_{2a}	σ_z	σ_{db}	
G			C_{2b}	σ_{da}	σ_z	
D			C_{2c}	σ_{db}	σ_{da}	
S, U			C_{2c}	σ_{de}	σ_y	
Z			C_{2x}	σ_z	σ_y	
	N		C_{2a}	C_{2z}	C_{2b}	
			σ_{da}	σ_z	σ_{db}	
C_{2v}	D_{2h}					
A_1	A_{1g}, A_{1u}		1	1	1	1
A_2	B_{1g}, B_{1u}		1	1	-1	-1
B_1	B_{2g}, B_{2u}		1	-1	1	-1
B_2	B_{3g}, B_{3u}		1	-1	-1	1

Δ, T

X

M

W

E	C_{2y}	C_{4y}^+	$\sigma_{(x,z)}$	$\sigma_d(e,c)$
{	E	C_{2y}	C_{4y}^+	$C_{2(x,z)} C_{2(c,e)}$
	I	σ_y	S_{4y}^-	$\sigma_{(x,z)}$ $\sigma_d(c,e)$
{	E	C_{2z}	C_{4z}^+	$C_{2(x,y)} C_{2(a,b)}$
	I	σ_z	S_{4z}^-	$\sigma_{(x,y)}$ $\sigma_d(a,b)$
E	C_{2x}	S_{4x}^+	$C_{2(d,f)}$	$\sigma_{(y,z)}$

 C_{4v} D_{4h} D_{2d}

A_1	A_{1g}, A_{1u}	A_1	1	1	1	1	1
A_2	A_{2g}, A_{2u}	A_2	1	1	1	-1	-1
B_1	B_{1g}, B_{1u}	B_1	1	1	-1	1	-1
B_2	B_{2g}, B_{2u}	B_2	1	1	-1	-1	1
E	E_g, E_u	E	2	-2	0	0	0

 $\wedge$

F

L

E	C_{31}^+	$\sigma_d(b,e,f)$
E	C_{34}^+	$\sigma_d(a,d,e)$
{	E	C_{31}^+
	I	S_{61}^-
		$C_2(b,e,f)$
		$\sigma_d(b,e,f)$

 C_{3v} D_{3h}

A_1	A_{1g}, A_{1u}	1	1	1
A_2	A_{2g}, A_{2u}	1	1	-1
E	E_g, E_u	2	-1	0

V		E	σ_{da}
C		E	σ_{db}
O		E	σ_e
J		E	σ_{de}
B		E	σ_y
	Q	E	C_{2F}
C_{1h}	C_2		
A'	A	1	1
A''	B	1	-1

A	E
C_1	
A	1

TABLE 2.3 THE TWO-DIMENSIONAL AND THREE-DIMENSIONAL REPRESENTATIONS OF THE CO-GROUPS OF THE k-VECTORS FOR ALL THE k-VECTORS OF THE CUBIC LATTICES.

Note: All the matrices correspond to operators in their active interpretation.

TABLE 2.3(a) THE TWO-DIMENSIONAL REPRESENTATIONS.

key	ε	λ	κ	ρ
	$\begin{bmatrix} 1 & \\ & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & \\ & -1 \end{bmatrix}$	$\begin{bmatrix} & 1 \\ 1 & \end{bmatrix}$	$\begin{bmatrix} & 1 \\ -1 & \end{bmatrix}$
	α	β	μ	ν
	$\begin{bmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} \\ -\frac{1}{2}\sqrt{3} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} & \frac{1}{2} \end{bmatrix}$

For the representations E , the matrices listed in the left (right) column under E correspond to the operations listed in the first (last) column of the table. For the points that admit representations E_g, E_u , both operations which are on the same row and are in the first and last columns of the table belong to the group. Only the matrices for the operations in the first column are given. Those for the corresponding operations of the last column are, for the E_g representations, the same and for the E_u representations the same matrices multiplied by -1 .

	Γ, H, R E_{Eu}	Δ, T E	Λ E	F E	P E	X E_{Eu}	M E_{Eu}	W E	L E_{Eu}	
E	ϵ	ϵ	ϵ	ϵ	ϵ	ϵ	ϵ	ϵ	ϵ	I
C_{31}^+	β		β		β				β	S_{61}^-
C_{31}^-	α		α		α				α	S_{61}^+
C_{32}^+	β				β					S_{62}^-
C_{32}^-	α				α					S_{62}^+
C_{33}^+	β				β					S_{63}^-
C_{33}^-	α				α					S_{63}^+
C_{34}^+	β			β	β					S_{64}^-
C_{34}^-	α			α	α					S_{64}^+
C_{2x}	ϵ	κ			ϵ	κ	λ	$-\epsilon$		σ_x
C_{2y}	ϵ	$-\epsilon$			ϵ	$-\epsilon$	$-\lambda$	λ		σ_y
C_{2z}	ϵ	$-\kappa$			ϵ	$-\kappa$	$-\epsilon$	$-\lambda$		σ_z
C_{4x}^+	μ				μ			$-\rho$		S_{4x}^-
C_{4x}^-	μ				μ			ρ		S_{4x}^+
C_{4y}^+	ν	$-\rho$			ν	$-\rho$				S_{4y}^-
C_{4y}^-	ν	ρ			ν	ρ				S_{4y}^+
C_{4z}^+	λ				λ		ρ			S_{4z}^-
C_{4z}^-	λ				λ		$-\rho$			S_{4z}^+
C_{2a}	λ			λ	λ		$-\kappa$			σ_{da}
C_{2b}	λ		λ		λ		κ		λ	σ_{db}
C_{2c}	ν	λ			ν	λ				σ_{dc}
C_{2d}	μ			μ	μ			$-\kappa$		σ_{dd}
C_{2e}	ν	$-\lambda$	ν	ν	ν	$-\lambda$			ν	σ_{de}
C_{2f}	μ		μ		μ			κ	μ	σ_{df}

TABLE 2.3(b) THE THREE-DIMENSIONAL REPRESENTATIONS.Notes.

(i) Column (1) The matrices of the operations listed in this column are those printed on the right of the symbol for the operation, for all the representations of Γ , H, R, and P.

(ii) Column (2) The matrices for the operations listed under this column are obtained by postmultiplying the matrix printed on the left of the symbol of the operation with the following matrices:

$$\begin{array}{l} \text{for } T_{1g}, T_{1u} \text{ of } \Gamma, H, R \text{ and } T_1 \text{ of P: } \begin{bmatrix} & 1 & \\ 1 & & \\ & & -1 \end{bmatrix} \\ \text{for } T_{2g}, T_{2u} \text{ of } \Gamma, H, R \text{ and } T_2 \text{ of P: } \begin{bmatrix} & -1 & \\ -1 & & \\ & & 1 \end{bmatrix} \end{array}$$

(iii) Primed columns For the operations in the columns (1') and (2') obtain first the matrices of the corresponding operations in the columns (1) and (2) respectively, by means of the above prescriptions. Then multiply the matrices thus obtained with $+1$ for T_{1g} , T_{2g} , and -1 for T_{1u} , T_{2u} .

Γ, H R, P (1)	Γ, H R (1')	Γ, H R (2)	Γ, H R (2')	P (2)	Γ, H R, P (1)	Γ, H R (1')	Γ, H R (2)	Γ, H R (2')	P (2)		
E	I	$\begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$	C_{2a}	σ_{da}	σ_{da}	C_{33}^-	S_{63}^+	$\begin{bmatrix} -1 & & \\ & 1 & \\ & & -1 \end{bmatrix}$	C_{2f}	σ_{df}	σ_{df}
C_{31}^+	S_{61}^-	$\begin{bmatrix} & & 1 \\ 1 & & \\ & 1 & \end{bmatrix}$	C_{4y}^-	S_{4y}^+	S_{4y}^+	C_{34}^+	S_{64}^-	$\begin{bmatrix} & & 1 \\ -1 & & \\ & -1 & \end{bmatrix}$	C_{2e}	σ_{de}	σ_{de}
C_{31}^-	S_{61}^+	$\begin{bmatrix} & 1 & \\ & & 1 \\ 1 & & \end{bmatrix}$	C_{4x}^+	S_{4x}^-	S_{4x}^-	C_{34}^-	S_{64}^+	$\begin{bmatrix} & -1 & \\ & & -1 \\ 1 & & \end{bmatrix}$	C_{2d}	σ_{dd}	σ_{dd}
C_{32}^+	S_{62}^-	$\begin{bmatrix} & & -1 \\ 1 & & \\ & -1 & \end{bmatrix}$	C_{4y}^+	S_{4y}^-	S_{4y}^-	C_{2x}	σ_x	$\begin{bmatrix} 1 & & \\ & -1 & \\ & & -1 \end{bmatrix}$	C_{4z}^-	S_{4z}^+	S_{4z}^+
C_{32}^-	S_{62}^+	$\begin{bmatrix} & 1 & \\ & & -1 \\ -1 & & \end{bmatrix}$	C_{4x}^-	S_{4x}^+	S_{4x}^+	C_{2y}	σ_y	$\begin{bmatrix} -1 & & \\ & 1 & \\ & & -1 \end{bmatrix}$	C_{4z}^+	S_{4z}^-	S_{4z}^-
C_{33}^+	S_{63}^-	$\begin{bmatrix} & & -1 \\ -1 & & \\ & 1 & \end{bmatrix}$	C_{2c}	σ_{dc}	σ_{dc}	C_{2z}	σ_z	$\begin{bmatrix} -1 & & \\ & -1 & \\ & & 1 \end{bmatrix}$	C_{2b}	σ_{db}	σ_{db}

TABLE 2.4 THE SYMMETRY-ADAPTED HARMONICS FOR THE CUBIC GROUPS.

Notes.

(i) Representations. The representations spanned by the bases given here are obtained from Table 2.2 (1-dimensional) and Table 2.3 (2- and 3-dimensional). Although these representations correspond to active operators, the bases listed here are also correct for the representations that correspond to passive operators.

(ii) Notation. The symmetry-adapted harmonics are given as linear combinations of the bases that span the representations of $m\bar{3}m$ (O_h), point Γ . These are obtained from Table 2.1. The successive partners of a multi-dimensional basis of $m\bar{3}m$ in Table 2.1 are identified with superscripts 1, 2, etc. The symmetry-adapted harmonics that span a multidimensional basis are linked together with braces. The resulting bases should be understood as row vectors.

To simplify the production of the Tables all symmetry adapted harmonics which are given as a sum of two or three terms have been denormalized. To normalize them one must therefore divide the functions concerned by the square root of the sum of the squares of the coefficients: thus

$T_{2u}^1 + T_{2u}^2 - 2T_{2u}^3$ should be read as $(T_{2u}^1 + T_{2u}^2 - 2T_{2u}^3)/\sqrt{6}$.

(iii) Example. The normalized harmonics up to $l=2$ that are obtained from those listed for A_1 of Δ are:

$$Y_1^0, \frac{1}{2}Y_2^0 + \frac{1}{2}3Y_2^{2,0}, Y_1^{1,S}.$$

(iv) Uses of the Tables. Although the symmetry-adapted harmonics given here are such that, on using the results of S2.2, they generate immediately all the lattice harmonics for all the cubic groups, they can also be used as symmetry-adapted harmonics for the point groups listed in Table 2.2, if the special setting used there is required, rather than the standard one.

Γ, H, R

Identical with those of $m\bar{3}m$ (O_h).

P

A_1	A_{1g}, A_{2u}
A_2	A_{2g}, A_{1u}
E	$\{E_g^1, E_g^2\}, \{E_u^2, -E_u^1\}$
T_1	$\{T_{1g}^1, T_{1g}^2, T_{1g}^3\}, \{T_{2u}^1, T_{2u}^2, T_{2u}^3\}$
T_2	$\{T_{2g}^1, T_{2g}^2, T_{2g}^3\}, \{T_{1u}^1, T_{1u}^2, T_{1u}^3\}$

ξ, K

A_1	$A_{1g}, E_g^1, T_{2g}^3, T_{2u}^1 - T_{2u}^2, T_{1u}^1 + T_{1u}^2$
A_2	$A_{1u}, E_u^1, T_{2u}^3, T_{2g}^1 - T_{2g}^2, T_{1g}^1 + T_{1g}^2$
B_1	$A_{2g}, E_g^2, T_{1g}^3, T_{2u}^1 + T_{2u}^2, T_{1u}^1 - T_{1u}^2$
B_2	$A_{2u}, E_u^2, T_{1u}^3, T_{2g}^1 + T_{2g}^2, T_{1g}^1 - T_{1g}^2$

G

$$\begin{array}{ll}
 A_1 & A_{1g}, E_g^1, T_{2g}^3, T_{2u}^1 + T_{2u}^2, T_{1u}^1 - T_{1u}^2 \\
 A_2 & A_{1u}, E_u^1, T_{2u}^3, T_{2g}^1 + T_{2g}^2, T_{1g}^1 - T_{1g}^2 \\
 B_1 & A_{2u}, E_u^2, T_{1u}^3, T_{2g}^1 - T_{2g}^2, T_{1g}^1 + T_{1g}^2 \\
 B_2 & A_{2g}, E_g^2, T_{1g}^3, T_{2u}^1 - T_{2u}^2, T_{1u}^1 + T_{1u}^2
 \end{array}$$

D

$$\begin{array}{ll}
 A_1 & A_{1g}, A_{2u}, E_g^1, E_u^2, T_{2g}^3, T_{1u}^3 \\
 A_2 & A_{2g}, A_{1u}, E_g^2, E_u^1, T_{1g}^3, T_{2u}^3 \\
 B_1 & T_{2g}^1 + T_{2g}^2, T_{1g}^1 - T_{1g}^2, T_{2u}^1 - T_{2u}^2, T_{1u}^1 + T_{1u}^2 \\
 B_2 & T_{2g}^1 - T_{2g}^2, T_{1g}^1 + T_{1g}^2, T_{2u}^1 + T_{2u}^2, T_{1u}^1 - T_{1u}^2
 \end{array}$$

S, U

$$\begin{array}{ll}
 A_1 & A_{1g}, E_g^1 + \sqrt{3}E_g^2, T_{2g}^2, T_{2u}^1 - T_{2u}^3, T_{1u}^1 + T_{1u}^3 \\
 A_2 & A_{1u}, E_u^1 + \sqrt{3}E_u^2, T_{2u}^2, T_{2g}^1 - T_{2g}^3, T_{1g}^1 + T_{1g}^3 \\
 B_1 & A_{2u}, -\sqrt{3}E_u^1 + E_u^2, T_{1u}^2, T_{2g}^1 + T_{2g}^3, T_{1g}^1 - T_{1g}^3 \\
 B_2 & A_{2g}, -\sqrt{3}E_g^1 + E_g^2, T_{1g}^2, T_{2u}^1 + T_{2u}^3, T_{1u}^1 - T_{1u}^3
 \end{array}$$

Z

$$\begin{array}{ll}
 A_1 & A_{1g}, A_{2g}, E_g^1, E_g^2, T_{2u}^1, T_{1u}^1 \\
 A_2 & A_{1u}, A_{2u}, E_u^1, E_u^2, T_{2g}^1, T_{1g}^1 \\
 B_1 & T_{2g}^3, T_{1g}^3, T_{2u}^2, T_{1u}^2 \\
 B_2 & T_{2g}^2, T_{1g}^2, T_{2u}^3, T_{1u}^3
 \end{array}$$

H

$$\begin{array}{ll}
A_g & A_{1g}, E_g^1, T_{2g}^3 \\
B_{1g} & T_{2g}^1 - T_{2g}^2, T_{1g}^1 + T_{1g}^2 \\
B_{2g} & A_{2g}, E_g^2, T_{1g}^3 \\
B_{3g} & T_{2g}^1 + T_{2g}^2, T_{1g}^1 - T_{1g}^2 \\
A_u & A_{1u}, E_u^1, T_{2u}^3 \\
B_{1u} & T_{2u}^1 - T_{2u}^2, T_{1u}^1 + T_{1u}^2 \\
B_{2u} & A_{2u}, E_u^2, T_{1u}^3 \\
B_{3u} & T_{2u}^1 + T_{2u}^2, T_{1u}^1 - T_{1u}^2
\end{array}$$

 Δ, T

$$\begin{array}{ll}
A_1 & A_{1g}, E_g^1 + \sqrt{3}E_g^2, T_{1u}^2 \\
A_2 & A_{1u}, E_u^1 + \sqrt{3}E_u^2, T_{1g}^2 \\
E_1 & A_{2g}, -\sqrt{3}E_g^1 + E_g^2, T_{2u}^2 \\
E_2 & A_{2u}, -\sqrt{3}E_u^1 + E_u^2, T_{2g}^2 \\
E & \{T_{2g}^1 - T_{2g}^3, T_{2g}^1 + T_{2g}^3\}, \{T_{1g}^1 + T_{1g}^3, T_{1g}^1 - T_{1g}^3\} \\
& \{-T_{2u}^1 - T_{2u}^3, T_{2u}^1 - T_{2u}^3\}, \{-T_{1u}^1 + T_{1u}^3, T_{1u}^1 + T_{1u}^3\}
\end{array}$$

W

$$\begin{array}{ll}
A_1 & A_{1g}, T_{2u}^1, E_g^1 - \sqrt{3}E_g^2 \\
A_2 & A_{2u}, T_{1g}^1, \sqrt{3}E_u^1 + E_u^2 \\
E_1 & A_{1u}, T_{2g}^1, E_u^1 - \sqrt{3}E_u^2 \\
E_2 & A_{2g}, T_{1u}^1, \sqrt{3}E_g^1 + E_g^2 \\
E & \{T_{2g}^2, T_{2g}^3\}, \{T_{1g}^2, -T_{1g}^3\}, \{T_{2u}^3, T_{2u}^2\}, \{-T_{1u}^3, T_{1u}^2\}
\end{array}$$

X

A_{1g}	$A_{1g}, E_g^1 + \sqrt{3}E_g^2$
A_{2g}	T_{1g}^2
B_{1g}	$A_{2g}, -\sqrt{3}E_g^1 + E_g^2$
B_{2g}	T_{2g}^2
A_{1u}	$A_{1u}, E_u^1 + \sqrt{3}E_u^2$
A_{2u}	T_{1u}^2
B_{1u}	$A_{2u}, -\sqrt{3}E_u^1 + E_u^2$
B_{2u}	T_{2u}^2
E_g	$\{T_{2g}^1 - T_{2g}^3, T_{2g}^1 + T_{2g}^3\}, \{T_{1g}^1 + T_{1g}^3, T_{1g}^1 - T_{1g}^3\}$
E_u	$\{T_{2u}^1 - T_{2u}^3, T_{2u}^1 + T_{2u}^3\}, \{T_{1u}^1 + T_{1u}^3, T_{1u}^1 - T_{1u}^3\}$

II

A_{1g}	A_{1g}, E_g^1
A_{2g}	T_{1g}^3
B_{1g}	A_{2g}, E_g^2
B_{2g}	T_{2g}^3
A_{1u}	A_{1u}, E_u
A_{2u}	T_{1u}^3
B_{1u}	A_{2u}, E_u^2
B_{2u}	T_{2u}^3
E_g	$\{T_{2g}^1, T_{2g}^2\}, \{T_{1g}^1, -T_{1g}^2\}$
E_u	$\{T_{2u}^1, T_{2u}^2\}, \{T_{1u}^1, -T_{1u}^2\}$

Λ

$$\begin{array}{ll}
A_1 & A_{1g}, A_{2u}, T_{2g}^1 + T_{2g}^2 + T_{2g}^3, T_{1u}^1 + T_{1u}^2 + T_{1u}^3 \\
A_2 & A_{1u}, A_{2g}, T_{1g}^1 + T_{1g}^2 + T_{1g}^3, T_{2u}^1 + T_{2u}^2 + T_{2u}^3 \\
E & \{E_g^1, E_g^2\}, \{-E_u^2, E_u^1\}, \{T_{1g}^1 - T_{1g}^2, T_{1g}^1 + T_{1g}^2 - 2T_{1g}^3\}, \\
& \{T_{2u}^1 - T_{2u}^2, T_{2u}^1 + T_{2u}^2 - 2T_{2u}^3\}, \\
& \{-T_{2g}^1 - T_{2g}^2 + 2T_{2g}^3, T_{2g}^1 - T_{2g}^2\}, \\
& \{-T_{1u}^1 - T_{1u}^2 + 2T_{1u}^3, T_{1u}^1 - T_{1u}^2\}
\end{array}$$

 E

$$\begin{array}{ll}
A_1 & A_{1g}, A_{2u}, T_{2g}^1 - T_{2g}^2 + T_{2g}^3, T_{1u}^1 - T_{1u}^2 + T_{1u}^3 \\
A_2 & A_{1u}, A_{2g}, T_{1g}^1 - T_{1g}^2 + T_{1g}^3, T_{2u}^1 - T_{2u}^2 + T_{2u}^3 \\
E & \{E_g^1, E_g^2\}, \{E_u^1, E_u^2\}, \{T_{2g}^1 - T_{2g}^2 - 2T_{2g}^3, -T_{2g}^1 - T_{2g}^2\}, \\
& \{T_{1u}^1 - T_{1u}^2 - 2T_{1u}^3, -T_{1u}^1 - T_{1u}^2\}, \\
& \{T_{1g}^1 + T_{1g}^2, T_{1g}^1 - T_{1g}^2 - 2T_{1g}^3\}, \\
& \{T_{2u}^1 + T_{2u}^2, T_{2u}^1 - T_{2u}^2 - 2T_{2u}^3\}
\end{array}$$

 L

$$\begin{array}{ll}
A_{1g} & A_{1g}, T_{2g}^1 + T_{2g}^2 + T_{2g}^3 \\
A_{2g} & A_{2g}, T_{1g}^1 + T_{1g}^2 + T_{1g}^3 \\
A_{1u} & A_{1u}, T_{2u}^1 + T_{2u}^2 + T_{2u}^3 \\
A_{2u} & A_{2u}, T_{1u}^1 + T_{1u}^2 + T_{1u}^3 \\
E_g & \{E_g^1, E_g^2\}, \{T_{2g}^1 + T_{2g}^2 - 2T_{2g}^3, T_{2g}^1 - T_{2g}^2\} \\
& \{T_{1g}^1 - T_{1g}^2, T_{1g}^1 + T_{1g}^2 - 2T_{1g}^3\} \\
E & \{E_u^1, E_u^2\}, \{T_{2u}^1 + T_{2u}^2 - 2T_{2u}^3, T_{2u}^1 - T_{2u}^2\} \\
& \{T_{1u}^1 - T_{1u}^2, T_{1u}^1 + T_{1u}^2 - 2T_{1u}^3\}
\end{array}$$

V

$$\begin{array}{l}
 A' \quad A_{1g}, A_{2u}, E_g^1, E_u^2, T_{2g}^3, T_{1u}^3, T_{1g}^1 + T_{1g}^2, \\
 \quad T_{2g}^1 - T_{2g}^2, T_{2u}^1 + T_{2u}^2, T_{1u}^1 - T_{1u}^2 \\
 A'' \quad A_{2g}, A_{1u}, E_g^2, E_u^1, T_{1g}^3, T_{2u}^3, T_{2g}^1 + T_{2g}^2, \\
 \quad T_{1g}^1 - T_{1g}^2, T_{1u}^1 + T_{1u}^2, T_{2u}^1 - T_{2u}^2
 \end{array}$$

C

$$\begin{array}{l}
 A' \quad A_{1g}, A_{2u}, E_g^1, E_u^2, T_{2g}^3, T_{1u}^3, T_{2g}^1 + T_{2g}^2, \\
 \quad T_{1g}^1 - T_{1g}^2, T_{2u}^1 - T_{2u}^2, T_{1u}^1 + T_{1u}^2 \\
 A'' \quad A_{1u}, A_{2g}, E_g^2, E_u^1, T_{1g}^3, T_{2u}^3, T_{2g}^1 - T_{2g}^2, \\
 \quad T_{1g}^1 + T_{1g}^2, T_{2u}^1 + T_{2u}^2, T_{1u}^1 - T_{1u}^2
 \end{array}$$

O

$$\begin{array}{l}
 A' \quad A_{1g}, A_{2g}, E_g^1, E_g^2, T_{2u}^1, T_{2u}^2, T_{1u}^1, T_{1u}^2, T_{2g}^3, T_{1g}^3 \\
 A'' \quad A_{1u}, A_{2u}, E_u^1, E_u^2, T_{2g}^1, T_{2g}^2, T_{1g}^1, T_{1g}^2, T_{2u}^3, T_{1u}^3
 \end{array}$$

J

$$\begin{array}{l}
 A' \quad A_{1g}, A_{2u}, E_g^1 + \sqrt{3}E_g^2, -\sqrt{3}E_u^1 + E_u^2, T_{2g}^1 + T_{2g}^3, \\
 \quad T_{2g}^2, T_{1g}^1 - T_{1g}^3, T_{2u}^1 - T_{2u}^3, T_{1u}^1 + T_{1u}^3, T_{1u}^2 \\
 A'' \quad A_{2g}, A_{1u}, -\sqrt{3}E_g^1 + E_g^2, E_u^1 + \sqrt{3}E_u^2, T_{2g}^1 - T_{2g}^3, \\
 \quad T_{1g}^1 + T_{1g}^3, T_{1g}^2, T_{2u}^1 + T_{2u}^3, T_{2u}^2, T_{1u}^1 - T_{1u}^3
 \end{array}$$

B

$$\begin{array}{l}
 A' \quad A_{1g}, A_{2g}, E_g^1, E_g^2, T_{2g}^2, T_{1g}^2, T_{2u}^1, T_{2u}^3, T_{1u}^1, T_{1u}^3 \\
 A'' \quad A_{1u}, A_{2u}, E_u^1, E_u^2, T_{2u}^2, T_{1u}^2, T_{2g}^1, T_{2g}^3, T_{1g}^1, T_{1g}^3
 \end{array}$$

Q

$$\begin{array}{l}
 \text{A} \quad A_{1g}, A_{1u}, E_g^1 - \sqrt{3}E_g^2, E_u^1 - \sqrt{3}E_u^2, T_{1g}^2 - T_{1g}^3, \\
 T_{1u}^2 - T_{1u}^3, T_{2g}^1, T_{2g}^2 + T_{2g}^3, T_{2u}^1, T_{2u}^2 + T_{2u}^3 \\
 \text{B} \quad A_{2g}, A_{2u}, -\sqrt{3}E_g^1 - E_g^2, -\sqrt{3}E_u^1 - E_u^2, T_{2g}^2 - T_{2g}^3, \\
 T_{2u}^2 - T_{2u}^3, T_{1g}^1, T_{1g}^2 + T_{1g}^3, T_{1u}^1, T_{1u}^2 + T_{1u}^3
 \end{array}$$

A

A all harmonics of Γ .

CHAPTER III. THE LATTICE HARMONICS FOR THE IRREDUCIBLE REPRESENTATIONS OF THE REMAINING CUBIC GROUPS.

3.1 Introduction.

In the previous chapter three particularly important cubic space groups were considered. And in this chapter we shall summarize the work on the rest of the cubic space groups. For reasons of space it has been necessary to omit from the present account all the detailed results which it is hoped to publish shortly anyway, and to confine the discussion to a description of what has been done, stating clearly at each stage where results have been omitted. A few random examples will be given therefore in lieu of the full results which would exceed, on their own, 100 pages of quarto typescript.

3.2 The Remaining Symmorphic Cubic Space Groups.

There remain twelve symmorphic space groups, namely those arising by associating each of the point groups 23 , $m\bar{3}$, $43m$, and 432 with each of the three cubic Bravais lattices. These can all be treated exactly as the three space groups considered in chapter II. In this case $\underline{G}^{\underline{k}}$ will be some subgroup of $\underline{G}^{\underline{k}}$ for the same $\underline{k}$ vector in the Brillouin Zone of the corresponding $m\bar{3}m$ type space group. The subgroup $\underline{G}^{\underline{k}}$ for, say, $F23$ will consist of those elements in $\underline{G}^{\underline{k}}$ for $Fm\bar{3}m$ which are also present in the point group 23 . It is thus possible, by inspection, to write down the results for $\underline{G}^{\underline{k}}$ for all these twelve space groups: this is done in Table 3.1.

TABLE 3.1 THE ELEMENTS OF THE GROUP OF THE k -VECTOR FOR ALL POINTS IN THE FIRST BRILLOUIN ZONE OF EACH OF THE 15 SYMMORPHIC CUBIC SPACE GROUPS.

Note:

In the Table $\underline{G}^k$ is given, it is explained in the text how to find $\underline{G}^k$, and thence $\underline{G}^k$ for the asymmetric cubic groups.

(P.T.O.)

(a) Primitive Bravais Lattice.

	P23	Pm3	P43m	P432	Pm3m
IR	ALL	ELEMENTS	OF POINT	GROUP.	
Σ	E	E, σ_z	E, σ_{db}	E, C_{2a}	$E, C_{2a}, \sigma_z, \sigma_{db}$
Δ, T	E, C_{2y}	$E, C_{2y}, \sigma_z, \sigma_x$	$E, C_{2y}, \sigma_{dc}, \sigma_{de}$	$E, C_{2y}, C_{4y}^{\pm}$	$E, C_{2y}, C_{4y}^{\pm}, \sigma_z, \sigma_x, \sigma_{de}$
Λ	$E, C_{31}^{\pm}$	$E, C_{31}^{\pm}$	$E, C_{31}^{\pm}, \sigma_{db}, \sigma_{dc}, \sigma_{de}$	$E, C_{31}^{\pm}$	$E, C_{31}^{\pm}, \sigma_{db}, \sigma_{dc}, \sigma_{de}$
S	E	E, σ_y	E, σ_{de}	E, C_{2e}	$E, C_{2c}, \sigma_y, \sigma_{de}$
X	$E, C_{2x}, C_{1y}, C_{1z}$	$E, C_{2y}, C_{2z}, C_{2x}, I, \sigma_y, \sigma_z, \sigma_x$	$E, C_{2y}, C_{2z}, C_{2x}, \sigma_{dy}^{\pm}, \sigma_{de}, \sigma_{de}$	$E, C_{4y}^{\pm}, C_{2y}, C_{2z}, C_{2x}, C_{2c}, C_{2e}$	$E, C_{4y}^{\pm}, C_{2m}, C_{2c}, C_{2e}, I, \sigma_{dy}^{\pm}, \sigma_m, \sigma_{dc}, \sigma_{de}$
M	∞X	$E, C_{2z}, C_{2x}, C_{1y}, I, \sigma_z, \sigma_x, \sigma_y$	$E, C_{2z}, C_{2x}, C_{2y}, \sigma_{dz}^{\pm}, \sigma_{de}, \sigma_{db}$	$E, C_{2z}, C_{2x}, C_{2y}, C_{2a}, C_{2b}, C_{4z}^{\pm}$	$E, C_{4z}^{\pm}, C_{2m}, C_{2a}, C_{2b}, I, \sigma_{dz}^{\pm}, \sigma_m, \sigma_{da}, \sigma_{db}$
Z	E, C_{2x}	$E, C_{2x}, \sigma_y, \sigma_z$	E, C_{2x}	E, C_{2x}	$E, C_{2x}, \sigma_y, \sigma_z$
C	E	E	E, σ_{db}	E	E, σ_{db}
O	E	E, σ_z	E	E	E, σ_z
T	E	E	E, σ_{de}	E	E, σ_{de}
B	E	E, σ_y	E	E	E, σ_y
A	E	E	E	E	E

(b)

Face-centred cubic Lattice.

	F23	Fm3	F43m	F432	Fm3m
Γ		ELEMENTS	OF POINT	GROUP.	
Σ, K	E	E, σ_z	E, σ_{db}	E, C_{2a}	$E, C_{2a}, \sigma_z, \sigma_{db}$
Δ	E, C_{2y}	$E, C_{2y}, \sigma_z, \sigma_x$	$E, C_{2y}, \sigma_{de}, \sigma_{dc}$	$E, C_{2y}, C_{4y}^{\pm}$	$E, C_{2y}, C_{4y}^{\pm}, \sigma_z, \sigma_x, \sigma_{de}, \sigma_{dc}$
Λ	$E, C_{31}^{\pm}$	$E, C_{31}^{\pm}$	$E, C_{31}^{\pm}, \sigma_{db}, \sigma_{df}, \sigma_{de}$	$E, C_{31}^{\pm}$	$E, C_{31}^{\pm}, \sigma_{db}, \sigma_{df}, \sigma_{de}$
S, H	E	E, σ_y	E, σ_{de}	E, C_{2c}	$E, C_{2c}, \sigma_y, \sigma_{de}$
X	AS	PRIMITIVE	LATTICE, X.		
Z	AS	PRIMITIVE	LATTICE, Z.		
W	E, C_{2x}	$E, C_{2x}, \sigma_y, \sigma_z$	$E, S_{4x}^{\pm}, C_{2x}$	$E, C_{2x}, C_{2d}, C_{2f}$	$E, S_{4x}^{\pm}, C_{2x}, \sigma_y, \sigma_z, C_{2d}, C_{2f}$
L	$E, C_{31}^{\pm}$	$E, C_{31}^{\pm}, I, S_{61}^{\pm}$	$E, C_{31}^{\pm}, \sigma_{db}, \sigma_{de}, \sigma_{df}$	$E, C_{31}^{\pm}, C_{2b}, C_{2e}, C_{2f}$	$E, C_{31}^{\pm}, \sigma_{db}, \sigma_{de}, \sigma_{df}, I, S_{61}^{\pm}, C_{2b}, C_{2e}, C_{2f}$
Q	E	E	E	E, C_{2f}	E, C_{2f}
C	E	E	E, σ_{db}	E	E, σ_{db}
O	E	E, σ_z	E	E	E, σ_z
T	E	E	E, σ_{de}	E	E, σ_{de}
B	E	E, σ_y	E	E	E, σ_y
A	E	E	E	E	E

	I 23	I m 3	I $\bar{4}$ 3 m OF POINT LATTICE, Δ .	I 4 3 2 GROUP.	I m 3 m
Γ	ALL	ELEMENTS	E, σ_{ab}		
Σ	E	E, σ_z	E, σ_{ab}	E, C_{2a}	E, $C_{2a}, \sigma_z, \sigma_{db}$
Δ	AS	PRIMITIVE	LATTICE, Δ .		
Λ	AS	PRIMITIVE	LATTICE, Λ .		
F	$E, C_{3a}^{\pm}$	$E, C_{3a}^{\pm}$	$E, C_{3a}^{\pm}, \sigma_{da}, \sigma_{db}, \sigma_{de}$	$E, C_{3a}^{\pm}$	$E, C_{3a}^{\pm}, \sigma_{da}, \sigma_{db}, \sigma_{de}$
G	E	E, σ_z	E, σ_{da}	E, C_{2b}	E, $C_{2b}, \sigma_z, \sigma_{da}$
D	E, C_{2z}	E, C_{2z}	$E, C_{2z}, \sigma_{da}, \sigma_{db}$	E, C_{2z}	$E, C_{2z}, \sigma_{da}, \sigma_{db}$
P	AS Γ .	AS I 23 Γ .	AS Γ	AS I 23 Γ	AS I $\bar{4}$ 3 m Γ
N	E, C_{2z}	E, C_{2a}, I, σ_z	$E, C_{2z}, \sigma_{da}, \sigma_{db}$	$E, C_{2a}, C_{2b}, C_{2z}$	$E, C_{2a}, C_{2b}, C_{2z},$ $I, \sigma_{da}, \sigma_{db}, \sigma_z$
V	E	E	E, σ_{da}	E	E, σ_{da}
C	E	E	E, σ_{db}	E	E, σ_{db}
O	E	E, σ_z	E	E	E, σ_z
T	E	E	E, σ_{de}	E	E, σ_{de}
A	E	E	E	E	E

Having found $\underline{G}^k$ it is possible to find matrix representatives for Γ , to perform the subduction process and thence to obtain the lattice harmonics exactly as in chapter II. The results have been obtained and are given as Appendix I to this chapter, which is arranged in the same way as Table 2.4 in chapter II.

3.3 The Asymorphic Cubic Space Groups.

Various asymorphic cubic space groups have been considered in detail, e.g. diamond by Herring (1942), several by Slater (1963) and, in a very different notation by some Russian workers. To achieve a unified treatment we have considered all the asymorphic space groups from the start; although this involves a certain duplication of a few space groups this was considered to be preferable to trying to adapt treatments of specific space groups using other notations, since there are variations in the labelling of the symmetry operations, in the labelling of the representations, and also in the choice of the representative portion of the Brillouin Zone to be used for the evaluation of $\underline{G}^k$, and of course, finally, there are some authors using left handed sets of axes and others using right handed sets of axes. The results of Herring (1942) for diamond, $Fd\bar{3}m$, have been compared with our own as a check on the general procedure, and all was found to be in order. If we consider all the operations ($\underline{R}/\underline{t}$) of one of the symorphic space groups it is possible to derive all the operations of those asymorphic space groups "isomorphous" to it, by taking all the $\underline{R}$'s as before and altering some ~~of~~

of the $\underline{t}$'s subject to the condition that the new elements still form a group. It is necessary to define what is meant by "isomorphous". A space group is said to be "isogonal" to a point group $\underline{G}$ if, on putting $\underline{t} = 0$ in all the operators of the space group, the result is the point group $\underline{G}$. And an asymorphic space group is said to be "isomorphous" to the symorphic space group which is obtained by associating the point group $\underline{G}$ with each lattice point of the original space group; where two orientations of the isogonal point group $\underline{G}$ on the Bravais Lattice are possible that one is chosen in which each operator ($\underline{R}_i/\underline{0}$) is in the same orientation as the original operator ($\underline{R}_i/\underline{t}$). It is realized that not everyone uses these definitions of the terms.

3.4 Elements of Asymorphic Space Groups.

As mentioned already the elements of any asymorphic space group are very closely related to those of the isomorphous space group. And the translations $\underline{t}$ associated with the elements of the asymorphic cubic space groups are listed in Table 3.2, which is adapted from the one given by Iyubarskii (1960). The notation has been changed from that of this reference so that $\underline{t}$ is now expressed in terms of the vectors $(a,0,0)$, $(0,a,0)$, and $(0,0,a)$ for all three cubic Bravais lattices, and one or two ambiguities have been removed. It will be noticed that the sense of the elements ($\underline{R}/\underline{t}$) as screw axes or glide planes has been lost, so that for a rotation $\underline{R}$, $\underline{t}$ is not necessarily along the axis of $\underline{R}$.

This is done so as to have all the axes and planes passing through the points of the Bravais lattice, which, if one adheres to strict screws and glides is not the case. Only one translation $\underline{t}$ is shown for each element in a given space group, but it may have added to it any translation of the appropriate Bravais lattice thus providing all the elements of the (infinite) space group.

TABLE 5.2 THE ELEMENTS (R/t) FOR THE ASYMMORPHIC CUBIC SPACE GROUPS.

Note.

The translations are given as (t_1, t_2, t_3) so that $\underline{t}$ is actually $a(t_1\underline{i} + t_2\underline{j} + t_3\underline{k})$ where a is the side of the unit cube and the basis vectors of the three lattices are:

P: $a(1,0,0)$	F: $a(0, \frac{1}{2}, \frac{1}{2})$	I: $a(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
$a(0,1,0)$	$a(\frac{1}{2}, 0, \frac{1}{2})$	$a(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$
$a(0,0,1)$	$a(\frac{1}{2}, \frac{1}{2}, 0)$	$a(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$

1.) 23 type.

$P2_13 (T^4)$.

$\{E/000\}$	$\{C_{31}^-/000\}$	$\{C_{31}^+/000\}$
$\{C_{2x}/\frac{1}{2}\frac{1}{2}0\}$	$\{C_{32}^-/\frac{1}{2}\frac{1}{2}0\}$	$\{C_{32}^+/0\frac{1}{2}\frac{1}{2}\}$
$\{C_{2y}/0\frac{1}{2}\frac{1}{2}\}$	$\{C_{33}^-/0\frac{1}{2}\frac{1}{2}\}$	$\{C_{33}^+/\frac{1}{2}0\frac{1}{2}\}$
$\{C_{2z}/\frac{1}{2}0\frac{1}{2}\}$	$\{C_{34}^-/\frac{1}{2}0\frac{1}{2}\}$	$\{C_{34}^+/\frac{1}{2}\frac{1}{2}0\}$

$I2_13 (T^5)$

$\{E/000\}$	$\{C_{31}^-/000\}$	$\{C_{31}^+/000\}$
$\{C_{2x}/00\frac{1}{2}\}$	$\{C_{32}^-/00\frac{1}{2}\}$	$\{C_{32}^+/00\frac{1}{2}\}$
$\{C_{2y}/\frac{1}{2}00\}$	$\{C_{33}^-/00\frac{1}{2}\}$	$\{C_{33}^+/00\frac{1}{2}\}$
$\{C_{2z}/0\frac{1}{2}0\}$	$\{C_{34}^-/0\frac{1}{2}0\}$	$\{C_{34}^+/00\frac{1}{2}\}$

For the rest of the space groups the elements are those of the space group listed in column 3 plus those same elements premultiplied by the operator shown in column 2.

2.) $m\bar{3}$ type.

1	2	3
T_h^2 $Pn\bar{3}$	$I/\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$P23$
T_h^6 $Pn\bar{3}$	$I/000$	$P2_13$
T_h^4 $Pn\bar{3}$	$I/\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$F23$
T_h^7 $Ia\bar{3}$	$I/000$	$I2_13$

3.) $\bar{4}3m$ type.

1	2	3
T_d^4 $F\bar{4}3c$	$\sigma_{ab}/\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$P23$
T_d^5 $F\bar{4}3c$	$\sigma_{ab}/\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$F23$
T_d^6 $I\bar{4}3d$	$\sigma_{ab}/\frac{1}{2}\frac{1}{2}\frac{1}{2}$	$I2_13$

4.) 432 type.

1	2	3
O^7 $P4_132$	$C_{4v}^-/\bar{4}22$	$P2_13$
O^2 $P4_232$	$C_{4v}^-/\bar{3}22$	$P2_13$
O^6 $P4_332$	$C_{4v}^-/\bar{2}22$	$P2_13$
O^4 $F4_132$	$C_{4v}^-/\bar{4}22$	$P23$
O^8 $I4_132$	$C_{4v}^-/\bar{4}2-2$	$I2_13$

5.) m3m type.

1	2	3
O_h^2 $Pn3n$	$\sigma_{db}/\bar{4}22$	$P432$
O_h^3 $Pm3n$	$\sigma_{db}/\bar{4}22$	$P4_232$
O_h^4 $Pn3m$	$\sigma_{db}/000$	$P4_232$
O_h^6 $Fm3c$	$\sigma_{db}/\bar{4}22$	$F432$
O_h^7 $Fd3m$	$\sigma_{db}/000$	$F4_132$
O_h^8 $Fd3c$	$\sigma_{db}/\bar{4}22$	$F4_132$
O_h^{10} $Ia3d$	$\sigma_{db}/\bar{4}2-2$	$I4_132$

3.5 The Brillouin Zones and G^k for Asymorphic Cubic Space Groups.

The Brillouin Zone is defined with reference to the basis vectors of the Bravais lattice on which the space group in question is constructed so that the Brillouin Zone for an asymorphic space group is exactly the same as for the isomorphous space group. The three zones have already been given in chapter II Figures 2.1, 2.2 and 2.3. The

group of the $\underline{k}$ -vector is the same as for the isomorphous space group which appears in Table 3.1, but it must be remembered that the results of Table 3.1 are only a shorthand for a group $\underline{G}^{\underline{k}}$ which is, in fact, infinite. For a symmorphic space group it was always possible to express this infinite group as a semi-direct product of the translation group of the Bravais lattice and a point group, i.e. $\underline{G}^{\underline{k}} = \underline{\Gamma} \wedge \underline{G}^{\underline{k}}$. For an asymmorphic space group it is still possible to write $\underline{G}^{\underline{k}} = \underline{\Gamma} \wedge \underline{G}^{\underline{k}}$ but $\underline{G}^{\underline{k}}$ which still exists may no longer be a point group, indeed it may not even be a group at all, in which case we may call it the "pseudo co-group". If $\underline{G}^{\underline{k}}$ is no longer a point group it will however still be simply related to a point group: for instance consider Table 3.1 point J of $F\bar{4}3m$, then the group $\underline{G}^{\underline{k}}$ is the semi-direct product of $(\underline{E}/\underline{t})$, the group of all lattice translations, with the group $(\underline{E}/0) + (\underline{\sigma}_{de}/0)$, this latter group being $\underline{G}^{\underline{k}}$. Now consider point J of $F\bar{4}3c$, $\underline{G}^{\underline{k}}$ consists of the infinite group of all elements of lattice translations $(\underline{E}/\underline{t})$ and all the elements $(\underline{E}/\underline{t})(\underline{\sigma}_{de}/\underline{t}')$ where $\underline{t}'$ is the translation specified in Table 3.2 for $\underline{\sigma}_{de}$ in this particular space group. $\underline{G}^{\underline{k}}$ is now thus $(\underline{E}/0) + (\underline{\sigma}_{de}/\underline{t}')$ which is not a point group. It can only be a point group usually if $\underline{t}'$ is zero, which is not the case here. The method of Herring (1942) however makes it possible to find the irreducible representations of an asymmorphic space group: in effect instead of writing $\underline{G}^{\underline{k}}$ as $\underline{\Gamma} \wedge \underline{G}^{\underline{k}}$ where $\underline{G}^{\underline{k}}$ is no

longer a group it is possible to express $\underline{G}^k$ as $\underline{\Gamma}^k \wedge \underline{C}^k$ where $\underline{\Gamma}^k$ is the subgroup of $\underline{\Gamma}$ defined by the property that the matrix representative of every element in $\underline{\Gamma}^k$ is 1, i.e. for $(\underline{R}/\underline{t})$ to be in $\underline{\Gamma}^k$ we have $\underline{k} \cdot \underline{t} = 2n\pi$, where n is some integer.

Now having expressed $\underline{G}^k$ as a genuine semi-direct product, where the co-group $\underline{C}^k$ is actually a group the process of reduction of the space group can be followed through just as in the case of the symmorphic groups, but with one slight complication in practice. This is the fact that the group $\underline{C}^k$ is not necessarily a point group and therefore it may be necessary to find the irreducible representations of $\underline{C}^k$ from first principles instead of, as in the symmorphic cases, referring to the published sets of character tables for the point groups. It is therefore necessary to describe briefly how this is done.

3.6 To Find the Character Table and Irreducible Representations of the Group $\underline{C}^k$

The preliminary investigation of an asymmorphic space group makes it possible to identify the group $\underline{\Gamma}^k$ and hence $\underline{C}^k$. In practice $\underline{C}^k$ is found by starting with the pseudo-co-group $\underline{C}^k$ and constructing the multiplication table, replacing any element of $\underline{\Gamma}^k$ when it appears, by $(\underline{R}/0)$ and introducing just enough extra elements to ensure the closure of the group. $\underline{C}^k$ will always be of order equal to some

integral multiple of the number of elements in the "pseudo-co-group" $\underline{G}^k$.

Assuming $\underline{C}^k$ given the character table can be constructed as follows. The theory of the method is well established and need not be given here.

(i) the elements of the group must be sorted into classes, i.e. for a given element R the products $X^{-1}RX$ are formed for all the elements X of the group, and the elements so formed constitute one of the classes of the group, this is done for enough of the R's to assign all the elements of the group to their classes,

(ii) having split the group into classes in this way the class multiplication coefficients are formed, c_{ijk} , where

$$\underline{C}_i \times \underline{C}_j = \sum_k c_{ijk} \underline{C}_k,$$

and $\underline{C}_i, \underline{C}_j, \underline{C}_k$ are classes of the group. These coefficients are evaluated for all i, j, k, i.e. $1 \leq i \leq m; 1 \leq j \leq m;$ and $1 \leq k \leq m$, where m is the number of classes in the group.

(iii) If the class $\underline{C}_i$ is of order h_i , then for the α th representation, of order n_α , we have the well known equations

$$h_i \chi_\alpha(\underline{C}_i) \cdot h_j \chi_\alpha(\underline{C}_j) = n_\alpha \sum_k c_{ijk} h_k \chi_\alpha(\underline{C}_k).$$

These form a set of m^2 equations for $\chi_\alpha(\underline{C}_i)$ for given n_α , so that with m variables $m(m-1)$ of them are redundant.

(iv) A set of solutions can be obtained for $\chi_\alpha(\underline{C}_i)$ in terms of n_α . But several of these sets of solutions may not be genuine solutions for there is the orthogonality condition to be satisfied as well, the first part of which is

that $\sum_i h_i \chi_{\alpha}^*(C_i) \chi_{\alpha}(C_i) = \text{order of the group}$. The solutions which, having satisfied this last condition, still remain can be put together to form the character table. It will be seen that just the right number of representations will have been obtained (i.e. this is equal to the number of classes). This provides a valuable check at this stage, as also does the rest of the orthogonality condition for the characters, namely $\sum_i h_i \chi_{\alpha}^*(C_i) \chi_{\beta}(C_i) = 0$, for all possible pairs of representations, so long as $\alpha \neq \beta$.

3.7 Summary of Results on Reduction of C_k^k .

The technique described above has been applied to all the asynorphic cubic and tetragonal space groups for all points, lines and planes of symmetry in the relevant Brillouin Zone. The working is very long, and the presentation of the results alone would be too bulky to include here. As an indication of the work involved the groups C_k^k occur with orders up to 96, there being three groups of order 96, six of order 48, etc., etc. A random example, one point of symmetry for one cubic space group will be given in the next section. This work on the cubic and tetragonal space groups, together with similar work by Dr C J Bradley on the space groups of the other five crystal systems will, it is hoped, be published shortly.

3.8 An Example of Reduction of the group C_k^k .

As an example, chosen at random from the massive

selection available, the case of point X for the space group $Pn\bar{3}m$, (O_h^4 , space group number 224) is considered.

At X: $k = 2\pi/a(0\frac{1}{2}0)$, so that if $(\underline{E}/\underline{t})$ is a member of $\underline{\Gamma}^k$ then:

$$\frac{2\pi}{a} (0\frac{1}{2}0) \cdot (t_1, t_2, t_3) = 2n\pi,$$

so that $t_2 = 2na$, and $\underline{\Gamma}^k$ has elements $(\underline{E}/\underline{t}_1, 2na, \underline{t}_3)$, where n is an integer.

The elements of $\underline{\Gamma}^k$ the pseudo-co-group for X are:

E	$\{\underline{E}/000\}$	P	$\{I/\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$
B	$\{C_{2x}/000\}$	Q	$\{\sigma_x/\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$
C	$\{C_{2y}/000\}$	R	$\{\sigma_y/\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$
D	$\{C_{2z}/000\}$	S	$\{\sigma_z/\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$
K	$\{C_{4y}^-/\frac{1}{4}\frac{1}{4}\frac{1}{2}\}$	T	$\{S_{4y}^+/000\}$
L	$\{C_{4y}^+/\frac{3}{4}\frac{3}{4}\frac{1}{2}\}$	U	$\{S_{4y}^-/000\}$
M	$\{C_{2c}/\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$	V	$\{\sigma_{dc}/000\}$
N	$\{C_{2c}/\frac{1}{2}\frac{1}{2}\frac{1}{2}\}$	W	$\{\sigma_{dc}/000\}$

where the letters E, B, C, etc., are used as a shorthand labelling of them; all translation components are written in terms of a, as in Table 3.2. It should be noticed that the values of $\underline{t}'$ appearing here are relatively simple; it is perfectly possible for example for C_{2x} , C_{2y} , C_{2z} to have different values of $\underline{t}'$, for instance in $Ia\bar{3}d$ they have $(00\frac{1}{2})$, $(\frac{1}{2}00)$, and $(0\frac{1}{2}0)$ respectively. Using the fact that the elements of $\underline{\Gamma}^k$ have been identified we attempt to construct the multiplication table using these 16 elements, but they do not form a group; for example $(C_{4y}^-/\frac{1}{4}\frac{1}{4}\frac{1}{2})(C_{4y}^-/\frac{1}{4}\frac{1}{4}\frac{1}{2}) =$

$$(C_{4y}^- C_{4y}^- / C_{4y}^- (\frac{1}{2}\frac{1}{2}\frac{1}{2}) + (\frac{1}{2}\frac{1}{2}\frac{1}{2})) \quad (i)$$

from the multiplication rule for Seitz space group operators. From Chapter I Appendix I it follows that $C_{4y}^- (\frac{1}{2}\frac{1}{2}\frac{1}{2}) = (-\frac{1}{2}\frac{1}{2}\frac{1}{2})$ so that (i) becomes $(C_{2y} / (-\frac{1}{2}\frac{1}{2}\frac{1}{2}) + (\frac{1}{2}\frac{1}{2}\frac{1}{2})) = (C_{2y} / 011)$. This is not a member of $\underline{C}^k$, although $(C_{2y} / 000)$ is. $\underline{C}^k$ is constructed by using the extended definition of the identity that if $(C_{2y} / 011)$ is equal to $(C_{2y} / 000)$ multiplied by an element of $\underline{\Gamma}^k$ it is possible to replace $(C_{2y} / 011)$ by $(C_{2y} / 000)$. In this way $\underline{C}^k$ is built up, and it may contain only as many elements as the pseudo-co-group $\underline{\Gamma}^k$. In this case, however, $(C_{2y} / 011) = (E / 011)(C_{2y} / 000)$ and $(E / 011)$ is not a member of $\underline{\Gamma}^k$. Therefore $(C_{2y} / 011)$ must appear in $\underline{C}^k$ as well as $(C_{2y} / 000)$. On doing this for all other possible products a closed group is obtained with in fact 32 elements, i.e. each element in $\underline{\Gamma}^k$ is duplicated; thus there are two "identity" operations $(E / 000)$ and $(E / 010)$. If $(E / 010)$ is denoted by E' and the product of element B with E' is denoted by B' and so on, the group multiplication table for this $\underline{C}^k$ is as shown in Table 3.3.

On forming the products $X^{-1}RX$ the elements divide themselves into 14 classes, so that there must be 14 irreducible representations. The classes are:

C_1	E	C_2	E'
C_3	$BDB'D'$		
C_4	θ	C_5	C'

TABLE 3.3 GROUP MULTIPLICATION TABLE FOR C^k FOR $X, Pn3m$.

E	B	C	D	K	L	M	N	P	Q	R	S	T	U	V	W
B	E	D	C	N'	M'	L'	K'	Q'	P'	S'	R'	W	V	U	T
C	D	E	B	L	K	N	M	R	S	P	Q	U	T	W	V
D	C	B	E	M'	N'	K'	L'	S'	R'	Q'	P'	V	W	T	U
K	M	L	N	C'	E'	D'	B'	T'	V'	U'	W'	R	P	S	Q
L	N	K	M	E'	C'	B'	D'	U'	W'	T'	V'	P	R	Q	S
M	K	N	L	B	D	E	C	V	T	W	U	Q	S	P	R
N	L	M	K	D	B	C	E	W	U	V	T	S	Q	R	P
P	Q	R	S	T	U	V	W	E	B	C	D	K	L	M	N
Q	P	S	R	W'	V'	U'	T'	B'	E'	D'	C'	N	M	L	K
R	S	P	Q	U	T	W	V	C	D	E	B	L	K	N	M
S	R	Q	P	V'	W'	T'	U'	D'	C'	B'	E'	M	N	K	L
T	V	U	W	R'	P'	S'	Q'	K'	M'	L'	N'	C	E	D	B
U	W	T	V	P'	R'	Q'	S'	L'	N'	K'	M'	E	C	B	D
V	T	W	U	Q	S	P	R	M	K	N	L	B	D	E	C
W	U	V	T	S	Q	R	P	N	L	M	K	D	B	C	E

Notes.

(i) This is only $\frac{1}{2}$ of the whole group multiplication table, the deduction of the rest is trivial since E' commutes with all elements of the group.

(ii) Though here the primed elements occur in sets together this is by no means always true, the table can, for another group, have primed and unprimed elements much more jumbled up with one another.

$$C_6 \quad KIK'L'$$

$$C_7 \quad MN'$$

$$C_8 \quad M'N$$

$$C_9 \quad PP'$$

$$C_{10} \quad QSQ'S'$$

$$C_{11} \quad RR'$$

$$C_{12} \quad TUT'U'$$

$$C_{13} \quad WV$$

$$C_{14} \quad W'V'$$

It is not necessary to list all the class multiplication coefficients c_{ijk} and a few examples only will be given; from the extracts from the group multiplication table given below one can see immediately that

a) $c_{111} = 1; \quad c_{11k} = 0, \quad k \neq 1.$

b) $c_{331} = 4$

$$c_{332} = 4$$

$$c_{334} = 4$$

$$c_{335} = 4; \quad c_{33k} = 0, \quad \text{all other } k \text{ values.}$$

c) $c_{3,11,10} = 2; \quad c_{3,11,k} = 0, \quad k \neq 10.$

(a)

	E
E	E

(b)

	B	D	B'	D'
B	E	C	B'	C'
D	C	E	C'	E'
B'	E'	C'	B	C
D'	C'	E'	C	E

(c)

	R	R'
B	S'	S
D	Q'	Q
B'	S	S'
D'	Q	Q'

$c_{111} = 1$ means, denoting $\chi(C_1)$ by x_1 , that $x_1^2 = nx_1$ or $x_1 = n$. Considering $c_{221} = 1$, this means that $x_2 \cdot x_2 = nx_1$, $x_2^2 = n^2$, or $x_2 = \pm n$. Continuing in this fashion, picking out only the coefficients which seem likely to lead to useful results one can quickly build up the solution in terms of n , the order of the representation. This appears in Table 3.4.

TABLE 3.4 SOLUTION OF CHARACTER EQUATIONS FOR x_i 's.

Order	x_i	Possible values.											
1	x_1	n											
1	x_2	n						$-n$					
4	x_3	n			$-n$			0			0		
1	x_4	n			$-n$			n			$-n$		
1	x_5	n			$-n$			$-n$			n		
4	x_6	n		$-n$		n		$-n$		0		0	
2	x_7	n		$-n$		$-n$		n		0		n $-n$	
2	x_8	n		$-n$		$-n$		n		0		0 $-n$ n	
2	x_9	n	$-n$	n	$-n$	n	$-n$	n	$-n$	n	$-n$	0	0
4	x_{10}	n	$-n$	n	$-n$	$-n$	n	$-n$	n	0	0	0	0
2	x_{11}	n	$-n$	n	$-n$	n	$-n$	n	$-n$	$-n$	n	0	0
4	x_{12}	n	$-n$	$-n$	n	n	$-n$	$-n$	n	0	0	0	0
2	x_{13}	n	$-n$	$-n$	n	$-n$	n	n	$-n$	0	0	n $-n$	0
2	x_{14}	n	$-n$	$-n$	n	$-n$	n	n	$-n$	0	0	$-n$ n	0

And the only values of n for which these solutions fit

the orthogonality conditions $\sum_i h_i \chi_i^* \chi_i = 32$ are, for the first 8 columns, $n = 1$, and for the last 6 columns $n = 2$, providing a total of 14 solutions, which is equal to the number of classes as required. In this particular case there are no redundant solutions at all. It will also be noticed that the sum of the squares of the orders of the representations is $8 \times (1)^2 + 6 \times (2)^2 = 8 + 24 = 32 = \text{order of the group}$, which it must do and this serves as another useful check.

The final result with n values inserted is shown in Table 3.5. The orthogonality of the characters can quite readily be checked, and will be found to be satisfied.

Of all the description included here for completeness, and the working which has, largely, been omitted the only necessities in a full table of results for all special points of the Brillouin Zone and all space groups is the identification of the elements in the classes and the final character table.

(P.T.O.)

TABLE 3.5 CHARACTER TABLE FOR C_h^k FOR X OF $Pn3m$.

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
A'_1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
B_1	1	1	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
B'_1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1
A_2	1	1	-1	1	1	1	-1	-1	1	-1	1	1	-1	-1
A'_2	1	1	-1	1	1	1	-1	-1	-1	1	-1	-1	1	1
B_2	1	1	-1	1	1	-1	1	1	1	-1	1	-1	1	1
B'_2	1	1	-1	1	1	-1	1	1	-1	1	-1	1	-1	-1
E	2	2	0	-2	-2	0	0	0	2	0	-2	0	0	0
E'	2	2	0	-2	-2	0	0	0	-2	0	2	0	0	0
ξ_1	2	-2	0	2	-2	0	0	0	0	0	0	0	2	-2
ξ_2	2	-2	0	2	-2	0	0	0	0	0	0	0	-2	2
ξ_3	2	-2	0	-2	2	0	2	-2	0	0	0	0	0	0
ξ_4	2	-2	0	2	2	0	-2	2	0	0	0	0	0	0

3.9 The Labelling of the Irreducible Representations.

The labelling of the irreducible representations of the point groups in their standard orientations according to certain well defined rules is already fully described in the literature and the tables presented, e.g. by Heine (1960). A slight extension is necessary to cover the cases of point groups in non-standard orientations, and where these

occured in the earlier sets of tables in chapter II the following rules were adopted in the labelling of the representations. For example with Δ of $Pm\bar{3}$ the group is $E, C_{2y}, \sigma_z, \sigma_x$, then keeping x, y, z , in cyclic order we replace the elements in the character table of $2m$ by those of the group in its new orientation, $2m^*$, the asterisk denotes that it is not in standard orientation, though it does not indicate the actual orientation. The character table therefore becomes:

$2m^*$	E	C_{2y}	σ_x	σ_z
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

A further possibility is given by N of $I\bar{4}3m$ which has $E, C_{2z}, \sigma_{da}, \sigma_{db}$, in this case the twofold axis is along the z axis still, but the other two axes are at 45° to their standard positions, and here the z, x, y , of the standard $2m$ must be replaced by z, a, b , in cyclic order; if z, a, b , is used instead a left handed set of axes would be in use, or an inconsistent scheme for labelling the representations would be in use, and a confusion between the suffices 1 and 2 would result.

This is sufficient to deal with all the symmorphic

space groups, but for asynorphic space groups further refinements are needed, and all the details of the notation are not finally worked out yet; obviously the sign of the character of E' is a very important property of a representation since only those representations with a given sign can be used simultaneously on any problem. The labels for the case X of $Pn3m$ were inserted in Table 3.5, and here the notation is explained only as much as it is relevant to this particular case. Representations A and B are distinguished by the sign of the character of the class containing rotations about the principle axis, i.e. class C_6 . The 2-dimensional representations are denoted by E. A prime denotes the fact that the character of the inversion (x_9) is negative, and italic letters are used for representations where the character of E' (the symmetry element) is negative. Suffices 1, 2, 3, . . . are used for the remaining differences.

3.10 The Representations of infinite groups C_{∞}^k , Koster's Theorem.

In an asynorphic space group, if one considers points on lines of symmetry in the Brillouin Zone, e.g. Δ , Λ , Σ , the group C_{∞}^k may be infinite. But it is possible to obtain the representations of this infinite group in terms of the finite group C_k for the isomorphous space group. Compatibility relationships must exist at the ends of the line of symmetry. For example Δ , for F type space groups, lies between Γ , $k = 0$,

and X , $\underline{k} = 2\pi/a(0,1,0)$, i.e. Δ is $2\pi/a(0,\delta,0)$; and treating Γ and X as special cases of Δ (with $\delta = 0,1$ respectively) must give the same result as taking the subgroup of the elements of Δ from the finite groups $C_{\underline{k}}$ of Γ and X . And so one can obtain the character tables for $C_{\underline{k}}$ for Δ from those for Δ at either end of the line, and the rule, if one works in terms of $C_{\underline{k}}$ at Γ is that the characters of the elements ($\underline{R}/\underline{t}$) must be multiplied by $\exp(-i\underline{k}.\underline{t})$ where $\underline{k}$ is the $\underline{k}$ -vector of Δ at which the characters are required. That these characters and representations are possible is the result of the theorem due to Koster (1957).

Koster's Theorem.

If $\underline{k}$ is a point in the Brillouin Zone, and if $\underline{R}$ is an element in the group of $\underline{k}$, then $\underline{Rk} = \underline{k} + \underline{K}_j$ where $\underline{K}_j$ is some $\underline{k}$ -space lattice translation; if $\underline{k}$ is not on the surface of the Brillouin Zone $\underline{K}_j = 0$. $\Gamma(\underline{R}/0)$ denotes a matrix representative of $C_{\underline{k}}$ for the same $\underline{k}$ -vector in the Brillouin Zone of the isomorphous space group.

Theorem: IF $D^{\underline{k}}(\underline{R}/\underline{t}) = \exp(-i\underline{k}.\underline{t}) \Gamma(\underline{R}/0)$ THEN $D(\underline{R}/\underline{t})$ IS AN IRREDUCIBLE REPRESENTATION OF $C_{\underline{k}}$.

Proof:

(i) the equation above is used to define the $D^{\underline{k}}(\underline{R}/\underline{t})$ and therefore the homomorphism $(\underline{R}/\underline{t}) \rightarrow D^{\underline{k}}(\underline{R}/\underline{t})$ is valid. (a)

$$(ii) \quad D^{\underline{k}}(\underline{R}_2/\underline{t}_2) \cdot D^{\underline{k}}(\underline{R}_1/\underline{t}_1) = \exp(-i\underline{k}.\underline{t}_2) \Gamma(\underline{R}_2/0) \cdot \exp(-i\underline{k}.\underline{t}_1) \Gamma(\underline{R}_1/0) =$$

$$\exp(-i\mathbf{k} \cdot (\mathbf{t}_2 + \mathbf{t}_1)) \Gamma(\mathbf{R}_2 \mathbf{R}_1 / 0) \quad (b)$$

$$\text{and } D^{\mathbf{k}}((\mathbf{R}_2/\mathbf{t}_2)(\mathbf{R}_1/\mathbf{t}_1)) = D^{\mathbf{k}}((\mathbf{R}_2 \mathbf{R}_1 / \mathbf{R}_2 \mathbf{t}_1 + \mathbf{t}_2)) \\ = \exp(-i\mathbf{k} \cdot (\mathbf{R}_2 \mathbf{t}_1 + \mathbf{t}_2)) \Gamma(\mathbf{R}_2 \mathbf{R}_1 / 0).$$

But $\mathbf{k} \cdot \mathbf{R} \mathbf{t} = \sum_i k_i (\mathbf{R} \mathbf{t})_i = \sum_{ij} k_i R_{ji} t_j$, and since $\mathbf{R}$ is unitary $R_{ji} = R_{ij}^{-1}$, therefore

$$\mathbf{k} \cdot \mathbf{R} \mathbf{t} = \sum_{ij} k_i R_{ij}^{-1} t_j \\ = \sum_j (\sum_i k_i R_{ij}^{-1}) t_j \\ = \sum_j (\mathbf{R}^{-1} \mathbf{k})_j t_j \\ = (\mathbf{R}^{-1} \mathbf{k}) \cdot \mathbf{t}.$$

Since $\mathbf{R}^{-1}$ is in the group of $\mathbf{k}$ then $\exp(-i(\mathbf{R}^{-1} \mathbf{k}) \cdot \mathbf{t}_2) = \exp(-i\mathbf{k} \cdot \mathbf{t}_2)$, so that:

$$D^{\mathbf{k}}(\mathbf{R}_2/\mathbf{t}_2) \cdot D^{\mathbf{k}}(\mathbf{R}_1/\mathbf{t}_1) = \exp(-i\mathbf{k} \cdot (\mathbf{t}_1 + \mathbf{t}_2)) \Gamma(\mathbf{R}_2 \mathbf{R}_1 / 0) \quad (c)$$

thus from (b) and (c) we have that:

$$\underline{D^{\mathbf{k}}(\mathbf{R}_2/\mathbf{t}_2) \cdot D^{\mathbf{k}}(\mathbf{R}_1/\mathbf{t}_1) = D^{\mathbf{k}}((\mathbf{R}_2/\mathbf{t}_2) \cdot (\mathbf{R}_1/\mathbf{t}_1))} \quad (d)$$

so that the multiplication rule is conserved under the homomorphism. The two results (a) and (b) therefore mean that $D^{\mathbf{k}}(\mathbf{R}/\mathbf{t})$ must be a representation of $\underline{C^{\mathbf{k}}}$. Furthermore if $\Gamma(\mathbf{R}/0)$ is an irreducible matrix representation of $\underline{C^{\mathbf{k}}}$ for the same $\mathbf{k}$ -vector in the isomorphous space group the only matrix which will commute with it is a constant times the identity, and therefore the only matrix which commutes with $D^{\mathbf{k}}(\mathbf{R}/\mathbf{t})$ is also a constant times the identity so that $D^{\mathbf{k}}(\mathbf{R}/\mathbf{t})$ is an irreducible representation of $\underline{C^{\mathbf{k}}}$. Q.E.D.

If $\underline{C^{\mathbf{k}}}$ is infinite this does not matter and the theorem is still valid, since no restriction to $\underline{C^{\mathbf{k}}}$ being finite was

used. Thus it is possible to write down for $C_{\underline{k}}$ even for infinite cases a part of the character table which is sufficient to give the character of any other element in the group by simply multiplying by a readily determined exponential factor; that is, if $\chi(R/t_1)$ is given then $\chi(R/t_2) = \exp(-i\underline{k} \cdot (\underline{t}_2 - \underline{t}_1)) \chi(R/t_1)$. As an example, in Table 3.6, is the character table for Δ of $Fd3m$ will be the same; at X, though a point of symmetry $h = \exp(-i\pi\delta) = -1$ so that the character tables are different for in the two groups.

TABLE 3.6 CHARACTER TABLES FOR Δ $Fd3m$ at $\underline{k} = 0$; $\underline{k} = \frac{2\pi}{a}(0, \delta, 0)$

$\underline{k} = 0$:		E	C_{2y}	C_{4y}^+	$\sigma_{x,z}$	$\sigma_{d(c,e)}$
	A_1	1	1	1	1	1
	A_2	1	1	1	-1	-1
	B_1	1	1	-1	1	-1
	B_2	1	1	-1	-1	1
	E	2	-2	0	0	0
$\underline{k} = 2\pi/a (0, \delta, 0)$:		E	C_{2y}	C_{4y}^+	$\sigma_{x,z}$	$\sigma_{d(c,e)}$
	A_1	1	1	h	h	1
	A_2	1	1	h	$-h$	-1
	B_1	1	1	$-h$	h	-1
	B_2	1	1	$-h$	$-h$	1
	E	2	-2	0	0	0

3.11 Matrix Representations of $C_{\underline{k}}$.

From the character tables and the group multiplication table it is possible to deduce matrix representatives for

each irreducible representation; these are obtained it must be admitted by using a certain amount of judicious guess-work. It is only necessary to choose matrices to represent the generating elements of each group, which must be of the right order and satisfy the generating relations. There is not necessarily any fixed unique group of matrix representatives of a given irreducible representation but it has to be decided which one is going to be used for the later consideration of the lattice harmonics.

Having found the irreducible representations, their characters, and groups of their matrix representatives, it remains to find the lattice harmonics, or symmetry adapted functions for these various space groups.

In chapter II are listed the tables of the lattice harmonics for three symmorphic cubic space groups, and at the end of this chapter for the remaining twelve groups; At the central point of each Brillouin Zone where $\underline{k} = 0$ the group of $\underline{k}$ consists of all the elements of the space group, and whether the space group is symmorphic or not it is possible to factor out the translation group entirely, and therefore the lattice harmonics for Γ in any of the cubic space groups are the same as the lattice harmonics of the isogonal point group and are therefore as given in chapter II, Table 2.1. In the case of a symmorphic space group the group $\underline{G}^{\underline{k}}$ for any point in the Brillouin Zone is a subgroup of $\underline{G}^{\underline{k}}$ for Γ , the central point of the Zone. It is therefore

possible to perform the process of subduction which was described in detail in S2.3, to find the lattice harmonics for any point in the Brillouin Zone in terms of those of Γ . But for an asymorphic space group this is not so since the groups of $\underline{k}$ for these other points will very often contain more than one "identity" element and so are not subgroups of $\underline{G}^{\underline{k}}$ at Γ . Therefore it is only possible to go by subduction from the harmonics of Γ to those for lines or planes through Γ . It is not possible to apply this process of subduction any farther from Γ . To cover the rest of the points in the Brillouin Zone one must induce their harmonics from those of the lines and planes we have just mentioned.

3.12 Induction.

This is really the reverse application of the process of subduction. $\underline{M}$ is found in the same way as before and $\phi = \psi \underline{M}^{-1}$ is constructed; but since one representation of $\underline{G}^{\underline{k}}$ on the line may be compatible with several of the representations of $\underline{G}^{\underline{k}}$ at the point at its end it is not true that all the harmonics ϕ produced in this way will belong to the α th representation of $\underline{G}^{\underline{k}}$ at the point. Some of them will be redundant and must be rejected; this is done by seeing which of the harmonics formed by $\psi \underline{M}^{-1}$ do not in fact transform under the operations of the group like the α th representation of the group; these are then rejected. Rather than looking at the effect of the operators of the group on the harmonics to see which ones are redundant

one can apply the symmetrising operators whose use is described later in the chapter on the empty lattice tests. Except for this extra complication of having to look at the harmonics and test their behaviour under the operations of the group the process of induction is no more complicated than that of subduction.

3.13 An Example, $\Gamma-\Delta-X$ for $Pn\bar{3}m$.

As an example we consider $\Gamma-\Delta-X$ for the space group $Pn\bar{3}m$; the character table was deduced in § 3.8. It so happens that this G^k is identical to G^k for the case of diamond $Fd\bar{3}m$. The only difference is that for X $Pn\bar{3}m$ E' is $(E/010)$ and for X $Fd\bar{3}m$ E' is $(E/0\frac{1}{2}\frac{1}{2})$. This one example will be enough to illustrate the special effects occurring with an asymorphic space group. The complete character table for X is given earlier in Table 3.5, but since the second identity element $(E/010)$ must be represented by the matrix $-E$ it must have character $-n$, where n is the dimension of the representation. The only part of the table which is of interest therefore is the last four representations $\xi_1, \xi_2, \xi_3, \xi_4$ or X_1, X_2, X_3, X_4 of Herring's notation (1942).

As already mentioned, a group of matrix representatives can be deduced by selecting the generating elements of the group and assigning to each of them a matrix of the required character and of the correct order; for example a matrix representation of $X\xi_1$ is:

$$\begin{aligned}
(E/O), (C_{2y}/O), (\sigma_{dc}/O), (\sigma_{de}/O) & \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\
(S_{4y}^+/O), (S_{4y}^-/O), (C_{2x}/O), (C_{2z}/O) & \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \\
(I/t), (\sigma_y/t), (C_{2c}/t), (C_{2e}/t) & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
(C_{4y}^-/t), (C_{4y}^+/t), (\sigma_x/t), (\sigma_z/t) & \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \\
\text{where } t = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}). & \\
(E/O, 1, 0) & \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}
\end{aligned}$$

And also, from the end of S3.10 the character table for Δ is as shown in Table 3.7, and a group of matrix representatives for representation E of Δ are given beside the character for that representation:

TABLE 3.7 CHARACTER TABLE AND MATRIX REPRESENTATIVES FOR Δ .

	A_1	A_2	E_1	E_2	E	matrices of E.
E/O	1	1	1	1	2	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
C_{2y}/O	1	1	1	1	-2	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
σ_{dc}/O	1	-1	-1	1	0	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$
σ_{de}/O	1	-1	-1	1	0	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$
C_{4y}^+/t	h	h	$-h$	$-h$	0	$\begin{pmatrix} 0 & -h \\ h & 0 \end{pmatrix}$
C_{4y}^-/t	h	h	$-h$	$-h$	0	$\begin{pmatrix} 0 & h \\ -h & 0 \end{pmatrix}$
σ_z/t	h	$-h$	h	$-h$	0	$\begin{pmatrix} -h & 0 \\ 0 & h \end{pmatrix}$
σ_x/t	h	$-h$	h	$-h$	0	$\begin{pmatrix} h & 0 \\ 0 & -h \end{pmatrix}$

$h = \exp(-i\pi/8)$

For Γ of course the matrix representatives are as already given for the symmorphic case $Fm\bar{3}m$ in chapter II, Table 2.3.

Even in the case of an asynorphic space group it is perfectly possible to subduce from Γ onto a line or plane through Γ : therefore at Γ , treated both as Γ and as Δ with $k = 0$, this means that $\exp(-i\pi\delta)$ is just 1, and straightway from the results of chapter II the harmonics of Δ are:

$$\begin{array}{ll}
 A_1 & A_{1g}, E_g^1 + \sqrt{3}E_g^2, T_{1u}^2 \\
 A_2 & A_{1u}, E_u^1 + \sqrt{3}E_u^2, T_{1g}^2 \\
 B_1 & A_{2g}, -\sqrt{3}E_g^1 + E_g^2, T_{2u}^2 \\
 B_2 & A_{2u}, -\sqrt{3}E_u^1 + E_u^2, T_{2g}^2 \\
 E & \{T_{2g}^1 - T_{2g}^3, T_{2g}^1 + T_{2g}^3\}, \{T_{1g}^1 + T_{1g}^3, T_{1g}^1 - T_{1g}^3\}, \\
 & \{T_{2u}^1 + T_{2u}^3, T_{2u}^1 - T_{2u}^3\}, \{T_{1u}^1 - T_{1u}^3, T_{1u}^1 + T_{1u}^3\}.
 \end{array}$$

Since X does not have C_k^k which is a subgroup of C_k^k for Γ the harmonics for X cannot be found by subduction from Γ ; they can however be found by induction from the point Δ on the line which ends at X , alternatively they can be found by projection ab initio. To induce from Δ onto X we need to know the matrices $\underline{M}$ which can be found in the same way as in going from Γ to Δ : using just the representation $\mathcal{E}_1$ for example the matrices are:

	$X \mathcal{E}_1$	Δ		$X \mathcal{E}_1$	Δ
E	$\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$	σ_z	$\begin{pmatrix} 1 & \\ -1 & \end{pmatrix}$	$\begin{pmatrix} -1 & \\ & 1 \end{pmatrix}$
C_{2y}	$\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$	σ_x	$\begin{pmatrix} 1 & \\ -1 & \end{pmatrix}$	$\begin{pmatrix} -1 & \\ & 1 \end{pmatrix}$
C_{4y}^+	$\begin{pmatrix} 1 & \\ -1 & \end{pmatrix}$	$\begin{pmatrix} -1 & \\ & i \end{pmatrix}$	σ_{de}	$\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$
C_{4y}^-	$\begin{pmatrix} 1 & \\ -1 & \end{pmatrix}$	$\begin{pmatrix} -1 & \\ & i \end{pmatrix}$	σ_{dc}	$\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & \\ & 1 \end{pmatrix}$
		$B_2 \ A_1$			$B_2 \ A_1$

$$\underline{M} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ 1 & -1 \end{pmatrix}$$

$$\underline{M}^{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} -i & 1 \\ -1 & -1 \end{pmatrix}$$

At X the character table for the special case of Δ being at X , is of course not the same as for Δ at Γ now that we are dealing with an asymorphic group. The harmonics for $X\mathcal{E}_1$ therefore are ρM^{-1} where ρ is the row vector of those of B_2, A_1 of Δ , i.e.

$$\frac{1}{\sqrt{2}}(\Delta B_2 + \Delta A_1), \frac{1}{\sqrt{2}}(\Delta B_2 - \Delta A_1).$$

The problem is now very similar to the one which occurs later in the theory of the empty lattice tests; namely to construct from a given function u a function possessing the symmetry of some stated group; i.e. transforming according to one of the irreducible representations of that group. This case is apparently simpler than the case of the empty lattice wave functions, in that rather than obtaining a linear combination of the u 's we are just going to throw away some of the functions and retain the rest; that means that of the functions $\frac{1}{\sqrt{2}}(B_2 + A_1)$ some will belong to $X\mathcal{E}_1$ and some will not.

The necessary functions can be deduced using the symmetrizing operator

$$W_{ts}^i = 1/h \sum_R D^i(R)^*_{ts} R,$$

acting on the function u . The function u is now made up of linear combinations of the basis functions of some of the irreducible representations of Γ whose transformation properties under operations R of the group are of course known already. Using the harmonics for Δ which were given above those for $X\mathcal{E}_1$ are:

$$\begin{aligned} & \Lambda_{1g} + \Lambda_{2u} \\ & E_g^1 + \sqrt{3}E_g^2 - \sqrt{5}E_u^1 + E_u^2 \\ & T_{1u}^2 + T_{2g}^2 \end{aligned}$$

since g type representations have only lattice harmonics of even l value, and u type those of odd l , there is no significance in the $+$ sign connecting the g and u type representations.

Taking the function u , and putting the dummy suffix t in W_{ts}^1 equal to s then the symmetrized function which we obtain is $W_{ss}^1 u = 1/n \sum_R D^1(R)_{ss}^* \cdot Ru$. In the particular case of $X\xi_1$ putting $t = s$ means that immediately half of the operators will contribute a null factor to their term in the summation. In Table 3.8 are listed Ru for all the R of the group excepting for those which, in this representation are not necessary for the reason just mentioned. The i in the W_{ts}^1 labels the representation according to which the function is being required to transform, in this case $X\xi_1$.

TABLE 3.8 Ru FOR OPERATIONS OF Δ , AND HARMONICS FOR $X\xi_1$.

	Λ_{1g}	Λ_{2u}	$(E_g^1 + \sqrt{3}E_g^2)$	$(\sqrt{5}E_u^1 + E_u^2)$	T_{1u}^2	T_{2g}^2
E	u	u	u	u	u	u
C_{2y}	u	u	u	u	u	u
σ_{dc}	u	$-u$	u	u	u	u
σ_{de}	u	$-u$	u	u	u	u
S_{xy}	u	$-u$	u	$-u$	$-u$	$-u$
S_{xy}	u	$-u$	u	$-u$	$-u$	$-u$
C_{2x}	u	u	u	$-u$	$-u$	$-u$
C_{2z}	u	u	u	$-u$	$-u$	$-u$

Also, in Table 5.9, are listed $D_{ss}^1(R)^*$ for representation $\mathcal{E}_1$ of X .

TABLE 5.9 $D_{ss}^1(R)^*$ FOR $X\mathcal{E}_1$.

	E	C_{2y}	σ_{dc}	σ_{de}	S_{4y}^-	S_{4y}^+	C_{2x}	C_{2z}
$D_{11}(R)^*$	1	1	1	1	1	1	1	1
$D_{22}(R)^*$	1	1	1	1	-1	-1	-1	-1

Therefore considering the case where u is a basis function of $\Gamma_{A_{1g}}$ we have $W_{ss}^{X\mathcal{E}_1} u = 8u/16 = \frac{1}{2}u$ and therefore the harmonics of A_{1g} of Γ are present in those of $X\mathcal{E}_1$, but for a function u belonging to $\Gamma_{A_{2u}}$ however $Wu = 0$. Similarly $X\mathcal{E}_1$ has $E_g^1 + \sqrt{3}E_g^2, T_{2g}^2$ but does not have $-\sqrt{3}E_u^1 + E_u^2, T_{1u}^2$. The functions which remain as basis functions for $X\mathcal{E}_1$ are:

$$A_{1g}, E_g^1 + \sqrt{3}E_g^2, T_{2g}^2.$$

Thus it will now be clear how, having induced the harmonics from any line or plane onto a point of high symmetry in the Brillouin Zone, but away from Γ , one can reject the "spare" ones which automatically creep in. One might of course, as an alternative procedure instead of using the harmonics for Δ , use all the harmonics for Γ and apply the symmetrizing operator W_{ts}^1 to obtain those of $X\mathcal{E}_1$, this is perfectly justifiable but, though it avoids having to get the harmonics for X in two stages, i.e. (i) $\Gamma \rightarrow \Delta$, and (ii) $\Delta \rightarrow X$, it does mean that W_{ts}^1 has to be applied to 20 types of function instead of to a much smaller number, i.e. in this case six.

That is, induction throws out many of the representations of Γ immediately.

Having now described the process of induction it is now possible to illustrate very easily how it applies to a symmorphic space group where of course its use is quite possible but un-necessary. For example we induce harmonics of X from those of Δ in the case of $Fm\bar{3}m$. From the matrices of X and Δ it follows that $XE_g \rightarrow \Delta E$ with $\underline{M} = \underline{E}$, and therefore the harmonics of XE_g are contained among those of ΔE , namely

$$T_{2g}^1 - T_{2g}^3, T_{1g}^1 + T_{1g}^3, T_{2u}^1 + T_{2u}^3, T_{1u}^1 - T_{1u}^3.$$

But it is a g type representation so that on taking the summation in $W_{\Delta g}^1$ over the operators $\underline{R}$, for every $\underline{R}$ there is also the operator $\underline{IR}$, and with a u type representation of Γ these two will just cancel each other out, leaving only the g type representations of Γ , so that the harmonics of XE_g^1 are:

$T_{2g}^1 - T_{2g}^3$, and $T_{1g}^1 + T_{1g}^3$, which are the same as one obtains by direct subtraction from Γ .

APPENDIX. THE LATTICE HARMONICS FOR THE CUBIC SPACE GROUPS

ISOGONAL TO 23, $m\bar{3}$, 432, $\bar{4}3m$, (SYMMORPHIC ONLY).

Note.

Some points of symmetry for space groups isogonal to $m\bar{3}m$ possess no special symmetry in the groups considered here, and where this happens the point is omitted from the Table.

P23:

Γ

The representations and harmonics are as for the point group 23, see chapter II.

Δ

A A, E^1, E^2, T^2

B T^1, T^3

Λ

A $A, T^1 + T^2 + T^3$

B $\{E^1, E^2\}, \{T^1 + \omega T^2 + \omega^2 T^3, T^1 + \omega^2 T^2 + \omega T^3\}$

X_M

A A, E^1, E^2

B_1 T^3

B_2 T^2

B_3 T^1

Z

A A, E^1, E^2, T^1

B T^2, T^3

I23:

89

Γ, Λ

as for P23.

E

A

$$A, T^1 - T^2 + T^3$$

B

$$\{E^1, E^2\}, \{T^1 - \omega T^2 + \omega^2 T^3, T^1 - \omega^2 T^2 + \omega T^3\}$$

D, H

A

$$A, E^1, E^2, T^3$$

B

$$T^1, T^2$$

F

as Γ .

P23:

$\Gamma, \Delta, \Lambda, X, Z$

as P23

H

A

$$A, E^1, E^2, T^1$$

B

$$T^2, T^3$$

I

as P23 Λ .

Pm3:

Γ

The representations and harmonics are as for the point group m3, see chapter II.

Σ

A

$$A, E_g^1, E_g^2, T_g^3, T_u^1, T_u^2$$

B

$$A, E_u^1, E_u^2, T_g^1, T_g^2, T_u^3$$

Δ

A_1

$$A, E_g^1, E_g^2, T_u^3$$

A_1

$$T_g^2, T_u^1$$

A_2

$$A_u, E_u^1, E_u^2, T_g^3$$

B

$$T_g^1, T_u^2$$

Λ

A

$$A_g, A_u, T_g^1 + T_g^2 + T_g^3, T_u^1 + T_u^2 + T_u^3$$

B

$$\{E_g^1, E_g^2\}, \{E_u^1, E_u^2\}, \{T_g^1 + \omega T_g^2 + \omega^2 T_g^3, T_g^1 + \omega^2 T_g^2 + \omega T_g^3\}, \\ \{T_u^1 + \omega T_u^2 + \omega^2 T_u^3, T_u^1 + \omega^2 T_u^2 + \omega T_u^3\}.$$

90
S, B

$$\begin{array}{l} A' \\ A'' \end{array} \quad \begin{array}{l} A_g, E_g^1, E_g^2, T_g^2, T_u^1, T_u^3 \\ A, E_u^1, E_u^2, T_g^1, T_g^3, T_u^2 \end{array}$$

X, M

$$\begin{array}{l} A_g \\ B_{1g} \\ B_{2g} \\ B_{3g} \end{array} \quad \begin{array}{l} A_g, E_g^1, E_g^2, T_g^3 \\ T_g^2 \\ T_g^1 \\ T_g^1 \end{array} \quad \begin{array}{l} A_u \\ B_{1u} \\ B_{2u} \\ B_{3u} \end{array} \quad \begin{array}{l} A_u, E_u^1, E_u^2 \\ T_u^3 \\ T_u^2 \\ T_u^1 \end{array}$$

Z

$$\begin{array}{l} A_1 \\ A_2 \end{array} \quad \begin{array}{l} A_g, E_g^1, E_g^2, T_u^1 \\ A_u, E_u^1, E_u^2, T_g^1 \end{array} \quad \begin{array}{l} B_1 \\ B_2 \end{array} \quad \begin{array}{l} T_g^2, T_u^3 \\ T_g^3, T_u^2 \end{array}$$

O

$$\begin{array}{l} A' \\ A'' \end{array} \quad \begin{array}{l} A_g, E_g^1, E_g^2, T_u^1, T_u^2, T_g^3 \\ A, E_u^1, E_u^2, T_g^1, T_g^2, T_u^3 \end{array}$$

In 31

$\Gamma, \Sigma, \Lambda, Q$ as Pn3.

E

$$\begin{array}{l} A \\ B \end{array} \quad \begin{array}{l} A_g, A_u, T_g^1 - T_g^2 + T_g^3, T_u^1 - T_u^2 + T_u^3 \\ \{E_g^1, E_g^2\}, \{E_u^1, E_u^2\}, \{T_g^1 - \omega T_g^2 + \omega^2 T_g^3, T_g^1 - \omega^2 T_g^2 + \omega T_g^3\}, \\ \{T_u^1 - \omega T_u^2 + \omega^2 T_u^3, T_u^1 - \omega^2 T_u^2 + \omega T_u^3\} \end{array}$$

G

as O.

D

$$\begin{array}{l} A \\ B \end{array} \quad \begin{array}{l} A, E_g^1, E_g^2, E_u^1, E_u^2, T_g^3, T_u^3 \\ T_g^1, T_g^2, T_u^1, T_u^2 \end{array}$$

$$A \quad A_g, A_u \quad E \quad \overline{E_g, E_u} \quad T \quad T_g, T_u.$$

$$\begin{array}{l} A_g \\ B_g \end{array} \quad \begin{array}{l} A_g, E_g^1, E_g^2, T_g^3 \\ T_g^1, T_g^2 \end{array} \quad \begin{array}{l} A_u \\ B_u \end{array} \quad \begin{array}{l} A_u, E_u^1, E_u^2, T_u^3 \\ T_u^1, T_u^2 \end{array}$$

Pm3:

$\Gamma, \xi, \Delta, \Lambda, S, X, Z, O, B$ as Pm3.

W as Z.

L

$$A_g, T_g^1 + T_g^2 + T_g^3.$$

$$A_u, T_u^1 + T_u^2 + T_u^3$$

$$E_g, \{E_g^1, E_g^2\}, \{T_g^1 + \omega T_g^2 + \omega^2 T_g^3, T_g^1 + \omega^2 T_g^2 + \omega T_g^3\}$$

$$E_u, \{E_u^1, E_u^2\}, \{T_u^1 + \omega T_u^2 + \omega^2 T_u^3, T_u^1 + \omega^2 T_u^2 + \omega T_u^3\}$$

P43m:

Γ

The representations and harmonics are as for the point group 43m, see chapter II.

ξ, C

$$A', A_1, E^1, T_1^1 - T_1^2, T_2^1 + T_2^2, T_2^3$$

$$A'', A_2, E^2, T_1^1 + T_1^2, T_1^3, T_2^1 - T_2^2$$

Δ

$$A_1, A_1, E^1 + \sqrt{3}E^2, T_2^2, B_1, T_1^1 + T_1^3, T_2^1 - T_2^3$$

$$A_2, A_2, -\sqrt{3}E^1 + E^2, T_1^2, B, T_1^1 - T_1^3, T_2^1 + T_2^3$$

Λ

$$A_1, A_1, T_2^1 + T_2^2 + T_2^3$$

$$A_2, A_2, T_1^1 + T_1^2 + T_1^3$$

$$E, \{E^1, E^2\}, \{T_1^1 - T_1^2, T_1^1 + T_1^2 - 2T_1^3\},$$

$$\{T_2^1 + T_2^2 - 2T_2^3, T_2^1 - T_2^2\}.$$

S, J

$$A', A_1, E^1 + \sqrt{3}E^2, T_1^1 - T_1^3, T_2^1 + T_2^3, T_2^2$$

$$A'', A_2, -\sqrt{3}E^1 + E^2, T_1^1 + T_1^3, T_1^2, T_2^1 - T_2^3$$

X

$$\begin{array}{ll}
 A_1 & A_1, T_1^1 + \sqrt{3}E^2. \\
 A_2 & T_1^2. \\
 B & \{T_1^1 + T_1^3, T_1^1 - T_1^3\}, \{T_2^1 - T_2^3, T_2^1 + T_2^3\}.
 \end{array}
 \quad
 \begin{array}{ll}
 B_1 & A_2, -\sqrt{3}E^1 + E^2 \\
 B_2 & T_2^2
 \end{array}$$

Z

$$\begin{array}{ll}
 A & A_1, A_2, E^1, E^2, T_1^1, T_2^1 \\
 B & T_1^2, T_1^3, T_2^2, T_2^3
 \end{array}$$

III

$$\begin{array}{ll}
 A_1 & A_1, E^1. \\
 B_1 & A_2, E^2. \\
 B & \{T_2^1, T_2^2\}, \{-T_1^1, T_1^2\}.
 \end{array}
 \quad
 \begin{array}{ll}
 A_2 & T_1^3 \\
 B_2 & T_2^3
 \end{array}$$

I43m: $\Gamma, P, \xi, \Lambda, \Sigma, C, J$ as P43m.F

$$\begin{array}{ll}
 A_1 & A_1, T_2^1 - T_2^2 + T_2^3 \\
 A_2 & A_2, T_1^1 - T_1^2 + T_1^3 \\
 B & \{E^1, E^2\}, \{T_1^1 + T_1^2, T_1^1 - T_1^2 - 2T_1^3\}, \\
 & \{T_2^1 - T_2^2 - 2T_2^3, T_2^1 + T_2^2\}.
 \end{array}$$

C.V

$$\begin{array}{ll}
 A' & A_1, E^1, T_1^1 + T_1^2, T_2^1 - T_2^2, T_2^3 \\
 A'' & A_2, E^2, T_1^1 + T_1^2, T_1^3, T_2^1 - T_2^2
 \end{array}$$

D.N

$$\begin{array}{ll}
 A_1 & A_1, E^1, T_2^3. \\
 A_2 & A_2, E^2, T_1^3. \\
 B_1 & T_1^1 + T_1^2, T_2^1 - T_2^2 \\
 B_2 & T_1^1 - T_1^2, T_2^1 + T_2^2
 \end{array}$$

P43m:

⁹³
r, p, z, Δ, Λ, S, X, Z, C, J as P43m.

W

$$\begin{aligned} A & A_1, E^1 - \sqrt{3}E^2, T_1^1 \\ B & A_2, \sqrt{3}E^1 + E^2, T_2^1 \\ E & \{T_1^2 + iT_1^3, T_1^2 - iT_1^3\}, \{iT_2^2 + T_2^3, -iT_2^2 + T_2^3\}. \end{aligned}$$

L

$$\begin{aligned} A_1 & A_1, T_2^1 + T_2^2 + T_2^3 \\ A_2 & A_2, T_1^1 + T_1^2 + T_1^3 \\ E & \{T_1^1 + T_1^2 - 2T_1^3, -T_1^1 + T_1^2\} \\ & \{T_2^1 - T_2^2, T_2^1 + T_2^2 - 2T_2^3\}. \end{aligned}$$

P432:

Γ

The representations and harmonics are as for the point group 432, see chapter II.

Σ

$$\begin{aligned} A & A_1, E^1, T_1^1 + T_1^2, T_2^1 - T_2^2, T_2^3 \\ B & A_2, E^2, T_1^1 - T_1^2, T_2^1 + T_2^2, T_2^3. \end{aligned}$$

Δ

$$\begin{aligned} A & A_1, A_2, E^1, E^2, T_1^2, T_2^2, \\ B & T_1^1, T_1^3, T_2^1, T_2^3 \end{aligned}$$

Λ

$$\begin{aligned} A & A_1, A_2, T_1^1 + T_1^2 + T_1^3, T_2^1 + T_2^2 + T_2^3 \\ E & \{E^1 + iE^2, E^1 - iE^2\}, \{T_1^1 + \omega T_1^2 + \omega^2 T_1^3, T_1^1 + \omega^2 T_1^2 + \omega T_1^3\} \\ & \{T_2^1 + \omega T_2^2 + \omega^2 T_2^3, T_2^1 + \omega^2 T_2^2 + \omega T_2^3\} \end{aligned}$$

S

$$\begin{aligned} A & A_1, E^1 + \sqrt{3}E^2, T_1^1 + T_1^3, T_2^1 + \sqrt{2}T_2^2 - T_2^3, T_2^1 - \sqrt{2}T_2^2 - T_2^3 \\ B & A_2, -\sqrt{3}E^1 + E^2, T_2^1 + T_2^3, T_1^1 + \sqrt{2}T_1^2 - T_1^3, T_1^1 - \sqrt{2}T_1^2 - T_1^3 \end{aligned}$$

CA
X

$$\begin{array}{ll} A_1 & A_1, E^1 + \sqrt{3}E^2. \\ B_1 & A_2, -\sqrt{3}E^1 + E^2. \\ E & \{T_2^1 - T_2^3, T_2^1 + T_2^3\}, \{T_1^1 + T_1^3, T_1^1 - T_1^3\}. \end{array}$$

Z

$$\begin{array}{ll} A & A_1, A_2, E^1, E^2, T_1^1, T_2^1 \\ B & T_1^2, T_1^3, T_2^2, T_2^3 \end{array}$$

W

$$\begin{array}{ll} A_1 & A_1, E^1. \\ A_2 & T_1^3 \\ B & \{T_2^1, T_2^2\}, \{T_1^1, -T_1^2\}. \end{array}$$

I432:

r, s, t as P432.

V

$$\begin{array}{ll} A & A_1, A_2, T_1^1 - T_1^2 + T_1^3, T_2^1 - T_2^2 + T_2^3 \\ B & \{E^1 + iE^2, E^1 - iE^2\}, \\ & \{T_1^1 - \omega T_1^2 + \omega^2 T_1^3, T_1^1 - \omega^2 T_1^2 + \omega T_1^3\} \\ & \{T_2^1 - \omega T_2^2 + \omega^2 T_2^3, T_2^1 - \omega^2 T_2^2 + \omega T_2^3\}. \end{array}$$

U

$$\begin{array}{ll} A & A_1, E^1, T_1^1 - T_1^2, T_2^1 + \sqrt{2}T_2^2 + T_2^3, T_2^1 + \sqrt{2}T_2^2 - T_2^3 \\ B & A, E^2, T_2^1 - T_2^2, T_1^1 + \sqrt{2}T_1^2 + T_1^3, T_1^1 + \sqrt{2}T_1^2 - T_1^3 \end{array}$$

T

$$\begin{array}{ll} A & A_1, A_2, E^1, E^2, T_2^3, T_1^3 \\ B & T_2^1, T_2^2, T_1^1, T_1^2 \end{array}$$

P

$$\begin{array}{ll} A & A_1, A_2 \\ B & \{E^1 + iE^2, E^1 - iE^2\} \\ T & \{T_1^1, T_1^2, T_1^3\}, \{T_2^1, T_2^2, T_2^3\}. \end{array}$$

A	$A_1, E^1, T_1^3.$	B_1	$T_1^1 - T_1^2, T_2^1 + T_2^2$
B	$T_1^1 + T_1^2, T_2^1 - T_2^2.$	B_3	T_2^3, A_2, E^2

P432: $r, z, \Delta, \Lambda, S, x, z$ as P432. II

A	$A_1, E^1, T_2^1.$	B_1	$T_2^2 + T_2^3, T_1^2 - T_1^3$
B_2	$T_1^2 + T_1^3, T_2^2 - T_2^3.$	B_3	A_2, E^2, T_1^1

L

A_1	$A_1, T_2^1 + T_2^2 + T_2^3$
A_2	$A_2, T_1^1 + T_1^2 + T_1^3$
B	$\{E^1, E^2\}, \{T_1^1 - T_1^2, T_1^1 + T_1^2 - 2T_1^3\},$ $\{T_2^1 + T_2^2 - 2T_2^3, -T_2^1 + T_2^2\}$

Q

A	$A_1, E^1 - \sqrt{3}E^2, T_1^2 - T_1^3, T_2^1, T_2^2 + T_2^3$
B	$A_2, \sqrt{3}E^1 - E^2, T_1^1, T_1^2 + T_1^3, T_2^2 + T_2^3$

PART 2.

COMPUTATIONS OF THE BAND STRUCTURE OF SOME FACE CENTRED CUBIC METALS, Al, Cu, Fe, & Co.

$$-\frac{1}{2} \sum_{\mathbf{r}} \psi^* (\mathbf{r}) \psi (\mathbf{r}) = 0$$

$$\psi^2 = \frac{1}{4} \left(\frac{1}{2} \psi^2 + \frac{1}{2} \psi^2 \right)$$

CHAPTER I. THEORY OF THE CELLULAR METHOD.

1.1 The Development of the Wigner-Seitz Method.

The previous part of this work was concerned with trying to find functions possessing some particular symmetry and now we come to consider an application of those results to a real physical problem.

The problem in question is the calculation of the band structure of a perfect cubic close packed metal at absolute zero. The first quantum mechanical approach to the consideration of the behaviour of the electrons in a metal was made by Wigner and Seitz (1933) who used a particularly simple model. They assumed that the metal consists of a regular array of fixed positive ions, that the electrons move independently within it (the independent particle model), and that, using Bloch's theorem one need only consider what happens in a unit cell of the structure; this unit cell was then, in their approximation, replaced by a sphere with volume equal to the volume of the cell. And, since they used sodium, a univalent metal, there is on average just one electron in each cell. Therefore the electron in the sphere has a wave function satisfying the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi = E \Psi \quad (1),$$

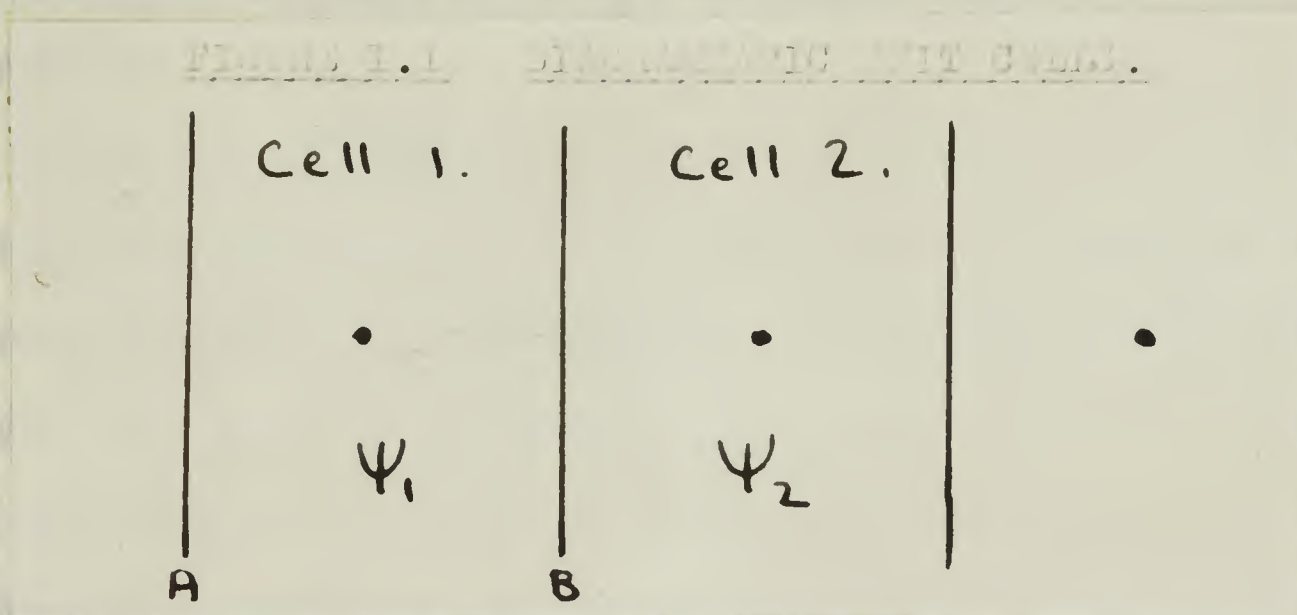
which has become simplified so as to be now just one

dimensional with $\nabla^2 = \frac{1}{r^2} \frac{d}{dr} (r^2 \frac{d}{dr})$

so that it is:

$$-\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) \right) + (V - E)\psi = 0$$

The boundary conditions to be satisfied by ψ are that both ψ and $\text{grad} \psi$ are continuous. Figure 1.1 represents a cell and one of its neighbours.



Since $\text{grad} \psi$ is continuous at the surface of the cell

$\left(\frac{\partial \psi_1}{\partial r} \right)_B = \left(\frac{\partial \psi_2}{\partial r} \right)_B = -e^{i\mathbf{k} \cdot \mathbf{r}} \left(\frac{\partial \psi_1}{\partial r} \right)_A$ from Bloch's theorem and considering the "ground state", i.e. $\mathbf{k} = 0$, representation

A_{1g} of Γ , then:

$$\left(\frac{\partial \psi_1}{\partial r} \right)_B = - \left(\frac{\partial \psi_1}{\partial r} \right)_A \quad (ii)$$

But the wave function ψ must transform according to the irreducible representation $\Gamma_{A_{1g}}$, so that under the inversion operator I ,

$$I \psi_B = D^{\Gamma_{A_{1g}}}(I) \psi_B = + \psi_B.$$

therefore $\left(\frac{\partial \psi}{\partial r} \right)_A = \left(\frac{\partial \psi}{\partial r} \right)_B \quad (iii)$

and from (ii) and (iii) $\text{grad} \psi = 0$ at the surface of the cell.

If then $V(r)$ is given numerically from a self-consistent field calculation the equation (i) can be integrated for a given E and therefore the value of $\text{grad} \psi$

at the surface of the cell can be found. E is then varied until the condition $\text{grad}\psi = 0$ is satisfied. The method is alright for the totally symmetrical representation of Γ , $k = 0$, i.e. Γ_{1g} , for which it yields reasonable results. For other points in the Brillouin Zone the method is less successful.

Slater (1934) suggested trying to take into account the actual shape of the cell and its symmetry instead of approximating to it by a sphere; this affects two things, the wave equation is no longer just one dimensional, and a more satisfactory treatment of the boundary conditions is possible and necessary. The method thus became known as the "cellular method." Later Shockley (1937) showed that using the special case of $V(\underline{r}) = 0$ one could solve the Schrödinger Equation analytically and thereby test the numerical methods used in integrating it by trying them on the case $V(\underline{r}) = 0$. This "empty lattice" test is of great value in ensuring that the very complicated numerical processes involved in a cellular calculation are correct ~~-----~~ it also gives one some idea of the limit of accuracy of the calculation for a real metal. It does not however detect any error in $V(\underline{r})$ and in fact, as will appear later, the choice of $V(\underline{r})$ is, within the limitations of the model, the sole surviving source of substantial errors.

1.2 The Cellular Method, Separation of Variables in the Schrödinger Equation.

Electrons moving in a lattice in real space are classified according to their $\underline{k}$ vectors, or their momentum vectors $\hbar \underline{k}$. Because they are Fermions and therefore obey an exclusion principle the electrons in a metal must all be in different $\underline{k}$ states, neglecting spin. Thus at absolute zero, if there are N electrons in the metal they occupy the N lowest $\underline{k}$ states in energy. The number of possible $\underline{k}$ states is infinite though $\underline{k}$ space for a finite number of electrons, i.e. for a finite lattice, is discrete. If one considers a given $\underline{k}$ vector, then the wave function of an electron with that $\underline{k}$ value can be expanded in terms of the basis functions of one of the representations of the group of $\underline{k}$, and the "coefficients" of these functions must take into account the radial variation of the wave function; i.e. if $\underline{r}$ is expressed in polar coordinates, (r, θ, ϕ) the complete lattice harmonic $f_e(r) \sum_m C_{evm} Y_e^m(\theta, \phi)$, is a suitable member of the set of basis functions for the expansion.

The wave function of an electron can therefore be written as $\psi(\underline{k}, \underline{r}) = \sum_{ev} B_{ev}^s \left(\sum_m C_{evm}^s Y_e^m(\theta, \phi) \right) R_e(r)$ where $\sum_m C_{evm}^s Y_e^m(\theta, \phi) = X_{ev}^s(\theta, \phi)$ which is one of the functions found in the previous part of this work. The B_{ev}^s are the numerical coefficients which it is one of the objects of the calculation to find. The $R_e(r)$ are the radial functions. An expansion of this form is possible because it

has been assumed that $V(\underline{r})$ is a function of r , and not of θ and ϕ , for it is this which makes the Schrödinger Equation separable:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi$$

$$\therefore -\frac{\hbar^2}{2m} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \psi}{\partial r}) + \frac{1}{r^2} \frac{\partial^2 \psi}{\partial \theta^2} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right\} + (V - E)\psi = 0$$

Put $\psi = R(r) X(\theta, \phi)$

$$\therefore -\frac{\hbar^2}{2mR} \frac{d}{dr} (r^2 \frac{dR}{dr}) - \frac{\hbar^2}{2mX} \left\{ \frac{\partial^2 X}{\partial \theta^2} + \cot \theta \frac{\partial X}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 X}{\partial \phi^2} \right\} + r^2 (V - E) = 0$$

OR

$$-\frac{\hbar^2}{2mR} \frac{d}{dr} (r^2 \frac{dR}{dr}) + r^2 (V - E) + \left\{ -\frac{\hbar^2}{2mX} \left[\frac{\partial^2 X}{\partial \theta^2} + \cot \theta \frac{\partial X}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2 X}{\partial \phi^2} \right] \right\} = 0$$

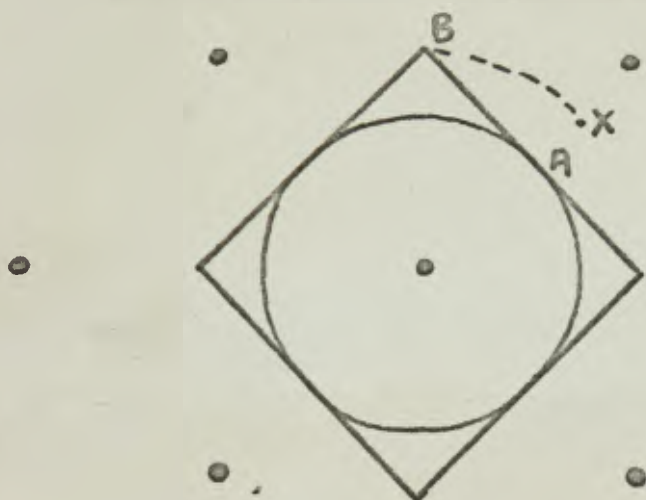
and this is separable only if V is not a function of θ and ϕ .

In other words, for this expansion for ψ to be valid $V(\underline{r})$ must be spherically symmetrical; this is alright near one of the ions **but** near the boundaries of the cell it is not completely realistic. It should be mentioned that the condition that $V(\underline{r})$ is spherically symmetrical is not essential to the cellular method, it would be possible to refine the method to consider V as non-centrosymmetric. This refinement one hopes will be within the scope of the next generation of computers.

1.3 The Potential Field.

In the picture of the two dimensional lattice shown in Figure 1.2 we must satisfy the condition that $V(\underline{r})$ is centro-symmetric.

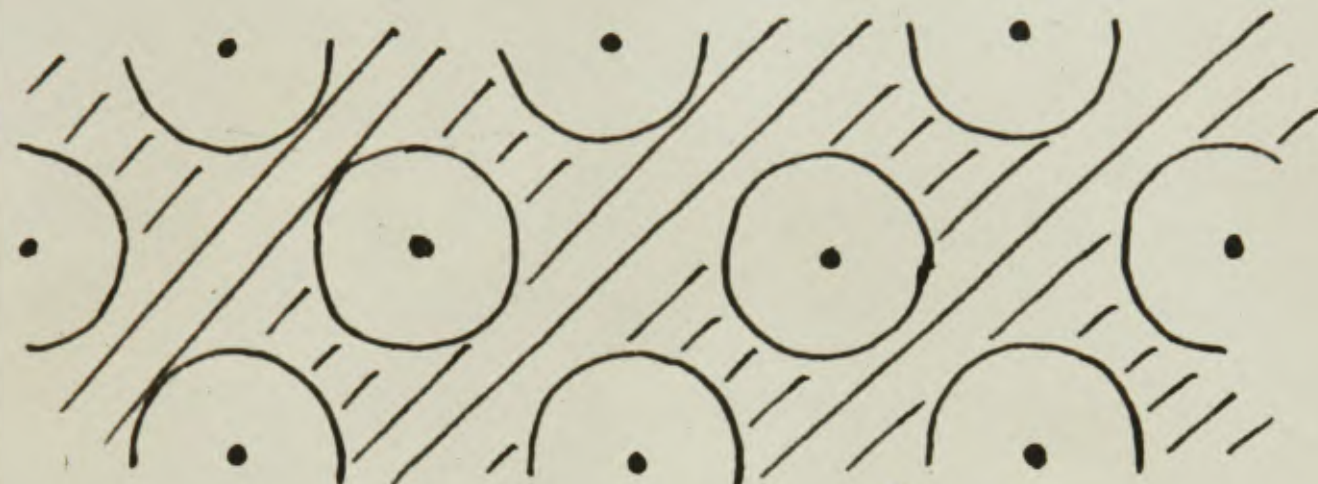
FIGURE 1.2 THE SPHERICAL SYMMETRY OF THE POTENTIAL.



If A is a point of contact of the cell face with the inscribed sphere then V will be spherically symmetrical inside that sphere. If we take point B, at the extreme corner of the cell and move $\underline{r}$, keeping its magnitude constant until $\underline{r}_B$ has been replaced by a vector of length r_B along the direction of $\underline{r}_A$, then we have moved $\underline{r}_B - \underline{r}_A$ into the next cell and spherical symmetry is only achieved if $V_B = V_X$ where X is a point $r_B - r_A$ away from A. For any other point in the shaded area V must be constant at any given value of $|\underline{r}|$ and this can only be satisfied if V is constant over the whole region outside the sphere of radius $r_A - (r_B - r_A)$. The potential then has a "muffin tin" appearance, as in Figure 1.3, and is spherically symmetrical like an ionic potential within

the spheres and constant in the shaded space.

FIGURE 1.7 THE ION-ION POTENTIAL.



Since the actual potential used is assumed to be that of the ion core right out to the extreme corners of the cell doubts have arisen about the validity of the expansion, e.g.

Saffron (1959). Some people, e.g. Ham (1960), are inclined to think that the departure from constancy of V in the outer regions of the cell (which is fairly small but certainly not negligible) may cause the expansion not to converge and it has been claimed that definite evidence of failure in convergence has been found. In the empty lattice tests of course the expansion is perfectly valid.

The actual ion core potential function used raises certain difficulties because the picture of a set of fixed ions and a set of perfectly free electrons definitely going into the conduction band is not completely realistic. It is a very good approximation in the case of the alkalis, but in the case of the transition metals one is a very long way from any closed shells and the distinction between bound electrons

and conduction electrons is not very sharp. Even if there is a definite ion core, the wave equation is that of a single electron moving in the field of an ion core and the other conduction electrons and so a correction to V is necessary. The potentials used are those of a free ion with the other conduction electrons smoothed out. The potential of the ion core includes exchange between the core electrons and the outer electrons, which go into the conduction band. The effect of correlation (that is the extent to which the particles do not obey the independent particle model) has been considered but it was found that addition of correlation made the energies worse rather than better. The reason for this is that by splitting the lattice up into cells and putting one electron in each cell (in the case of sodium) we have not considered the possibility of there being a second conduction electron in the cell at all so that we have constrained the electrons to stay apart more than they would really and have thereby already over-compensated for correlation effects; introduction of a special correlation term will then make the situation worse. A more detailed discussion of the potential field appears later, after the consideration of the empty lattice tests, when the use of the programme for real metals is considered.

1.4 The Representative Fraction of the Cell.

Turning our consideration to the angular part of the wave function we find that for k vectors of high symmetry the

expansion of ψ in terms of $X_{1\nu}(\theta, \phi)$ is more economical than that in terms of all the $Y_l^m(\theta, \phi)$ which was the object of using the lattice harmonics; by more economical is meant that for a given number of terms in the expansion one gets to higher l values than one would do using the full expansion. By using a function of the required symmetry it follows that one does not need to fit the boundary conditions on ψ over the whole of the surface of the cell but only over $1/n$ th of it, where n is the number of elements in the group of k , e.g. for $\Gamma(A_{1g})$ only $1/48$ th of the cell is necessary. This is only true in the case of degenerate representations if the matrix representatives $D^\alpha(R)_{ij}$ are diagonal; if they are not diagonal then it is necessary to know the wave functions ~~for~~ for the other degenerate representations over the $1/n$ th fraction of the cell chosen: $R\phi_j = \sum_i \phi_i D^\alpha(R)_{ij}$

So that in practice in cellular calculations where one only handles the boundary conditions for one representation at a time one has to fit ψ for $1/n$ th of the whole cell where n is the number of symmetry operators of the group of k which have diagonal matrix representatives.

1.5 The Least Squares Procedure.

When the equation (i), Schrödinger's equation, is made to satisfy the boundary conditions imposed by a particular problem it will only have non trivial solutions for certain values of E . The early cellular calculations

used the empty lattice energies to determine the coefficients $B_{1\nu}^0$ in the expansion of ψ by having just enough boundary condition equations for the number of unknown coefficients present. It was then argued that in a real metal the coefficients $B_{1\nu}^0$ could be assumed to be the same as in the free electron case, and therefore one could find the E value for this wave function using V for the metal and equation (1). There is little justification for this assumption and in fact the answers were found to be very sensitive to the selection of points at which the boundary conditions were fitted, von der Lage & Bethe (1947) and Howarth & Jones (1952). A comparison between the coefficients in the expansions for the empty lattice and a real metal appears later.

A better method was suggested by Altmann (1958).

This involves using more boundary condition equations than unknowns; the unknowns are the $B_{1\nu}^0$. A boundary condition equation will be of the form $\psi_1 = a\psi_2$ or

$$\sum_{e\nu} B_{e\nu}^S X_{e\nu}^S(\theta_1, \phi_1) R_e(r_1) = a \sum_{e\nu} B_{e\nu}^S X_{e\nu}^S(\theta_2, \phi_2) R_e(r_2)$$

and can be written in the form $\sum_{e\nu} B_{e\nu}^S \{S_{e\nu}\} = 0$

or $\sum_r a_{sr} x_r = 0$ with unknowns $x_r = B_{1\nu}^0$. By

using more equations than there are x_r the system of equations is heavily overdetermined; if the s th equation is :

$$\sum_{r=1}^{r=q} a_{sr} x_r = 0 \quad 1 \leq r \leq q, \quad 1 \leq s \leq p, \quad p > q$$

and one takes an arbitrary set of x_r the equation becomes

$$\sum_r a_{sr} x_r = p_s, \text{ and the ideal solution would occur with all}$$

the $p_s = 0$. This is clearly impossible in practice because

one has small errors in the a_{sr} as a result of the radial integrations especially. Some kind of least squares method of finding the best fit is thus needed and one tries to minimise $\sum_s p_s^2$. And if the wave function is then also to be normalized there is the subsidiary condition that $\sum_r x_r^2 = 1$. i.e. we have to minimise $S^2 = \sum_s p_s^2$, subject to $\sum_r x_r^2 = 1$.

Therefore if λ is a Lagrange undetermined multiplier we have

to minimise $W = S^2 - \lambda \{ \sum_r (x_r)^2 - 1 \}$

where $S^2 = \sum_s p_s^2 = \sum_s \left(\sum_r a_{sr} x_r \right)^2$

$$W = \sum_s \left[\sum_r a_{sr} x_r \right]^2 - \lambda \left[\sum_r x_r^2 - 1 \right]$$

$$\therefore \frac{\partial W}{\partial x_p} = \frac{\partial}{\partial x_p} \left\{ \sum_s \left(\sum_r a_{sr} x_r \right)^2 \right\} - 2 \lambda x_p = 0.$$

$$\therefore \sum_s \sum_r a_{sr} x_r a_{sp} - \lambda x_p = 0.$$

$$\therefore \sum_r \left[\sum_s a_{sr} a_{sp} \right] x_r - \lambda \delta_{pr} x_r = 0.$$

$$\therefore \sum_r \left[\sum_s (a^T)_{ps} a_{sr} \right] x_r - \lambda \delta_{pr} x_r = 0.$$

$$\therefore \sum_r \left(\underline{A}^T \underline{A} \right)_{pr} x_r - \lambda \delta_{pr} x_r = 0$$

$$\text{OR } \{ \underline{A}^T \underline{A} - \lambda \underline{E} \} \underline{x} = 0.$$

That is, the best fit occurs when the coefficients in the wave function, the x_r , form an eigenvector of the matrix $\underline{A}^T \underline{A}$, where $\underline{A}$ is the matrix a_{sr} . There are of course q eigenvectors where q = number of terms in the expansion, but one is not concerned with them all but only those likely to correspond

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to occupied states, these will be states of lowest energy and will correspond to the smallest eigenvalue λ of the matrix $\underline{A}^T \underline{A}$. The minimum value of the minimum eigenvalue of $\underline{A}^T \underline{A}$ will thus locate the energy which is a possible solution of Schrödinger's equation under these conditions. The calculation thus consists in tracing the curve of λ as a function of energy and interpolating to find the minimum value of λ ; finally using this interpolated energy λ is recalculated and the calculation can be made to go on until these two values agree to some prescribed order of accuracy. In fact solutions of the Schrödinger equation corresponding to the minima of the the next few lowest eigenvalues of the matrix $\underline{A}^T \underline{A}$ are sometimes required. This becomes especially important when levels at points of low symmetry, and especially general points in the Brillouin Zone are computed.

1.6 The Boundary Conditions.

In conclusion before describing the details of the programming of the calculation for a computer a little must be said about the boundary conditions themselves. The points at which the boundary conditions are fitted may be at corners, on edges or just anywhere on the faces of the Wigner-Seitz unit cell. Because of the presence of operators R in the group of $\underline{k}$ the wave function at one of these points will be related to the wave function at some other point on the surface of the cell, i.e. $R\phi_j = \sum_i \phi_i D^d(R)_{ij}$ and limiting ourselves to cases of $D^d(R)$ being diagonal then

$$R\phi_j = D^{\frac{106}{2}}(R)_{jj}\phi_j$$

If the two points so connected already have wave functions related by a Bloch factor $\exp(-ik \cdot \underline{t})$ these two conditions may only be able to be satisfied by having $\psi = 0$ for this point. This is similar to the argument used in the original Wigner-Seitz calculations. Similar considerations may lead to the replacement of the Bloch condition on $\text{grad}\psi$ by the condition $\text{grad}\psi = 0$ at the point concerned. In fact the analysis of the boundary conditions for all types of point on the cell's surface and for all the representations of all the possible types of $\underline{k}$ vector is very tedious. In the light of the experience of Bradley (1962) using a similar programme for hexagonal close packed metals it was concluded that a substantial saving both in programming time, and in machine operating time could be achieved by only considering points in general positions on the faces of the cell. The estimated gain of speed is probably about 50% from this source and as the empty lattice tests show there is certainly no loss of accuracy on this score.

CHAPTER II. THE CELLULAR PROGRAMME FOR FACE-CENTERED CUBIC METALS, SPACE GROUP $Fm\bar{3}m$.

2.1 The Ferranti "Mercury" Computer.

In the last chapter the general theory of the cellular calculation was considered and here we consider the details of the programme itself.

The programme is written for a Ferranti "Mercury" computer using a fairly simple input routine (IMP, due to Dr J S Rollett) and starting, chapter changing and checking routines due to Dr S L Altmann, Dr C J Bradley and Mr J E Jeacocke. These are very economical of storage space in the magnetic drum store of the machine and enable one to write programmes directly in machine (octal) instructions thus avoiding time wastage in a compiler routine. It is this saving of time by not using a compiler and the much more economical use which can be made of the fairly scarce amount of storage space in the magnetic drums which makes it worthwhile to use this method of programming. Of course the programming itself using basic machine instructions is much more tedious than using for example autocode.

The whole programme is stored in the machine and, provided no sector of it is overwritten by accident, it is possible to do many successive calculations by just feeding in the new data without refeeding all the programme tapes.

Before proceeding it is as well to mention that it is easier to refer to all numbers involved in the arrangement of the programme in octal rather than decimal form, i.e. a number is expressed to base 8 rather than base 10; this is because the basic unit of the machine is 2 and a convenient grouping of 2's is in 8's. Thus five hundred and eleven is 777_8 , i.e. $511 = 7 \times 64 + 7 \times 8 + 7 \times 1$. Because the programme is made to fit so exactly into the machine so that as little as possible of the magnetic drum storage space is wasted we find it easier to think in terms of these octal numbers. As mentioned already the programme's various chapters occupy a large portion of the total storage space available. There are altogether 1000_8 sectors in the magnetic drums (labelled 0 - 777_8) and about 250_8 of these (i.e. well over $\frac{1}{2}$ of them) are used to store programme. A further 140_8 sectors are used to store various codes connected with the geometry and boundary conditions for the various representations, and about 20_8 sectors for the input routines. The rest is used as temporary storage space for numbers produced and used at various stages in the calculation.

2.2 The Master Routine.

The whole calculation is controlled by a master routine which can be entered in various places by means of a flexible entry. This is achieved by using a small one-sector programme which is entered manually and can then be made to

enter the master routine at one of several points which can be selected on the handswitches of the machine. This is useful for several reasons (a) one can start the programme manually without needing to use a special starting tape, (b) in case of machine failure it makes it possible very often to restart a calculation without going right back to the beginning again and hence reduces wasted time, (c) if there are several eigenvalues for a given representation and one of them has been found it is possible to feed in, on tape, a new energy value and restart the calculation without wasting time calculating the harmonics $X_{1\nu}(\theta, \phi)$ all over again, (d) and it is possible for a given representation of a line of symmetry to move to another point and compute the levels at the new k value without having to re-compute the harmonics. This, together with the permanent storage of the programme in the machine and the consequent ease with which successive calculations may be done represents probably a gain of 50% in speed over the programme for hexagonal close packed metals described by Bradley (1962). These savings together with the simplification in the boundary conditions mentioned in the previous chapter probably represent a doubling of the speed of the programme compared with the hexagonal close packed metals' programme.

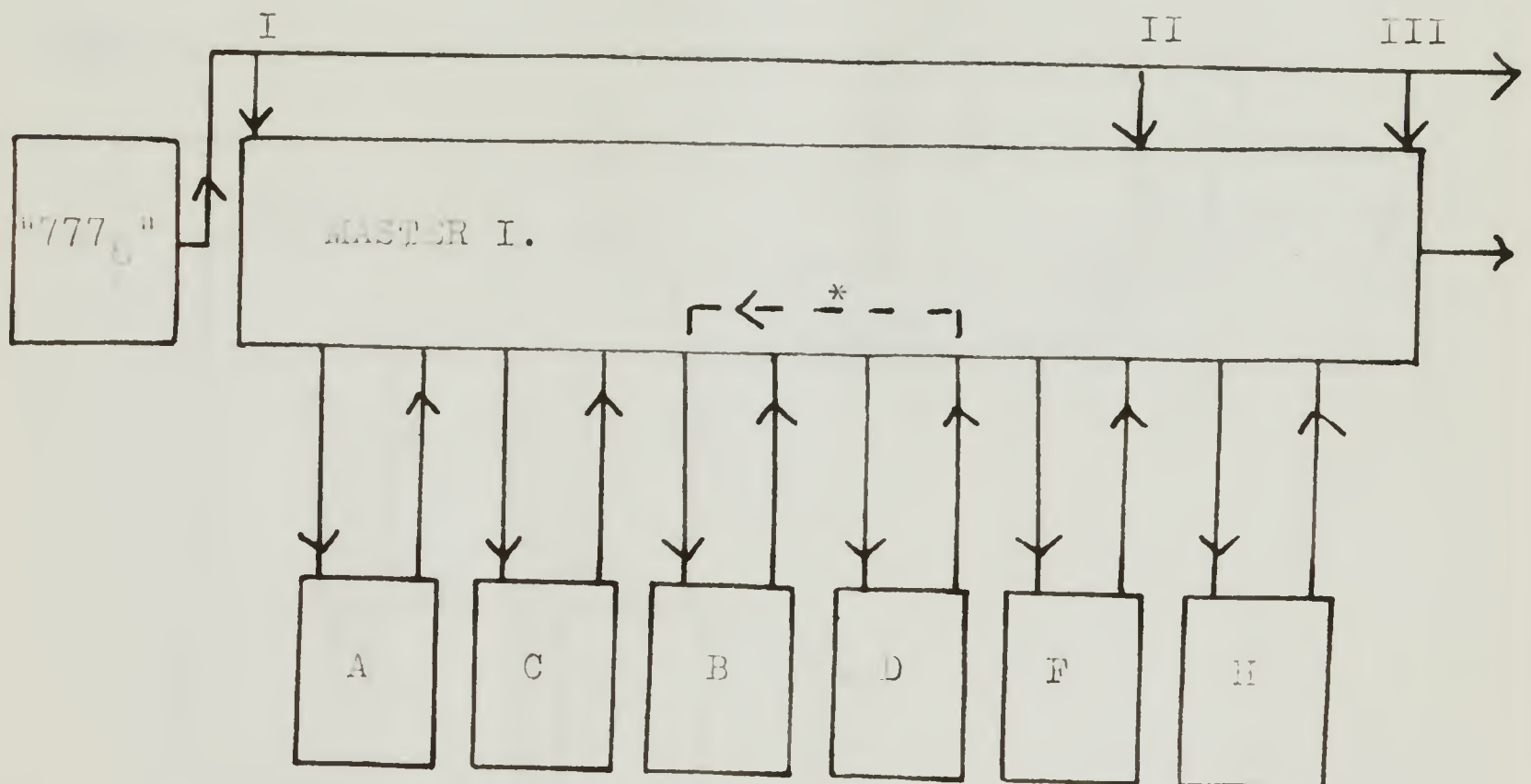
The layout of the programme is shown in Figure 2.1. The master routines set the data for the subchapters of the programme and store miscellaneous items in one sector kept

FIGURE 2.1 FLOW DIAGRAM OF CELLULAR PROGRAMME (Fm3m).

There are several entry points from the routine in sector 777₈,

- I Start calculation,
- II Continue with new k for same representation,
- III Continue at start of large cycle, new energy, same representation, same k .
- IV Print Ψ and finish.

Others can be inserted very easily.



A Geometry of Wigner-Seitz Cell.

C Select coefficients C_{lv}^m .

F Form X_{lv} , Y_{lv} , Z_{lv} .

B Form $P_l^m(\cos\theta)$.

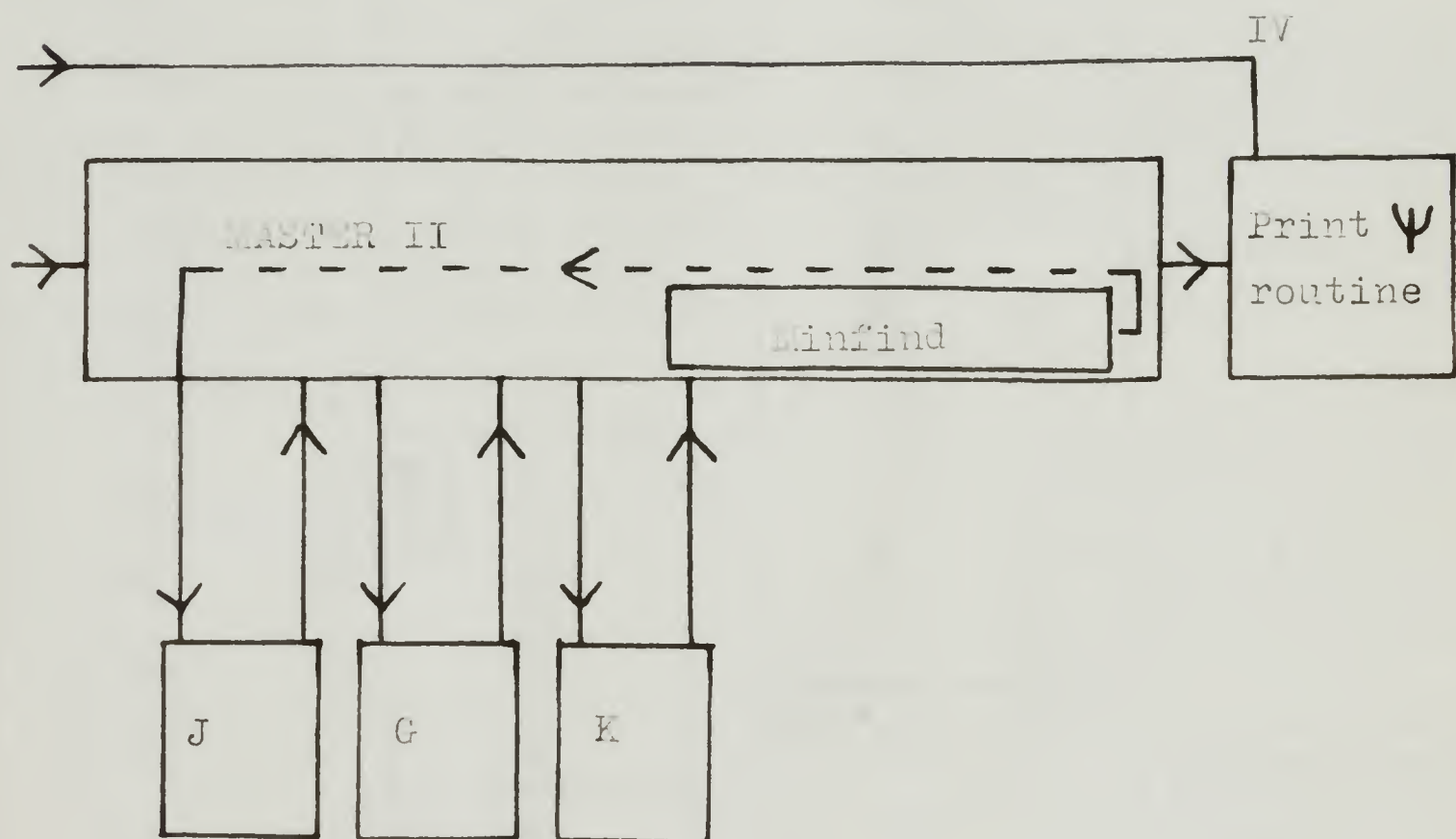
D Form X_{lv} etc.

H $Z \rightarrow Z_0$.

* repeats (n-1) times.

(P.T.O.)

FIGURE 2.1 (continued)



- J Outwards integration -- $G_1(\rho)$, $G_1'(\rho)$.
G Boundary conditions.
K Latent Roots.

TABLE 2.1 CODE NUMBERS OF THE REPRESENTATIONS OF
THE GROUP OF k (F_{432}).

Point & Code	Point & Code	Point & Code	Point & Code
Repn.	Repn.	Repn.	Repn.
Γ A_{1g} 1	Δ A_2 52	X E_g^1 101	L E_g^2 131
A_{2g} 2	B_1 53	E_g^2 137	A_{1u} 132
E_g^1 3	B_2 54	A_{1u} 102	A_{2u} 133
E_g^2 4	E^1 55	A_{2u} 103	E_u^1 134
T_{2g}^1 5	E^2 120	B_{1u} 104	E_u^2 135
T_{2g}^2 6	Λ A_1 56	B_{2u} 105	Q A_g 111
T_{2g}^3 7	A_2 57	E_u^1 106	A_u 112
T_{1g}^1 10	E^1 60	E_u^2 140	C A' 107
T_{1g}^2 11	E^2 136	Z A_1 65	A'' 110
T_{1g}^3 12	$\{ \begin{smallmatrix} \Sigma \\ K \end{smallmatrix} \}$ A_1 61	A_2 66	O A' 121
A_{1u} 13	A_2 62	B_1 67	A'' 122
A_{2u} 14	B_1 63	B_2 70	J A' 123
E_u^1 15	B_2 64	W A_1 113	A'' 124
E_u^2 16	$\{ \begin{smallmatrix} S \\ u \end{smallmatrix} \}$ A_1 71	A_2 114	A A 125
T_{2u}^1 17	A_2 72	B_1 115	B A' 126
T_{2u}^2 20	B_1 73	B_2 116	A'' 127
T_{2u}^3 21	B_2 74	E^1 117	
T_{1u}^1 22	X A_{1g} 75	E^2 141	
T_{1u}^2 23	A_{2g} 76	L A_{1g} 120	
T_{1u}^3 24	B_{1g} 77	A_{2g} 127	
Δ A_1 51	B_{2g} 100	E_g^1 130	

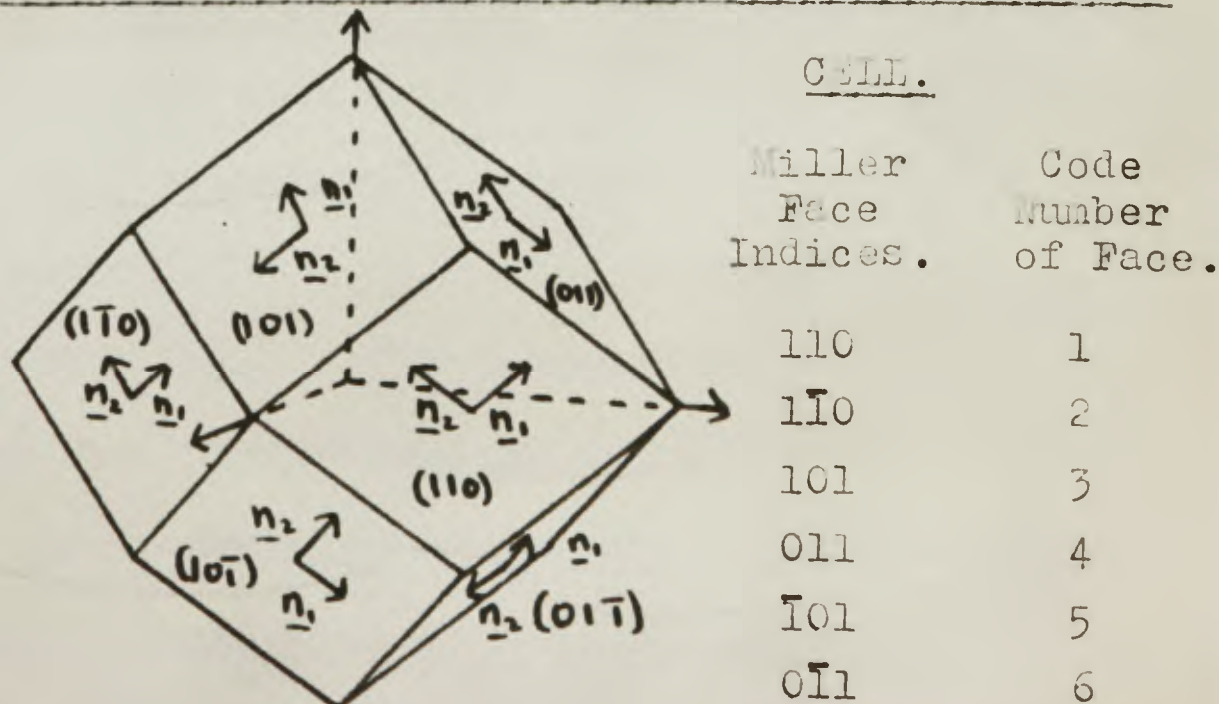
specially for that purpose (sector 776_8 - PARAMETERS); they also do some odd little bits of arithmetic and control the printing of the results.

For each representation of the group of the $\underline{k}$ -vector at each point in the Brillouin Zone there is one sector of code which contains details of (a) the fraction of the Wigner-Seitz cell which needs to be considered (b) the lattice harmonics for this representation in terms of those of the representations of Γ and (c) the boundary conditions used in the calculation. Each irreducible representation is given an arbitrary code number p_8 and the sector of code relevant to this representation is to be found in sector $400_8 + p_8$. Table 2.1 shows the code numbers given to the irreducible representations.

2.3 Subchapter A.

This subchapter deals with the geometry of the Wigner-Seitz unit cell which is shown in Figure 2.2.

FIGURE 2.2 LOCAL COORDINATES ON THE FACE OF WIGNER-SEITZ



As indicated here each face is given a code number and a system of local coordinate axes is set up on each face of the cell as shown in Figure 2.2. Faces opposite to those numbered 1-6 are given numbers 11-16 respectively. A point on the surface of the cell is then specified by the code number of the face on which it finds itself together with its local coordinates p, q referred to the axes $\underline{n}_1, \underline{n}_2$ on that face. In fact the programme is given a set of coordinates in one quadrant (i.e. both p and q are positive) and then the face and quadrant number of a point must be specified; the signs of p, q values for each quadrant are given in Table 2.2.

TABLE 2.2 LABELLING OF QUADRANTS OF FACES OF
WIGNER-SEITZ CELL.

	quadrant 1	quadrant 2	quadrant 3	quadrant 4
p	+	-	-	+
q	+	+	-	-

The same set of absolute values of p and q are used for each representation but they are arranged automatically over different fractions of the cell by the programme. Because of the symmetry it is only necessary to use $1/48$ th of the whole cell for some representations; while for k values of low symmetry the whole cell is needed. The fraction of the cell over which the points are distributed is specified in the code sector for the representation concerned. There is no reason why the whole cell should not be used for all representations

provided the precaution is taken that the points used are not related to one another by some symmetry operation of the group of $\underline{k}$. This is automatically guarded against in the programme.

The quantities calculated by the programme are r, θ, ϕ , the ordinary spherical polar coordinates of the points, and l_1, l_2, l_3 the direction cosines of the face normal with respect to axes at r, θ, ϕ . Also the radius of the sphere of volume equal to that of the Wigner-Seitz cell, r_{eq} , is found. The lattice spacing is provided to this subchapter by the master routine in the form of the side of the ordinary unit cell of the structure as normally quoted in the literature; this is a cube containing the equivalent of four atoms.

2.4 Theory of Subchapter A:

$|p|$ and $|q|$ are specified and using the code number of the quadrant signs are attached to these to form p and q .

The vector connecting the origin to the point in question is then $\underline{r} = r_0 \underline{n}_0 + p \underline{n}_1 + q \underline{n}_2$, where $\underline{n}_0, \underline{n}_1, \underline{n}_2$, are unit vectors along the face normal, and axes 1 and 2 on the face. If $\underline{i},$

$\underline{j}, \underline{k}$, are unit vectors along the x, y, z , axes then $x = \underline{r} \cdot \underline{i}$,

$y = \underline{r} \cdot \underline{j}$, $z = \underline{r} \cdot \underline{k}$, or

$$r \sin \theta \cos \phi = (r_0 \underline{n}_0 + p \underline{n}_1 + q \underline{n}_2) \cdot \underline{i}$$

$$r \sin \theta \sin \phi = (r_0 \underline{n}_0 + p \underline{n}_1 + q \underline{n}_2) \cdot \underline{j}$$

$$r \cos \theta = (r_0 \underline{n}_0 + p \underline{n}_1 + q \underline{n}_2) \cdot \underline{k}$$

and putting $r = r_0$, $p = u r_0$, $q = v r_0$, and $\underline{i} \cdot \underline{n}_0 = a_{11}$,

$\underline{i} \cdot \underline{n}_1 = a_{12}, \underline{i} \cdot \underline{n}_2 = a_{13}, \underline{i} \cdot \underline{n}_0 = a_{21}$ etc., we have

$$\Delta \sin \theta \cos \phi = a_{11} + u a_{12} + v a_{13},$$

$$\Delta \sin \theta \sin \phi = a_{21} + u a_{22} + v a_{23},$$

$$\Delta \cos \theta = a_{31} + u a_{32} + v a_{33}.$$

$$\text{therefore } \Delta = ((a_{11} + u a_{12} + v a_{13})^2 + (a_{21} + u a_{22} + v a_{23})^2 + (a_{31} + u a_{32} + v a_{33})^2)^{1/2}.$$

$$\text{and } r = \Delta r_0,$$

$$\theta = \cos^{-1} \left\{ \frac{a_{31} + u a_{32} + v a_{33}}{\Delta} \right\}$$

$$\phi = \cos^{-1} \left\{ \frac{a_{11} + u a_{12} + v a_{13}}{(a_{11} + u a_{12} + v a_{13})^2 + (a_{21} + u a_{22} + v a_{23})^2} \right\}.$$

The a_{ij} will depend on the face of the cell in use and the a_{ij} for the various faces represented are shown in Table 2.3.

For $\underline{l}_1, \underline{l}_2, \underline{l}_3$, if $\underline{i}', \underline{j}', \underline{k}'$, are unit basis vectors of the set of axes formed from $\underline{i}, \underline{j}, \underline{k}$, by the rotations through angles θ and ϕ and since the normal to the face is

$a_{11}\underline{i} + a_{21}\underline{j} + a_{31}\underline{k}$ then $\underline{l}_1 = \underline{n}_0 \cdot \underline{i}' = \underline{i}' \cdot (a_{11}\underline{i} + a_{21}\underline{j} + a_{31}\underline{k})$ etc., and by evaluating $\underline{i}' \cdot \underline{i}$ etc., one finds that

$$\underline{l}_1 = a_{11} \sin \theta \cos \phi + a_{21} \sin \theta \sin \phi + a_{31} \cos \theta$$

$$\underline{l}_2 = a_{11} \cos \theta \cos \phi + a_{21} \cos \theta \sin \phi - a_{31} \sin \theta$$

$$\underline{l}_3 = -a_{11} \sin \phi + a_{21} \cos \phi.$$

For r_{eq} , the radius of the sphere of volume equal to that of the Wigner-Seitz cell, we have

$$\frac{4}{3} \pi r_{eq}^3 = \frac{1}{8} a^3 = \text{volume of cell},$$

$$\text{so that } r_{eq} = a \times (3/16\pi)^{1/3}.$$

The entire programme is capable of dealing with 40₈n

TABLE 2.3 a_{ij} FOR FACES OF THE CELL.

Face		a_{11}	a_{12}	a_{13}	a_{21}	a_{22}	a_{23}	a_{31}	a_{32}	a_{33}
1	110	c	-d	d	c	d	-d	0	d	d
2	$\bar{1}10$	-c	d	-d	c	d	-d	0	d	d
3	101	c	-d	d	0	-d	-d	c	d	-d
4	011	0	-d	-d	c	d	-d	c	-d	d
5	10 $\bar{1}$	c	-d	d	0	d	d	-c	-d	d
6	01 $\bar{1}$	0	d	d	-c	d	-d	c	d	-d
11	$\bar{1}\bar{1}0$	-c	-d	d	-c	d	-d	0	d	d
12	1 $\bar{1}0$	c	d	-d	-c	d	-d	0	d	d
13	$\bar{1}0\bar{1}$	-c	-d	d	0	-d	-d	-c	d	-d
14	0 $\bar{1}\bar{1}$	0	-d	-d	-c	d	-d	-c	-d	d
15	10 $\bar{1}$	c	-d	d	0	d	d	-c	-d	d
16	01 $\bar{1}$	0	d	-d	c	d	-d	-c	d	-d

$$c = 1/3^{\frac{1}{2}}, d = 1/2^{\frac{1}{2}}.$$

(P.T.O.)

(i.e. 32_{10}^n) points where $n = 1, 2, 3$, and it is only entered once and does 40_8 , 100_8 , or 140_8 points according to the value of n specified to it.

2.5 Subchapter C.

This subchapter is a routine which uses the results of part I of this present work to select from the complete set of lattice harmonics of Γ those which are present in the representation actually under consideration. The results of part I chapter 2 are coded in the appropriate sector of code so that this chapter selects only those $C_{1\nu}^n$ needed and forms a compact store of them together with a list of their l, ν, n values and also a digit specifying whether the harmonic is Y_1^{mc} or Y_1^{ms} , where $X_{1\nu} = \sum_{m=1}^n Y_1^{mc/s}$. The details of the code are not very important, but basically each representation of Γ is listed together with a coding of the coefficient multiplying it in the lattice harmonics of the representation in question.

2.6 Subchapter D.

This subchapter of the programme calculates the $P_1^n(\cos\theta)$ (see previous chapter for details for them), values of θ are given and it is a routine kindly supplied by Dr C J Bradley; no material alteration has been made to it. It is therefore not necessary to describe in detail how it works; it only handles 40_8 θ values at a time and therefore this routine, together with subchapter B, has to run n times. An

accuracy of at least 7 figures is claimed for this routine.

2.7 Subchapter D.

From the results of the previous two subchapters this routine is enabled to form the lattice harmonics $X_{lv}(\theta, \phi)$ and their derivatives $\frac{\partial X_{lv}}{\partial \theta}$ and $\frac{\partial X_{lv}}{\partial \phi}$, where

$$X_{lv} = \sum_m C_{lv}^m P_l^m(\cos \theta) \Phi_m(\phi)$$

with

$$\begin{aligned} \Phi_m(\phi) &= 2^{\frac{1}{2}} \cos m\phi \text{ or } 2^{\frac{1}{2}} \sin m\phi, \text{ if } m \neq 0 \\ &= 1 \quad \text{or} \quad 0 \quad \text{if } m = 0. \end{aligned}$$

The ϕ dependence is listed with the coefficients C_{lv}^m in their store.

There are thus two sets of possibilities:

$$\begin{aligned} X_{lv} &= \sqrt{2} \sum_m C_{lv}^m P_l^m(\cos \theta) \cos m\phi \\ \frac{\partial X_{lv}}{\partial \theta} &= \sqrt{2} \sum_m C_{lv}^m \frac{dP_l^m(\cos \theta)}{d\theta} \cos m\phi \\ \frac{\partial X_{lv}}{\partial \phi} &= -\sqrt{2} \sum_m C_{lv}^m P_l^m(\cos \theta) \sin m\phi, \\ \text{and} \quad X_{lv} &= \sqrt{2} \sum_m C_{lv}^m P_l^m(\cos \theta) \sin m\phi, \\ \frac{\partial X_{lv}}{\partial \theta} &= \sqrt{2} \sum_m C_{lv}^m \frac{dP_l^m(\cos \theta)}{d\theta} \sin m\phi, \\ \frac{\partial X_{lv}}{\partial \phi} &= \sqrt{2} \sum_m m C_{lv}^m P_l^m(\cos \theta) \cos m\phi, \end{aligned}$$

and these can be made to cover all m values by adopting the artifice that $\cos m\phi = 2^{\frac{1}{2}}$ if $m = 0$.

From the store of $P_l^m(\cos \theta)$ left by the subchapter B this routine selects those it needs, and with the C_{lv}^m and its

code giving the θ dependence left by subchapter C it forms the functions $X_{\ell\nu}$, $\frac{\partial X_{\ell\nu}}{\partial \theta}$, and $\frac{\partial X_{\ell\nu}}{\partial \phi}$. Again this routine only works for $40_8 n$ points at a time but it stores the $X_{\ell\nu}$ for $40_8 n$ points in blocks of n sectors; i.e. for the first term in the expansion of ψ it stores all the $X_{\ell\nu}$ for $40_8 n$ points followed by the $\frac{\partial X_{\ell\nu}}{\partial \theta}$ for $40_8 n$ points and this in turn is followed by $\frac{\partial X_{\ell\nu}}{\partial \phi}$ for $40_8 n$ points. Following this are the $3n$ sectors of $X_{\ell\nu}$, $\frac{\partial X_{\ell\nu}}{\partial \theta}$, $\frac{\partial X_{\ell\nu}}{\partial \phi}$, for the next lattice harmonic in the expansion. The routine also leaves a directory for these functions indicating where they are to be found in the drum and what are the l and ν values.

2.6 Subchapter F.

There are several small things done by this chapter which works just once.

(i) It uses the $X_{\ell\nu}$, $\frac{\partial X_{\ell\nu}}{\partial \theta}$, $\frac{\partial X_{\ell\nu}}{\partial \phi}$ and they are replaced by $X_{\ell\nu}$, $Y_{\ell\nu}$, $Z_{\ell\nu}$, where

$$Y_{\ell\nu} = l_1 X_{\ell\nu}$$

and
$$Z_{\ell\nu} = l_2 \frac{\partial X_{\ell\nu}}{\partial \theta} + l_3 \operatorname{cosec} \theta \frac{\partial X_{\ell\nu}}{\partial \phi}$$

for all the $40_8 n$ values for each of the terms in the

(ii) It forms $\cos(\underline{k} \cdot \underline{R})$ and $\sin(\underline{k} \cdot \underline{R})$ for all the pairs of point and companion point, where companion points are related to the starting point by a reflexion in a plane through the origin and parallel to a plane of the cell.

(iii) It forms a table of $40_8 n$ values of $D^{\lambda}(\sigma)_{jj}$ and

another table of 40_8n coded values of $\exp(\underline{ik.R})$ and stores them in the drum. These are for each of the 40_8n points in turn. The code used for $\exp(\underline{ik.R})$ is:

$$1 \quad \text{if } \underline{k.R} = 2n$$

$$-1 \quad \text{if } \underline{k.R} = (2n+1) \quad (n \text{ is an integer})$$

0 if $k.R$ has any other value. This information is used later in sorting out which of the boundary conditions are applicable.

2.9 Subchapters H and J.

These two chapters together form the part of the programme concerned with the formation of the radial part of the wave function $R_\ell(r)$, and its derivative $\frac{dR_\ell(r)}{dr}$. These routines have been kindly supplied by Dr C J Bradley. In fact they work in terms of $G_\ell(e)$ and $G'_\ell(e)$ where $e = \log_e r$ and therefore $R_\ell(r) = G_\ell(e)\exp(-\frac{1}{2}e)$ and $\frac{dR_\ell(r)}{dr} = (G'_\ell(e) - \frac{1}{2}G_\ell(e))\exp(-\frac{3}{2}e)$. A self consistent potential field for the ion core which is assumed to exist (and which is kindly supplied by Dr D Mayers of the Oxford University Computing Laboratory) is supplied to the programme which from this produces the effective potential for an electron moving in the field of the ion core and the other conduction electrons in the cell; it is only in fact a "smoothed out" correction which is applied for the field contribution due to these other electrons. This part is outside the iterative cycle of the programme.

The second part uses a particular value of E and integrates the radial wave equation to produce $G_l(\rho)$ and $G_l'(\rho)$. This is done only for those l values needed but must of course be done afresh with each new trial energy.

2.10 Subchapter G.

This subchapter assembles the rectangular matrix; the theory of this was dealt with earlier, where it was seen that just 4 types of entry in the rectangular matrix are possible. Firstly the programme picks up the code number of the face on which the point in question is to be found and it tests the coded boundary conditions for the representation under consideration to see whether the group of k has a symmetry plane with diagonal matrix representative parallel to this face. If there is no such plane the boundary conditions are simply:

$$\psi_2 = \exp(i\mathbf{k} \cdot \mathbf{R}) \psi_1 \quad (i)$$

$$\nabla \psi_2 = -\exp(i\mathbf{k} \cdot \mathbf{R}) \nabla \psi_1 \quad (ii)$$

where $\mathbf{R}$ is the translation vector $\mathbf{r}_2 - \mathbf{r}_1$. If there is a plane of symmetry with diagonal matrix representative then the programme tests whether $D^\lambda(\sigma)_{jj}$ is equal to $\exp(i\mathbf{k} \cdot \mathbf{R})$ for this face; if this is so then equation (i) still applies, but if it is not true then, since $\psi_2 = D^\lambda(\sigma)_{jj} \psi_1$, this can only mean that ψ_2 and ψ_1 are both zero. For the boundary condition on $\text{grad } \psi$, if a plane of symmetry with diagonal matrix representative is present the programme tests for $D^\lambda(\sigma)_{jj} = -\exp(i\mathbf{k} \cdot \mathbf{R})$; if this is so then equation (ii)

still holds but if it is not true then for this point $\text{grad } \psi_2$ and $\text{grad } \psi_1$ are both zero.

As described in the previous chapter the actual functions produced are of the form:

$$(X_1 \psi_1)_2 = \cos(\underline{k} \cdot \underline{R}) \cdot (X_1 \psi_1)_1 \quad \text{etc.}$$

Because there are many more boundary condition equations than there are variables (the coefficients of the various terms in the expansion) the rectangular matrix, though large is long and narrow so that on forming $\underline{A}^T \underline{A}$, which is done at the end of the subchapter, a fairly small square matrix results.

2.11 Subchapter K.

This subchapter, due to Dr J S Rollett of Oxford University Computing Laboratory, finds the minimum eigenvalue or the eigenvector corresponding to the minimum eigenvalue (i.e. the wave function coefficients) of the matrix $\underline{A}^T \underline{A}$ left by the previous subchapter. This is a standard "Mercury" Autocode Library programme and further details about it are available from the manual of those Library programmes.

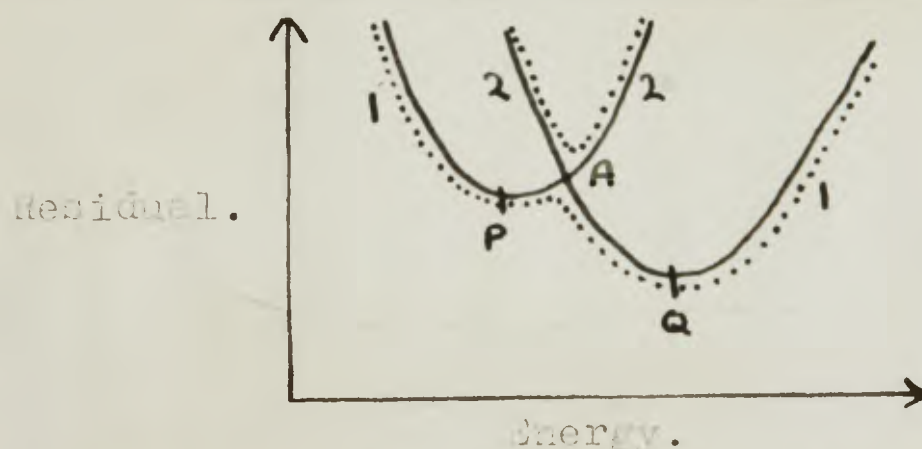
2.12 General Comments.

The programme is fully automatic; given a starting energy E and an increment ΔE it will either handle several representations and print out the residuals for each representation at $E + m\Delta E$ until it reaches the final value of E specified; $m = 0, 1, 2, \text{ etc.}$, (SCAN). Alternatively, handling just one representation it will find the residuals

at $E + m\Delta E$ until the minimum is bracketed when it will do a series of parabolic interpolations to find the minimum E to a stated degree of accuracy (MINFIND). In practice for a real metal one uses SCAN and a large ΔE to give a rough idea of the locations of the levels and this gives one sufficiently good starting values of E to feed to MINFIND, which can then proceed at a much smaller ΔE and locate the minimum to several figures of accuracy. With the empty lattice tests (see next chapter) there is however no need of SCAN since the correct answers are known beforehand.

One drawback of the method is that sometimes the lowest eigenvalue is masked by the sudden appearance of the second eigenvalue of the square matrix and the two may change over causing an apparent point of inflexion rather than a genuine minimum, as shewn in Figure 2.3.

FIGURE 2.3 THE CROSSING OF CURVES OF TWO EIGENVALUES.



If the first two eigenvalues of the matrix were found they would be seen to come very close together at A where in fact what was the lowest becomes the next lowest and vice versa. As a refinement it would be possible in cases like this, (i) to determine the point A, and then (ii) to use curve 1 on the

left of A and curve 2 on the right of A to find the minimum of 1-2 at P, and curve 2 on the left of A and curve 1 on the right of A to find the next minimum, on 2-1, at Q. This problem is particularly serious for the future development of cellular calculations when all points will be treated as general points with only 1 representation and a consequent crowding together of the eigenvalues.

A consideration of the accuracy of the programme will be given after the description of the empty lattice tests.

CHAPTER III. EMPTY LATTICE TESTS.

3.1 The Reciprocal Lattice.

The Cellular Method is capable of being tested in a very exhaustive way, by using the potential $V(r) = 0$ in the Schrödinger Equation. An exact analytical solution is possible for this case which can therefore be compared with the computed values: this is called the "empty lattice test" and was first suggested by Shockley (1937). An exact description of the energy bands is possible for the various points, lines, planes and general points in the Brillouin Zone. A good description of the outlines of the theory was given by Jones (1960) — though the treatment is not complete and only the line $\Gamma-\Lambda-L$ was considered. Here that treatment will be followed and extended to cover the whole of the Brillouin Zone; we list wave functions and energies for the lowest few levels at each point of symmetry in the Zone.

If $\underline{a}_1, \underline{a}_2, \underline{a}_3$, are the basis vectors of a Bravais Lattice then a general lattice point is

$$\begin{aligned} & n_1 \underline{a}_1 + n_2 \underline{a}_2 + n_3 \underline{a}_3, \\ &= \begin{bmatrix} a_{1x} & a_{2x} & a_{3x} \\ a_{1y} & a_{2y} & a_{3y} \\ a_{1z} & a_{2z} & a_{3z} \end{bmatrix} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix} \\ &= \underline{A} \underline{n}, \text{ where } n_1, n_2, n_3, \text{ are integers.} \end{aligned}$$

Thus any lattice point can be expressed as some matrix $\underline{A}$, characteristic of the Bravais lattice concerned operating on a vector consisting of 3 integers. For the face centred cubic

$$\text{lattice } \underline{a}_1 = (0, a/2, a/2)$$

$$\underline{a}_2 = (a/2, 0, a/2)$$

$$\underline{a}_3 = (a/2, a/2, 0)$$

$$\text{and so } \underline{A} = \begin{bmatrix} 0 & \frac{1}{2}a & \frac{1}{2}a \\ \frac{1}{2}a & 0 & \frac{1}{2}a \\ \frac{1}{2}a & \frac{1}{2}a & 0 \end{bmatrix}.$$

The reciprocal lattice with basis vectors $\underline{b}_1, \underline{b}_2, \underline{b}_3$, is defined by $\underline{b}_i \cdot \underline{a}_j = \delta_{ij}$, and the basis vectors of $\underline{k}$ space are $2\pi\underline{b}_1, 2\pi\underline{b}_2, 2\pi\underline{b}_3$. Therefore $\underline{b}_1 = 1/a(\bar{1}, 1, 1)$

$$\underline{b}_2 = 1/a(1, \bar{1}, 1)$$

$$\underline{b}_3 = 1/a(1, 1, \bar{1}).$$

Therefore one can write a point in $\underline{k}$ space as $l_1\underline{k}_1 + l_2\underline{k}_2 + l_3\underline{k}_3$

$$= 2\pi\underline{l} \cdot \underline{B}, \text{ where } \underline{B} = \begin{bmatrix} b_{1x} & b_{1y} & b_{1z} \\ b_{2x} & b_{2y} & b_{2z} \\ b_{3x} & b_{3y} & b_{3z} \end{bmatrix}, \text{ and the Matrix}$$

$\underline{K}$ is defined as $2\pi\underline{B}$. If we are dealing with a finite lattice in real space then $\underline{k}$ space is discrete and not continuous, but if we have an infinite lattice in real space then $\underline{k}$ space can be considered to be continuous.

There are two slightly different approaches to Brillouin Zone theory, one is to use the whole of $\underline{k}$ space, and the other is to use the reduced zone scheme. In the first case one gets just one wave function at each point in $\underline{k}$ space

corresponding to $\underline{l} = (0,0,0)$, i.e. $\Psi = \exp(i\underline{k}_f \cdot \underline{r})$ where $\underline{k}_f$ is the $\underline{k}$ vector in the full zone scheme. For all the equivalent points in $\underline{k}$ space these $\underline{k}$'s are related to one another by a reciprocal lattice vector and therefore possess the same symmetry and therefore the various wave functions will belong to the various irreducible representations of the same group, namely the common group shared by all the $\underline{k}$ vectors. Since this is so it has become customary often to use the reduced zone scheme where one takes, for given $\underline{k}$, solutions with $\underline{l}$ values other than $(0,0,0)$ and therefore getting an infinite number of levels and functions at any point in $\underline{k}$ space. The two descriptions, either considering only one level at each point in the whole of $\underline{k}$ space or considering all $\underline{l}$ values at only points within the first Brillouin Zone, are completely equivalent even by the time one writes down the wave function and energy, for the $\underline{k}_f$ of the full zone description is just the $(\underline{k}_T - \underline{lK})$ of the reduced zone scheme, the energy E is $\underline{k}_f^2$, or $|\underline{k}_T - \underline{lK}|^2$ and $\Psi = \exp(i\underline{k}_f \cdot \underline{r})$ or $\exp(i(\underline{k}_T - \underline{lK}) \cdot \underline{r})$. The first Brillouin Zone is thus the "unit cell" of $\underline{k}$ space and it has its opposite faces separated by a reciprocal lattice vector.

3.2 Solution of Schrödinger's Equation for $V(\underline{r}) = 0$.

If we now consider the Schrödinger Equation:

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V \Psi = E \Psi,$$

and use the form of the wave function obtained from Bloch's theorem $\Psi(\underline{r}) = u(\underline{r}) \exp(i\underline{k} \cdot \underline{r})$, then

$$-\frac{\hbar^2}{2m} \nabla^2 (e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r})) + V(\mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}) - E e^{i\mathbf{k} \cdot \mathbf{r}} u(\mathbf{r}) = 0$$

$$\text{i.e. } \frac{\hbar^2}{2m} \{ e^{i\mathbf{k} \cdot \mathbf{r}} \nabla^2 u + 2i\mathbf{k} \cdot e^{i\mathbf{k} \cdot \mathbf{r}} \nabla u - k^2 e^{i\mathbf{k} \cdot \mathbf{r}} u \} - V e^{i\mathbf{k} \cdot \mathbf{r}} u + E e^{i\mathbf{k} \cdot \mathbf{r}} u = 0$$

$$\therefore \nabla^2 u + 2i\mathbf{k} \cdot \nabla u + \frac{2m}{\hbar^2} (E - V - \frac{\hbar^2 k^2}{2m}) u = 0$$

u & V being functions of $\mathbf{r}$. For empty lattice tests we put

$V(\mathbf{r}) = 0$ so that

$$\nabla^2 u + 2i\mathbf{k} \cdot \nabla u + \frac{2m}{\hbar^2} (E - \frac{\hbar^2 k^2}{2m}) u = 0$$

then if $u = \exp(-i\mathbf{p} \cdot \mathbf{r})$

$$(-i\mathbf{p})^2 + 2i\mathbf{k} \cdot (-i\mathbf{p}) + \frac{2m}{\hbar^2} (E - \frac{\hbar^2 k^2}{2m}) = 0$$

or if $\mathbf{p} = \mathbf{k}$ then

$$\frac{2mE}{\hbar^2} = \mathbf{k}^2 - 2\mathbf{k} \cdot \mathbf{k} - \mathbf{k}^2$$

or $E = |\mathbf{k} - \mathbf{k}|^2$,

and $\psi(\mathbf{k}, \mathbf{r}) = \exp(i(\mathbf{k} - \mathbf{k}) \cdot \mathbf{r})$.

The first Brillouin Zone for face centred cubic lattices is as shown in part 1, figure 2.3. The values of $\mathbf{k}$ for the special points of symmetry in the Brillouin Zone are listed in Table 3.1.

To simplify the empty lattice tests the special value of $a = 2\pi$ is taken, so that if $\mathbf{k} = 2\pi/a(\xi, \eta, \zeta)$ this becomes just (ξ, η, ζ) so that

$$E = (\xi - n_1)^2 + (\eta - n_2)^2 + (\zeta - n_3)^2$$

and $\psi = \exp(i\{(\xi - n_1)x + (\eta - n_2)y + (\zeta - n_3)z\})$,

where $\mathbf{n} = \mathbf{k}$,

i.e. for this lattice $n_1 = -l_1 + l_2 + l_3$,

$$n_2 = l_1 - l_2 + l_3,$$

$$n_3 = l_1 + l_2 - l_3.$$

In Tables 3.2 and 3.3 are listed values of $\mathbf{k} - \mathbf{n}$, and

TABLE 5.1 POINTS OF SYMMETRY IN BRILLOUIN ZONE.

k .	Point of BZ.	Point group	Symmetry Elements present.
0, 0, 0	Γ	$m\bar{3}m$	all cubic elements.
π , 1, 0	U	$2mm^*$	$E, C_{2c}, \sigma_y, \sigma_{dc}$.
π , π , 0	K	$2mm^*$	$E, C_{2a}, \sigma_z, \sigma_{db}$.
0, 1, 0	X	$4/mmm^*$	$E, C_{2y}, C_{4y}^{\pm}, C_{2z}, C_{2x}, C_{2c}, C_{2e},$ $I, \sigma_y, S_{4y}^{\mp}, \sigma_z, \sigma_x, \sigma_{dc}, \sigma_{de}$.
π , 1, 0	Δ	$\bar{4}2m^*$	$E, S_{4x}^{\pm}, C_{2x}, \sigma_y, \sigma_z, C_{2d}, C_{2f}$.
π , π , π	L	$\bar{3}m^*$	$E, C_{3l}^{\pm}, \sigma_{db}, \sigma_{de}, \sigma_{df},$ $I, S_{6l}^{\mp}, C_{2b}, C_{2e}, C_{2f}$.

N.B. k is in units of $2\pi/a$.

* denotes a point group in the non-standard orientation.

TABLE 3.2

$$\{(5 - n_1), (\eta - n_2), (3 - n_3)\}.$$

$\underline{e}$	$\underline{n}$	Γ	X	L	W	K	U
000	000	000	010	$1/2 1/2 1/2$	$1/2 10$	$3/4 3/4 0$	$1/4 1 1/4$
100	$\bar{1}11$	1-1-1	10-1	$3/2 -1/2 -1/2$	$3/2 0-1$	$7/4 -1/4 1$	$5/4 0 -3/4$
010	1 $\bar{1}1$	-11-1	121	$-1/2 3/2 -1/2$	$-1/2 2-1$	$-1/4 7/4 -1$	$-3/4 2 -3/4$
001	11 $\bar{1}$	-1-11	-101	$-1/2 -1/2 3/2$	$-1/2 01$	$-1/4 -1/4 1$	$-3/4 0 5/4$
$\bar{1}00$	1 $\bar{1}\bar{1}$	-111	-121	$-1/2 3/2 3/2$	$-1/2 21$	$-1/4 7/4 1$	$-3/4 2 5/4$
0 $\bar{1}0$	$\bar{1}1\bar{1}$	1-11	101	$3/2 -1/2 3/2$	$3/2 01$	$7/4 -1/4 1$	$5/4 0 5/4$
00 $\bar{1}$	$\bar{1}\bar{1}1$	11-1	12-1	$3/2 3/2 -1/2$	$3/2 2-1$	$7/4 7/4 -1$	$5/4 2 -3/4$
011	200	-200	-210	$-3/2 1/2 1/2$	$-3/2 10$	$-5/4 3/4 0$	$-1/4 1 1/4$
101	020	0-20	0-10	$1/2 -3/2 1/2$	$1/2 -10$	$3/4 -5/4 0$	$1/4 -1 1/4$
110	002	00-2	01-2	$1/2 1/2 -3/2$	$1/2 1-2$	$3/4 3/4 -2$	$1/4 1 -7/4$
0 $\bar{1}\bar{1}$	$\bar{2}00$	200	210	$5/2 1/2 1/2$	$5/2 10$	$11/4 3/4 0$	$9/4 1 1/4$
$\bar{1}0\bar{1}$	0 $\bar{2}0$	020	030	$1/2 5/2 1/2$	$1/2 30$	$3/4 11/4 0$	$1/4 3 1/4$
$\bar{1}\bar{1}0$	00 $\bar{2}$	002	012	$1/2 1/2 5/2$	$1/2 12$	$3/4 3/4 2$	$1/4 1 9/4$
111	111	-1-1-1	-101	$-1/2 -1/2 -1/2$	$-1/2 0-1$	$-1/4 -1/4 -1$	$-3/4 0 -3/4$
$\bar{1}\bar{1}\bar{1}$	$\bar{1}\bar{1}\bar{1}$	111	121	$3/2 3/2 3/2$	$3/2 21$	$7/4 7/4 1$	$5/4 2 5/4$
01 $\bar{1}$	0 $\bar{2}2$	02-2	03-2	$1/2 -3/2 5/2$	$1/2 32$	$3/4 -5/4 2$	$1/4 3 -7/4$
0 $\bar{1}1$	02 $\bar{2}$	0-22	0-12	$1/2 5/2 -3/2$	$1/2 -1-2$	$3/4 11/4 -2$	$1/4 -1 9/4$
10 $\bar{1}$	$\bar{2}02$	20-2	21-2	$-3/2 1/2 5/2$	$-3/2 12$	$-5/4 3/4 2$	$9/4 1 -7/4$
$\bar{1}01$	20 $\bar{2}$	-202	-212	$5/2 1/2 -3/2$	$5/2 1-2$	$11/4 3/4 -2$	$-7/4 1 9/4$
1 $\bar{1}0$	$\bar{2}20$	2-20	2-10	$-3/2 5/2 1/2$	$-3/2 30$	$-5/4 11/4 0$	$9/4 -1 1/4$
$\bar{1}10$	2 $\bar{2}0$	-220	-230	$5/2 -3/2 1/2$	$5/2 -10$	$11/4 -5/4 0$	$-7/4 3 1/4$

TABLE 3.3 R FOR EMPTY LATTICE TESTS.

l	n	r	X	L	W	K	U
0 0 0	0 0 0	0	1	$\frac{2}{3}$	$1\frac{1}{3}$	$1\frac{1}{3}$	$1\frac{1}{3}$
1 0 0	$\bar{1}$ 1 1	3	2	$2\frac{2}{3}$	$3\frac{1}{3}$	$4\frac{1}{3}$	$2\frac{2}{3}$
0 1 0	1 $\bar{1}$ 1	3	6	$2\frac{2}{3}$	$5\frac{1}{3}$	$4\frac{1}{3}$	$5\frac{1}{3}$
0 0 1	1 1 $\bar{1}$	3	2	$2\frac{2}{3}$	$1\frac{1}{3}$	$1\frac{1}{3}$	$2\frac{2}{3}$
$\bar{1}$ 0 0	1 $\bar{1}$ $\bar{1}$	3	6	$4\frac{2}{3}$	$5\frac{1}{3}$	$4\frac{1}{3}$	$6\frac{1}{3}$
0 $\bar{1}$ 0	$\bar{1}$ 1 $\bar{1}$	3	2	$4\frac{2}{3}$	$3\frac{1}{3}$	$4\frac{1}{3}$	$3\frac{1}{3}$
0 0 $\bar{1}$	$\bar{1}$ $\bar{1}$ 1	3	6	$4\frac{2}{3}$	$7\frac{1}{3}$	$7\frac{1}{3}$	$6\frac{1}{3}$
0 1 1	2 0 0	4	5	$2\frac{2}{3}$	$3\frac{1}{3}$	$2\frac{2}{3}$	$4\frac{1}{3}$
1 0 1	0 2 0	4	1	$2\frac{2}{3}$	$1\frac{1}{3}$	$2\frac{2}{3}$	$1\frac{1}{3}$
$\bar{1}$ 1 0	0 0 2	4	5	$2\frac{2}{3}$	$5\frac{1}{3}$	$5\frac{1}{3}$	$4\frac{1}{3}$
0 $\bar{1}$ $\bar{1}$	$\bar{2}$ 0 0	4	5	$6\frac{2}{3}$	$7\frac{1}{3}$	$8\frac{1}{3}$	$6\frac{1}{3}$
$\bar{1}$ 0 $\bar{1}$	0 $\bar{2}$ 0	4	9	$6\frac{2}{3}$	$9\frac{1}{3}$	$8\frac{1}{3}$	$9\frac{1}{3}$
$\bar{1}$ $\bar{1}$ 0	0 0 $\bar{2}$	4	5	$6\frac{2}{3}$	$5\frac{1}{3}$	$5\frac{1}{3}$	$6\frac{1}{3}$
1 1 1	1 1 1	3	2	$\frac{2}{3}$	$1\frac{1}{3}$	$1\frac{1}{3}$	$1\frac{1}{3}$
$\bar{1}$ $\bar{1}$ $\bar{1}$	$\bar{1}$ $\bar{1}$ $\bar{1}$	3	6	$6\frac{2}{3}$	$7\frac{1}{3}$	$7\frac{1}{3}$	$7\frac{1}{3}$
0 1 $\bar{1}$	0 $\bar{2}$ 2	8	13	$8\frac{2}{3}$	$13\frac{1}{3}$	$12\frac{1}{3}$	$12\frac{1}{3}$
0 $\bar{1}$ 1	0 2 $\bar{2}$	8	5	$8\frac{2}{3}$	$5\frac{1}{3}$	$6\frac{1}{3}$	$6\frac{1}{3}$
1 0 $\bar{1}$	$\bar{2}$ 0 2	8	9	$8\frac{2}{3}$	$11\frac{1}{3}$	$12\frac{1}{3}$	$9\frac{1}{3}$
$\bar{1}$ 0 1	2 0 $\bar{2}$	8	9	$8\frac{2}{3}$	$7\frac{1}{3}$	$6\frac{1}{3}$	$9\frac{1}{3}$
1 $\bar{1}$ 0	$\bar{2}$ 2 0	8	5	$8\frac{2}{3}$	$7\frac{1}{3}$	$9\frac{1}{3}$	$6\frac{1}{3}$
$\bar{1}$ 1 0	2 $\bar{2}$ 0	8	13	$8\frac{2}{3}$	$11\frac{1}{3}$	$9\frac{1}{3}$	$12\frac{1}{3}$

and E for various $\underline{l}$ values at the special points of the zone. It will be seen that there are often several values of $\underline{l}$ leading to each energy level at the point concerned in most cases, but there is no reason why the particular $\underline{l}$ values chosen for these tables should be the only ones leading to the energies shown. In practice the symmetrizing operator which is mentioned later will usually discover any other $\underline{l}$ values leading to the same energy which may have been missed.

3.3 Symmetrizing Operators.

The wave function found above, $\psi = \exp i \{ (\xi - n_1)x + (\eta - n_2)y + (\zeta - n_3)z \}$ will not usually transform according to any of the irreducible representations of the group of $\underline{k}$ but it is possible to form linear combinations of the several degenerate functions at the given level with the required symmetry. This is necessary to enable one to tell which representations have levels at the energy value in question. If the function ϕ^i is some linear combination of the $u_1, u_2, \dots$ which are the functions already found, and it is to transform according to the i th irreducible representation then $\underline{R}\phi_s^i = \sum_{\underline{r}} \phi_{\underline{r}}^i D^i(\underline{R})_{rs}$, where $\underline{R}$ is an operator corresponding to any element of the group of $\underline{k}$, and ϕ_s^i is the s th function of the row vector ϕ^i and $D^i(\underline{R})_{rs}$ are the elements of the matrix representative of $\underline{R}$ in the i th representation.

It is shown in S3.2 of Altmann (1962) that the operator $\underline{W}_{ts}^i = 1/h \sum_{\underline{R}} D^i(\underline{R})_{ts}^* \underline{R}$ acting on an arbitrary function produces a function of the required symmetry, i.e. belonging to the s th

column of the i th irreducible representation of the group.

The function so produced may be identically zero. So that if we apply all the 20 operators for the 20 columns of the representations of Γ to the functions u_i then some of the operators acting on some of the functions will produce a total number of symmetrized functions ϕ^i equal in number to the u_i with which we started and the rest will produce zeros.

Because the operator W_{ts}^i produces a nontrivial function from one of the u_i 's this is no guarantee that it will do so with all the rest of the u_i 's though it may do so. And conversely because a given W_{ts}^i produces a trivial ϕ^i from one of the u_i 's this is no guarantee that there is no function of the necessary symmetry derivable from any of the other u_i 's using that W_{ts}^i .

It should be mentioned that the suffix t is redundant and it is possible to take the matrix elements $D(R)_{ts}^*$ belonging to any of the rows t so long as these elements are in the s th column. In practice we shall put $t = s$.

3.4 Example: Γ , $E = 3$.

As a detailed example of this procedure the 8 degenerate levels of Γ at $E = 3$ are considered. The 1 values leading to solutions of Schrödinger's equation at this value of E are tabulated below with their wave functions, Table 3.4.

(P.T.O.)

TABLE 3.4 THE 8 DEGENERATE WAVE FUNCTIONS AT Γ , $E = 3$.

<u>l</u>	<u>n</u>	ψ	label
111	111	$\exp i(-x -y -z)$	u_1
001	11 $\bar{1}$	$\exp i(-x -y +z)$	u_2
010	1 $\bar{1}$ 1	$\exp i(-x +y -z)$	u_3
100	$\bar{1}$ 11	$\exp i(x -y -z)$	u_4
$\bar{1}\bar{1}\bar{1}$	$\bar{1}\bar{1}\bar{1}$	$\exp i(x +y +z)$	u_5
00 $\bar{1}$	$\bar{1}\bar{1}$ 1	$\exp i(x +y +z)$	u_6
0 $\bar{1}$ 0	$\bar{1}$ 1 $\bar{1}$	$\exp i(x -y +z)$	u_7
$\bar{1}$ 00	1 $\bar{1}\bar{1}$	$\exp i(-x +y +z)$	u_8

Two more tables follow; these are Table 3.5 with the results of the operation R on all the 8 u_i 's by all the 48 elements of the group $m\bar{3}m (O_h)$, and Table 3.6 with the matrix elements $D_{tt}^1(R)^*$ for each element of all the irreducible representations of the group $m\bar{3}m (O_h)$. In deriving the first of these two tables the Jones' faithful representation of the operators was used (see chapter I Appendix I). The functions ϕ formed by the operators W_{tt}^1 operating on, for example, u_1 can thus be found from these two tables:

e.g. for Λ_{1g} we get

$$\begin{aligned}
 & u_1 + u_8 + u_7 + u_6 + u_1 + u_7 + u_6 + u_8 + u_2 + u_8 + u_7 + u_6 \\
 & + u_3 + u_2 + u_4 + u_2 + u_4 + u_3 + u_2 + u_5 + u_3 + u_4 + u_5 + u_5 \\
 & + u_5 + u_4 + u_3 + u_2 + u_5 + u_3 + u_2 + u_4 + u_5 + u_4 + u_3 + u_2 \\
 & + u_7 + u_6 + u_8 + u_6 + u_8 + u_7 + u_6 + u_1 + u_7 + u_8 + u_1 + u_1 \\
 & = 6(u_1 + u_2 + u_3 + u_4 + u_5 + u_6 + u_7 + u_8),
 \end{aligned}$$

TABLE 3.5 m_1 FOR ALL THE ELEMENTS R IN THE GROUP $m\bar{3}m (O_h)$.

Element	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_8	Element	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_8
E	u_1	u_2	u_3	u_4	u_5	u_6	u_7	u_8	I	u_5	u_6	u_7	u_8	u_1	u_2	u_3	u_4
C_{2x}	u_8	u_3	u_2	u_5	u_4	u_7	u_6	u_1	O_x	u_4	u_7	u_6	u_1	u_8	u_3	u_2	u_5
C_{2y}	u_7	u_4	u_5	u_2	u_3	u_8	u_1	u_6	O_y	u_3	u_8	u_1	u_6	u_7	u_4	u_5	u_2
C_{2z}	u_6	u_5	u_4	u_3	u_2	u_1	u_8	u_7	O_z	u_2	u_1	u_8	u_7	u_6	u_5	u_4	u_3
C_{31}^-	u_1	u_4	u_2	u_3	u_5	u_8	u_6	u_7	S_{61}^+	u_5	u_8	u_6	u_7	u_1	u_4	u_2	u_3
C_{32}^-	u_7	u_2	u_4	u_5	u_3	u_8	u_1	u_6	S_{62}^+	u_3	u_6	u_8	u_1	u_7	u_4	u_5	u_2
C_{33}^-	u_6	u_3	u_5	u_4	u_2	u_7	u_1	u_8	S_{63}^+	u_2	u_7	u_1	u_8	u_6	u_3	u_5	u_4
C_{34}^-	u_8	u_5	u_3	u_2	u_4	u_1	u_7	u_6	S_{64}^+	u_4	u_1	u_7	u_6	u_8	u_5	u_3	u_2
C_{31}^+	u_1	u_3	u_4	u_2	u_5	u_7	u_8	u_6	S_{61}^-	u_5	u_7	u_8	u_6	u_1	u_3	u_4	u_2
C_{32}^+	u_8	u_2	u_5	u_3	u_4	u_6	u_1	u_7	S_{62}^-	u_4	u_6	u_1	u_7	u_8	u_2	u_5	u_3
C_{33}^+	u_7	u_5	u_2	u_4	u_3	u_1	u_6	u_8	S_{63}^-	u_3	u_1	u_6	u_8	u_7	u_5	u_2	u_4
C_{34}^+	u_6	u_4	u_3	u_5	u_2	u_8	u_7	u_1	S_{64}^-	u_2	u_8	u_7	u_1	u_6	u_4	u_3	u_5
C_{4x}^-	u_3	u_1	u_8	u_6	u_7	u_5	u_4	u_2	S_{4x}^+	u_7	u_5	u_4	u_2	u_3	u_1	u_8	u_6
C_{4y}^-	u_2	u_7	u_8	u_1	u_6	u_3	u_4	u_5	S_{4y}^+	u_6	u_3	u_4	u_5	u_2	u_7	u_8	u_1
C_{4z}^-	u_4	u_7	u_1	u_6	u_8	u_3	u_5	u_2	S_{4z}^+	u_8	u_3	u_5	u_2	u_4	u_7	u_1	u_6
C_{4x}^+	u_2	u_8	u_1	u_7	u_6	u_4	u_5	u_3	S_{4x}^-	u_6	u_4	u_5	u_3	u_2	u_8	u_1	u_7
C_{4y}^+	u_4	u_1	u_6	u_7	u_8	u_5	u_2	u_3	S_{4y}^-	u_8	u_5	u_2	u_3	u_4	u_1	u_6	u_7
C_{4z}^+	u_3	u_8	u_6	u_1	u_7	u_4	u_2	u_5	S_{4z}^-	u_7	u_4	u_2	u_5	u_3	u_8	u_6	u_1
C_{2a}	u_2	u_1	u_7	u_8	u_6	u_5	u_3	u_4	O_{da}	u_6	u_5	u_3	u_4	u_2	u_1	u_7	u_8
C_{2b}	u_5	u_6	u_8	u_7	u_1	u_2	u_4	u_3	O_{db}	u_1	u_2	u_4	u_3	u_5	u_6	u_8	u_7
C_{2c}	u_3	u_6	u_1	u_8	u_7	u_2	u_5	u_4	O_{dc}	u_7	u_2	u_5	u_4	u_3	u_6	u_1	u_8
C_{2d}	u_4	u_6	u_7	u_1	u_8	u_2	u_3	u_5	O_{dd}	u_8	u_2	u_3	u_5	u_4	u_6	u_7	u_1
C_{2e}	u_5	u_8	u_7	u_6	u_1	u_4	u_3	u_2	O_{de}	u_1	u_4	u_3	u_2	u_5	u_8	u_7	u_6
C_{2f}	u_5	u_7	u_6	u_8	u_1	u_3	u_2	u_4	O_{df}	u_1	u_3	u_2	u_4	u_5	u_7	u_6	u_8

TABLE 3.6 $D_{tt}^1(R)^*$ FOR ELEMENTS OF $m3m (O_h)$.

Only half the table is given here;

for g-type representations $D_{tt}^1(IR)^* = +D_{tt}^1(R)^*$

and u-type representations $D_{tt}^1(IR)^* = -D_{tt}^1(R)^*$.

Element.	A_1	A_2	E^1	E^2	T_2^1	T_2^2	T_2^3	T_1^1	T_1^2	T_1^3
E	1	1	1	1	1	1	1	1	1	1
C_{2x}	1	1	1	1	1	-1	-1	1	-1	-1
C_{2y}	1	1	1	1	-1	1	-1	-1	1	-1
C_{2z}	1	1	1	1	-1	-1	1	-1	-1	1
C_{31}^-	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0
C_{32}^-	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0
C_{33}^-	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0
C_{34}^-	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0
C_{31}^+	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0
C_{32}^+	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0
C_{33}^+	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0
C_{34}^+	1	1	$-\frac{1}{2}$	$-\frac{1}{2}$	0	0	0	0	0	0
C_{4x}^-	1	-1	$-\frac{1}{2}$	$\frac{1}{2}$	-1	0	0	1	0	0
C_{4y}^-	1	-1	$-\frac{1}{2}$	$\frac{1}{2}$	0	-1	0	0	1	0
C_{4z}^-	1	-1	1	-1	0	0	-1	0	0	-1
C_{4x}^+	1	-1	$-\frac{1}{2}$	$\frac{1}{2}$	-1	0	0	1	0	0
C_{4y}^+	1	-1	$-\frac{1}{2}$	$\frac{1}{2}$	0	-1	0	0	1	0
C_{4z}^+	1	-1	1	-1	0	0	-1	0	0	1
C_{2a}	1	-1	1	-1	0	0	1	0	0	-1
C_{2b}	1	-1	1	-1	0	0	1	0	0	-1
C_{2c}	1	-1	$-\frac{1}{2}$	$\frac{1}{2}$	0	1	0	0	-1	0
C_{2d}	1	-1	$-\frac{1}{2}$	$\frac{1}{2}$	1	0	0	-1	0	0
C_{2e}	1	-1	$-\frac{1}{2}$	$\frac{1}{2}$	0	1	0	0	-1	0
C_{2f}	1	-1	$-\frac{1}{2}$	$\frac{1}{2}$	1	0	0	-1	0	0

and for E_g^1 ,

$$\begin{aligned}
 & u_1 + u_8 + u_7 + u_6 - \frac{1}{2}(u_1 + u_7 + u_8 + u_6 + u_1 + u_8 + u_3 + u_2) \\
 & - \frac{1}{2}(u_7 + u_6) + u_4 - \frac{1}{2}(u_2 + u_4) + u_3 + u_2 + u_5 - \frac{1}{2}(u_3 + u_4 + 2u_5) \\
 & + u_5 + u_4 + u_3 + u_2 - \frac{1}{2}(u_5 + u_3 + u_2 + u_4 + u_5 + u_4 + u_3 + u_2) \\
 & - \frac{1}{2}(u_7 + u_6) + u_8 - \frac{1}{2}(u_6 + u_8) + u_7 + u_6 + u_1 - \frac{1}{2}(u_7 + u_8 + 2u_1) \\
 & = 0.
 \end{aligned}$$

The results for all those irreducible representations which give non-trivial ϕ^1 are then tabulated in Table 3.7. All the other representations have W_{tt}^1 which give trivial ϕ^1 when acting on u_1 , and if we had used one of the other u_i as the function acted on by W_{tt}^1 we should still have arrived at the same table of functions as that given here. These functions can be put into a more familiar form e.g. for

A_{1g} ,

$$\begin{aligned}
 \phi &= u_1 + u_2 + u_3 + u_4 + u_5 + u_6 + u_7 + u_8 \\
 &= \cos(x+y+z) + \cos(x+y-z) + \cos(x-y+z) + \cos(-x+y+z) \\
 &= \cos(x+y)\cos z + \cos(x-y)\cos z \\
 &= \cos x \cos y \cos z, \text{ neglecting numerical factors.}
 \end{aligned}$$

In fact the 8 symmetrized functions for the level $S = 3$ of Γ can be shown to reduce to the form given in Table 3.8 and this can be compared with Jones (1960) p 125.

TABLE 3.7 THE SYMMETRIZED FUNCTIONS FOR Γ AT $E = 3$.

Repn. of Γ .	Function.
A_{1g}	$u_1 + u_2 + u_3 + u_4 + u_5 + u_6 + u_7 + u_8$
A_{2u}	$u_1 - u_2 - u_3 - u_4 - u_5 + u_6 + u_7 + u_8$
T_{2g}^1	$u_1 - u_2 - u_3 + u_4 + u_5 - u_6 - u_7 + u_8$
T_{2g}^2	$u_1 - u_2 + u_3 - u_4 + u_5 - u_6 + u_7 - u_8$
T_{2g}^3	$u_1 + u_2 - u_3 - u_4 + u_5 + u_6 - u_7 - u_8$
T_{1u}^1	$u_1 + u_2 + u_3 - u_4 - u_5 - u_6 - u_7 + u_8$
T_{1u}^2	$u_1 + u_2 - u_3 + u_4 - u_5 - u_6 + u_7 - u_8$
T_{1u}^3	$u_1 - u_2 + u_3 + u_4 - u_5 + u_6 - u_7 - u_8$

TABLE 3.8 SYMMETRIZED FUNCTIONS FOR Γ AT $E = 3$.

Repn. of Γ .	Function.	Jones' notation.
A_{1g}	$\cos x \cos y \cos z$	Γ_1
A_{2u}	$\sin x \sin y \sin z$	Γ_2'
T_{2g}^1	$\cos x \sin y \sin z$	
T_{2g}^2	$\sin x \cos y \sin z$	Γ_{25}'
T_{2g}^3	$\sin x \sin y \cos z$	
T_{1u}^1	$\sin x \cos y \cos z$	
T_{1u}^2	$\cos x \sin y \cos z$	Γ_{15}
T_{1u}^3	$\cos x \cos y \sin z$	

3.5 Empty Lattice Solutions of Schrödinger's Equation.

The example just considered shows in detail how the degenerate levels are assigned to the various irreducible representations of the group of $\underline{L}$, and for the rest of the special points in the Brillouin Zone we just quote the functions u_i , ϕ^i and the representations to which the ϕ^i belong, in Table 3.9.

TABLE 3.9 CLASSIFICATION OF THE SOLUTIONS OF SCHRÖDINGER'S EQUATION WITH $V(r) = 0$ FOR POINTS OF SYMMETRY.

Γ

$E = 0$: $\Psi = \text{constant}$, and belongs to $\Gamma_{A_{1g}}$.

$E = 3$: see Table 3.4 and Table 3.7.

$E = 4$:

ℓ	Ψ	
0 1 1	$\exp i2x$	u_1
1 0 1	$\exp i2y$	u_2
1 1 0	$\exp i2z$	u_3
0-1-1	$\exp -i2x$	u_4
-1 0-1	$\exp -i2y$	u_5
-1-1 0	$\exp -i2z$	u_6
Repn of Γ .	ϕ^i	
A_{1g}	$u_1 + u_2 + u_3 + u_4 + u_5 + u_6$	
E_g	$u_1 + u_2 - 2u_3 + u_4 + u_5 - 2u_6$	
E_g	$u_1 - u_2 + u_4 - u_5$	
T_{1u}	$u_1 - u_4$	
T_{1u}	$u_2 - u_5$	
T_{1u}	$u_3 - u_6$	

L.E = 1:

<u>l</u>	<u>ψ</u>	
0 0 0	$\exp -i(x+y+z)$	u_1
1 1 1	$\exp i(x+y+z)$	u_2
Repn of L.	ϕ^1	
A_{1E}	$u_1 + u_2$	
A_{2u}	$u_1 - u_2$	

E = 2:

<u>l</u>	<u>ψ</u>	
1 0 0	$\exp -i(3x-y-z)$	u_1
0 1 0	$\exp -i(-x+3y-z)$	u_2
0 0 1	$\exp -i(-x-y+3z)$	u_3
0 1 1	$\exp -i(-3x+y+z)$	u_4
1 0 1	$\exp -i(x-3y+z)$	u_5
1 1 0	$\exp -i(x+y-3z)$	u_6
Repn of L.	ϕ^1	
A_{1E}	$u_1 + u_2 + u_3 + u_4 + u_5 + u_6$	
A_{2u}	$u_1 + u_2 + u_3 - u_4 - u_5 - u_6$	
E_1	$u_1 + u_2 - 2u_3$	
E_2	$u_1 - u_2$	
E_3	$u_1 - u_2 - u_4 + u_5$	
E_{u_1}	$u_1 + u_2 - 2u_3 - u_4 - u_5 + 2u_6$	
E_{u_2}		
E_u		

E = 42:

<u>l</u>	Ψ	
-1 0 0	$\exp -\frac{1}{2}i(-x+3y+3z)$	u_1
0 -1 0	$\exp -\frac{1}{2}i(3x-y+3z)$	u_2
0 0 -1	$\exp -\frac{1}{2}i(3x+3y-z)$	u_3
2 1 1	$\exp -\frac{1}{2}i(x-3y-3z)$	u_4
1 2 1	$\exp -\frac{1}{2}i(-3x+y-3z)$	u_5
1 1 2	$\exp -\frac{1}{2}i(-3x-3y+z)$	u_6
Repn of L.	$\emptyset^1$	
$A_{1\mathcal{L}}$	$u_1+u_2+u_3+u_4+u_5+u_6$	
A_{2u}	$u_1+u_2+u_3-u_4-u_5-u_6$	
E_1	$u_1+u_2-2u_3+u_4+u_5-2u_6$	
E_2	$u_1-u_2+u_4-u_5$	
E_1	$u_1-u_2-u_4+u_5$	
E_u	$u_1+u_2-2u_3-u_4-u_5+2u_6$	
E_u^2		

X.E = 1:

<u>l</u>	Ψ	
0 0 0	$\exp -iy$	u_1
0 2 0	$\exp iy$	u_2
Repn of X.	$\emptyset^1$	
$A_{1\mathcal{L}}$	u_1+u_2	
A_{2u}	u_1-u_2	

E = 2:

<u>l</u>	<u>ψ</u>	
1 0 0	$\exp -i(x-z)$	u_1
0 0 1	$\exp -i(-x+z)$	u_2
0-1 0	$\exp -i(x+z)$	u_3
1 1 1	$\exp -i(-x-z)$	u_4
Repn of X.	$\emptyset^1$	
A_{1E}	$u_1 + u_2 + u_3 + u_4$	
B_{2E}	$u_1 + u_2 - u_3 - u_4$	
E_{u_2}	$u_3 - u_4$	
E_u	$u_1 - u_2$	

E = 5:

<u>l</u>	<u>ψ</u>	
0 1 1	$\exp i(2x-y)$	u_1
1 1 0	$\exp i(-y+2z)$	u_2
0-1-1	$\exp i(-2x-y)$	u_3
-1-1 0	$\exp i(-y-2z)$	u_4
0-1 1	$\exp i(y-2z)$	u_5
1-1 0	$\exp i(-2x+y)$	u_6
1 1 2	$\exp i(2x+y)$	u_7
2 1 1	$\exp i(y+2z)$	u_8
Repn of X.	$\emptyset^1$	
A_{1E}	$u_1 + u_2 + u_3 + u_4 + u_5 + u_6 + u_7 + u_8$	
A_{2u}	$u_1 + u_2 + u_3 + u_4 - u_5 - u_6 - u_7 - u_8$	
B_{1E}	$u_1 - u_2 + u_3 - u_4 - u_5 + u_6 + u_7 - u_8$	
B_{2u}	$u_1 - u_2 + u_3 - u_4 + u_5 - u_6 - u_7 + u_8$	
E_{E_1}	$u_1 - u_2 - u_3 + u_4 - u_5 + u_6 - u_7 + u_8$	
E_{E_2}	$u_1 + u_2 - u_3 - u_4 + u_5 + u_6 - u_7 - u_8$	
E_{E_1}	$u_1 + u_2 - u_3 - u_4 - u_5 - u_6 + u_7 + u_8$	
E_u	$u_1 - u_2 - u_3 + u_4 + u_5 - u_6 + u_7 - u_8$	

Addendum. $\mathbb{K} = \mathbb{F}_4$

$\underline{l}$	ψ
1 1 2	$\exp -5i(x+y)/4.$ u_1
norm of $K.$	$\emptyset^1$
Λ_1	u_1

$$E = 1\frac{1}{2}i$$

$\underline{l}$	ψ	
0 0 0	$\exp-i(x+iy)$	u_1
0 0 1	$\exp-i(-ix-iy+z)$	u_2
1 1 1	$\exp-i(-ix-iy-z)$	u_3
Repn of K.	ρ^1	
A_1	u_1	
A_1	u_2+u_3	
B_2	u_2-u_3	

$$E = 2\frac{1}{2}i$$

$\underline{l}$	ψ	
0 1 1	$\exp-i(-5x+3y)$	u_1
1 0 1	$\exp-i(3x-5y)$	u_2
Repn of K.	ρ^1	
A_1	u_1+u_2	
B_1	u_1-u_2	

$$E = 4\frac{1}{2}i$$

$\underline{l}$	ψ	
1 0 0	$\exp-i(7x-y-4z)$	u_1
0 1 0	$\exp-i(-x+7y-4z)$	u_2
-1 0 0	$\exp-i(-x+7y+4z)$	u_3
0 -1 0	$\exp-i(7x-y+4z)$	u_4
Repn of K.	ρ^1	
A_1	$u_1+u_2+u_3+u_4$	
A_2	$u_1-u_2+u_3-u_4$	
B_1	$u_1-u_2-u_3+u_4$	
B_2	$u_1+u_2-u_3-u_4$	

E = 5i:

<u>l</u>	<u>ψ</u>	
1 1 0	$\exp -i2z$	u_1
-1 -1 0	$\exp i2z$	u_2
Repn of K.	ϕ^i	
A_1	$u_1 + u_2$	
B_2	$u_1 - u_2$	

W.E = 1i:

<u>l</u>	<u>ψ</u>	
0 0 0	$\exp -i(\frac{1}{2}x+y)$	u_1
0 0 1	$\exp -i(-\frac{1}{2}x+z)$	u_2
1 0 1	$\exp -i(\frac{1}{2}x-y)$	u_3
1 1 1	$\exp -i(-\frac{1}{2}x-z)$	u_4
Repn of W	ϕ^i	
A_1	$u_1 + u_2 + u_3 + u_4$	
B_2	$u_1 - u_2 + u_3 - u_4$	
E^1	$u_1 + u_2 - u_3 - u_4$	
E^2	$u_1 - u_2 - u_3 + u_4$	

E = 3i:

<u>l</u>	<u>ψ</u>	
0 1 1	$\exp -\frac{1}{2}i(-3x+2y)$	u_1
0 -1 0	$\exp -\frac{1}{2}i(3x+2z)$	u_2
1 0 0	$\exp -\frac{1}{2}i(3x-2z)$	u_3
1 1 2	$\exp -\frac{1}{2}i(-3x-2y)$	u_4
Repn of W.	ϕ^i	
A_1	$u_1 + u_2 + u_3 + u_4$	
B_2	$u_1 - u_2 - u_3 + u_4$	
E^1	$u_1 + u_2 - u_3 - u_4$	
E^2	$u_1 - u_2 + u_3 - u_4$	

$\mathbb{H} = 5\mathbb{A}:$

$\underline{l}$	Ψ	
0 1 0	$\exp(-i(-\frac{1}{2}x+2y-z))$	u_1
-1 0 0	$\exp(-i(-\frac{1}{2}x+2y+z))$	u_2
1 1 0	$\exp(-i(\frac{1}{2}x+y-2z))$	u_3
-1 -1 0	$\exp(-i(\frac{1}{2}x+y+2z))$	u_4
0 -1 1	$\exp(-i(\frac{1}{2}x-y-2z))$	u_5
0 1 -1	$\exp(-i(\frac{1}{2}x-y+2z))$	u_6
2 1 2	$\exp(-i(-\frac{1}{2}x-2y-z))$	u_7
1 0 2	$\exp(-i(-\frac{1}{2}x-2y+z))$	u_8
Repn of W .	ϕ^1	
A_1	$u_1+u_2+u_3+u_4+u_5+u_6+u_7+u_8$	
A_2	$u_1-u_2-u_3+u_4+u_5-u_6-u_7+u_8$	
B_1	$u_1-u_2+u_3-u_4-u_5+u_6-u_7+u_8$	
B_2	$u_1+u_2-u_3-u_4-u_5-u_6+u_7+u_8$	
E^1_1	$u_1-u_3+u_6-u_8$	
E^2_1	$u_1+u_3-u_6-u_8$	
E^1_2	$u_2+u_4-u_5-u_7$	
E^2_2	$u_2-u_4+u_5-u_7$	

U. $\mathbb{H} = 1\mathbb{A}:$

$\underline{l}$	Ψ	
0 0 0	$\exp(-i(\frac{1}{2}x+y+\frac{1}{2}z))$	u_1
1 0 1	$\exp(-i(\frac{1}{2}x-y+\frac{1}{2}z))$	u_2
1 1 1	$\exp(-i(-\frac{1}{2}x-\frac{1}{2}z))$	u_3
Repn of U .	ϕ^1	
A_1	u_1+u_2	
B_1	u_1-u_2	
A_1	u_3	

B = 2:

<u>l</u>	<u>ψ</u>	
1 0 0	$\exp - i(5x - 3z)$	u_1
0 0 1	$\exp - i(-3x + 5z)$	u_2
Repn of U.	ϕ^i	
A_1	$u_1 + u_2$	
B_2	$u_1 - u_2$	

B = 3:

<u>l</u>	<u>ψ</u>	
0 -1 0	$\exp - i(5x + 5z)$	u_1
Repn of U.	ϕ^i	
A_1	u_1	

B = 4:

<u>l</u>	<u>ψ</u>	
0 1 1	$\exp - i(-7z + 4y + z)$	u_1
1 1 0	$\exp - i(x + 4y - 7z)$	u_2
1 1 2	$\exp - i(-7x - 4y + z)$	u_3
2 1 1	$\exp - i(x - 4y - 7z)$	u_4
Repn of U.	ϕ^j	
A_1	$u_1 + u_2 + u_3 + u_4$	
A_2	$u_1 - u_2 - u_3 + u_4$	
B_1	$u_1 + u_2 - u_3 - u_4$	
B_2	$u_1 - u_2 + u_3 - u_4$	

$E = 5\hbar$

$\underline{q}$	ψ	
2 1 2	$\exp - i(-3x-8y-3z)$	u_1
0 1 0	$\exp - i(-3x+8y-3z)$	u_2
Repr of U.	ϕ^1	
A_1	u_1+u_2	
B_1	u_1-u_2	

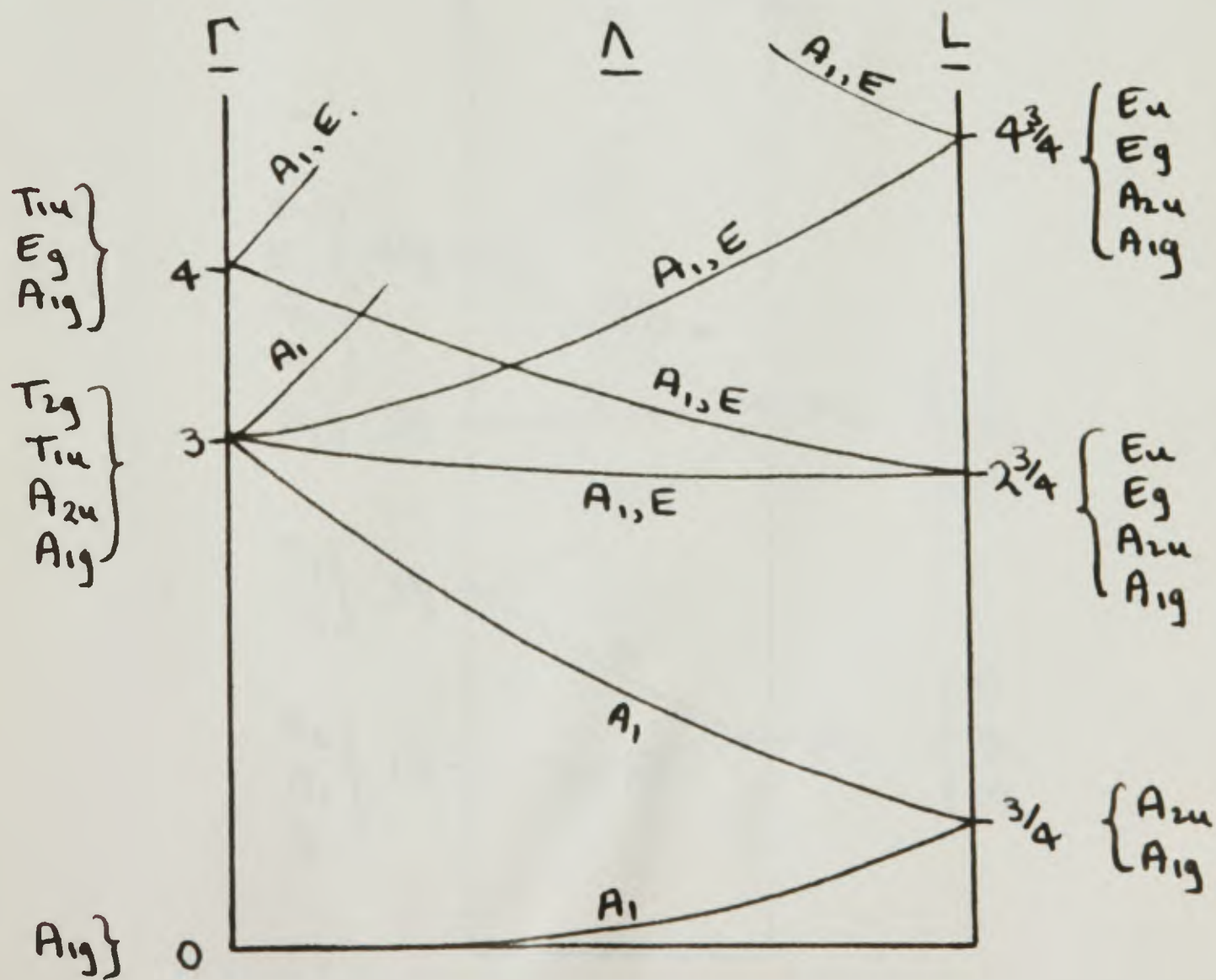
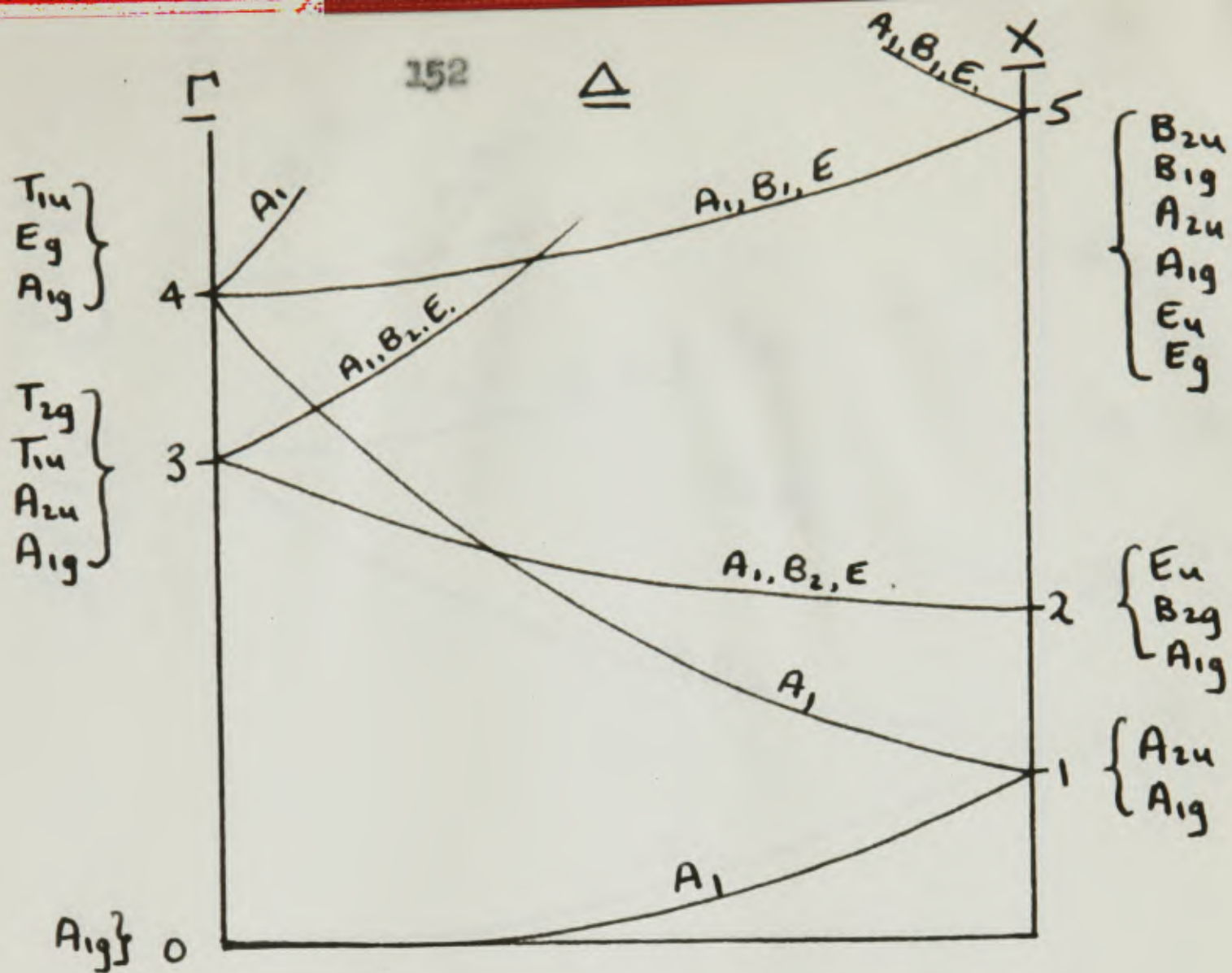
3.6 Diagrams of Empty Lattice Bands.

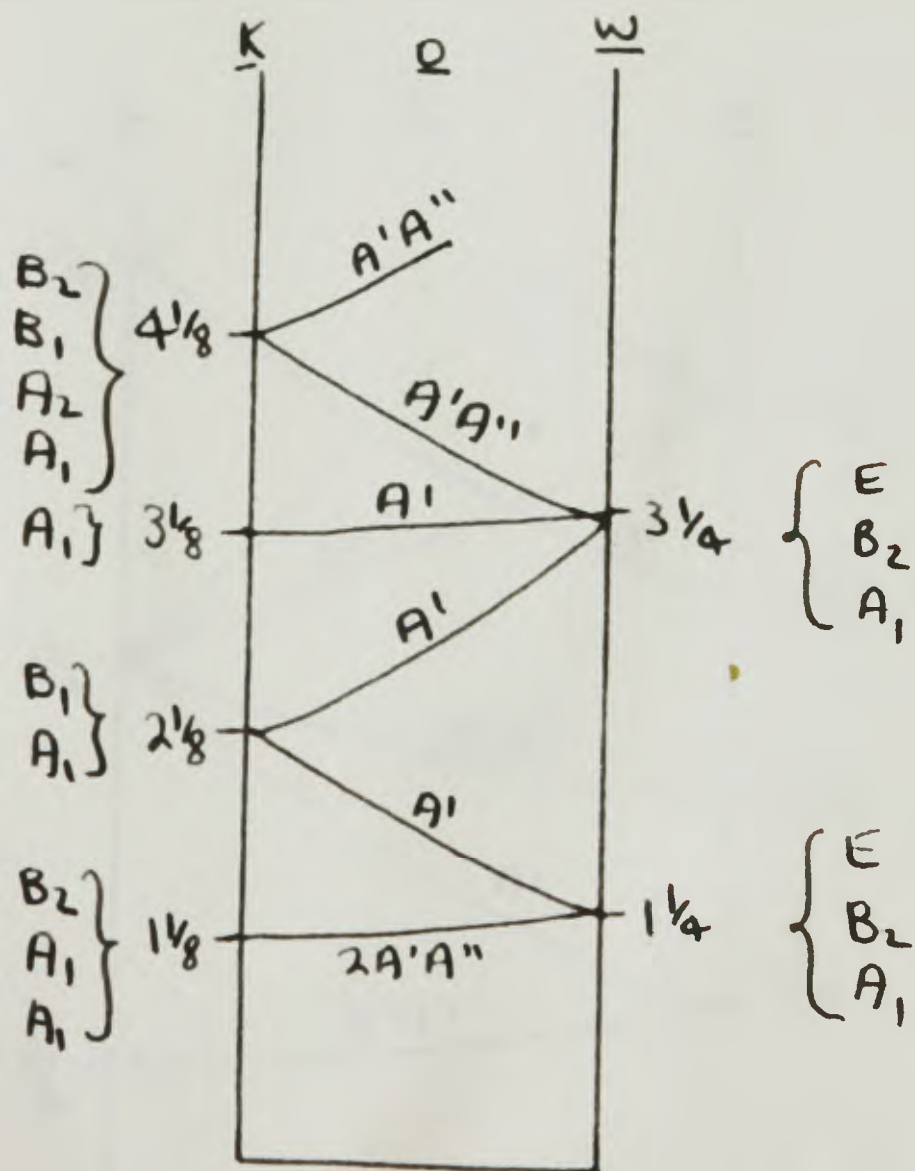
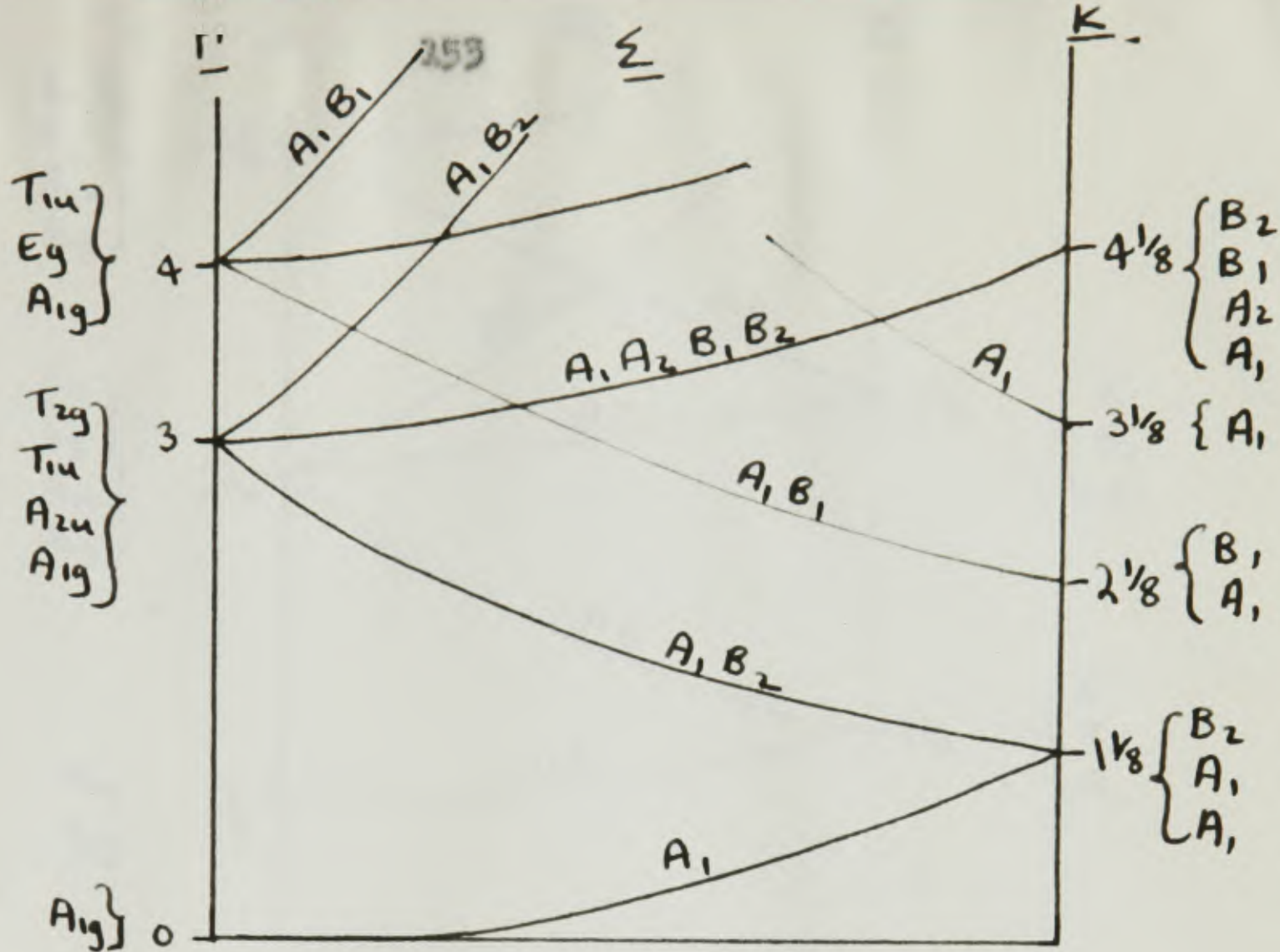
Sketches of all these levels along the lines joining these special points are given in the graphs in Figure 3.1. They are drawn to scale using the lengths (in units of $2\pi/a$):

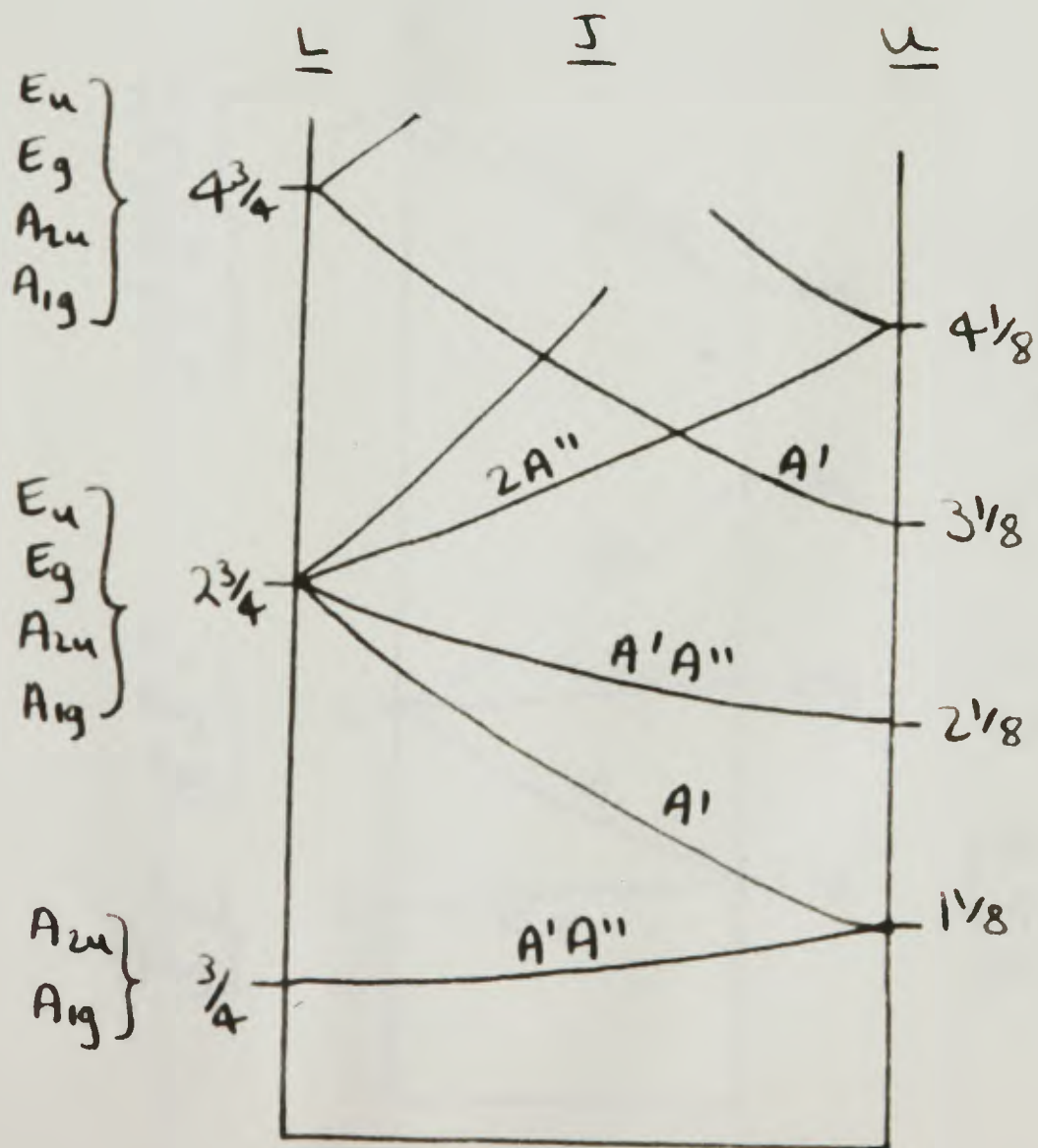
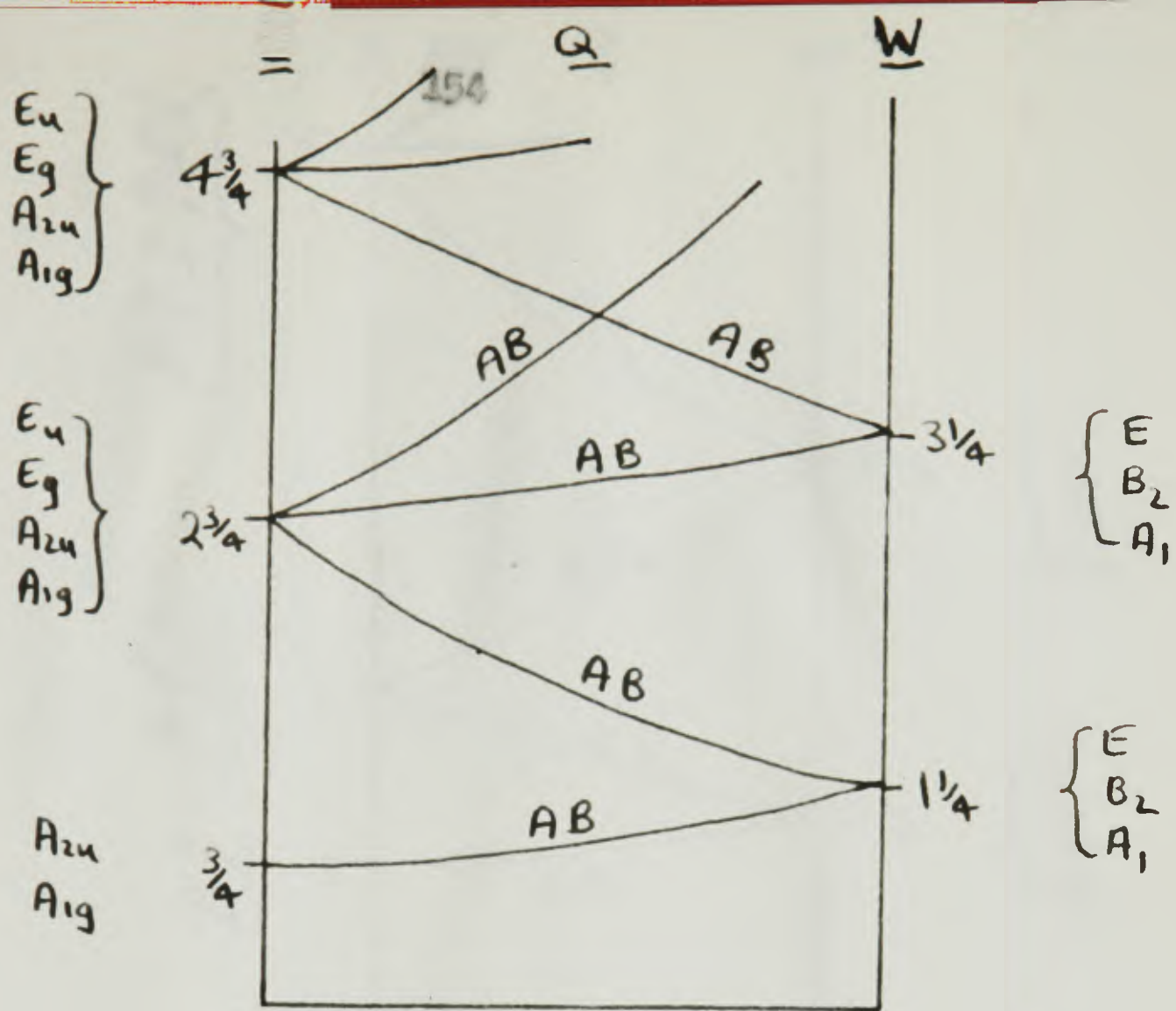
$$\begin{array}{llll}
 \Gamma X = 1 & = 1.000 & \Gamma L = \frac{1}{2}(3)^{\frac{1}{2}} & = 0.866 \\
 \Gamma K = \frac{1}{2}(2)^{\frac{1}{2}} & = 1.061 & W X = \frac{1}{2} & = 0.500 \\
 X U = \frac{1}{2}(2)^{\frac{1}{2}} & = 0.354 & L K = \frac{1}{2}(6)^{\frac{1}{2}} & = 0.612 \\
 L U = \frac{1}{2}(6)^{\frac{1}{2}} & = 0.612 & L W = \frac{1}{2}(2)^{\frac{1}{2}} & = 0.707 \\
 K W = \frac{1}{2}(2)^{\frac{1}{2}} & = 0.354. & &
 \end{array}$$

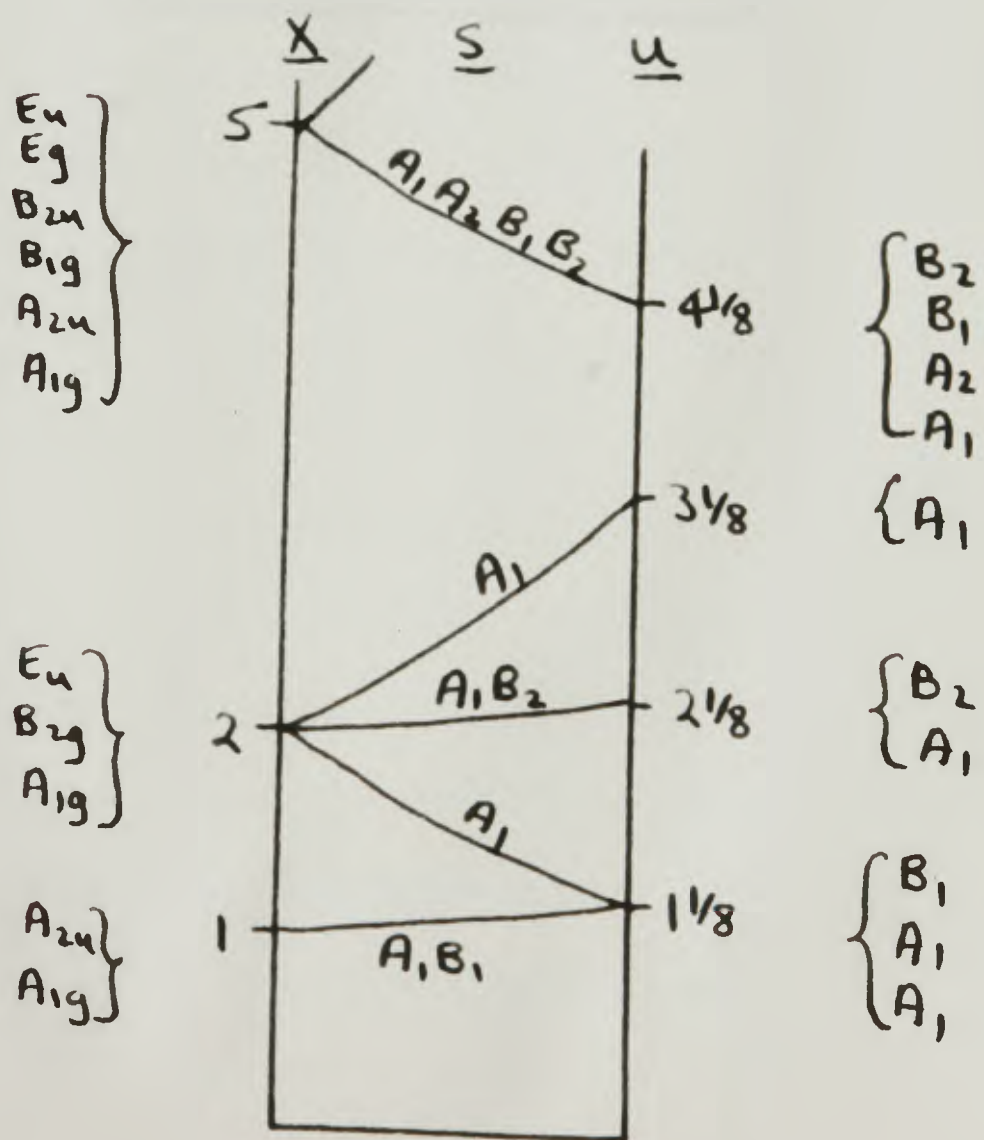
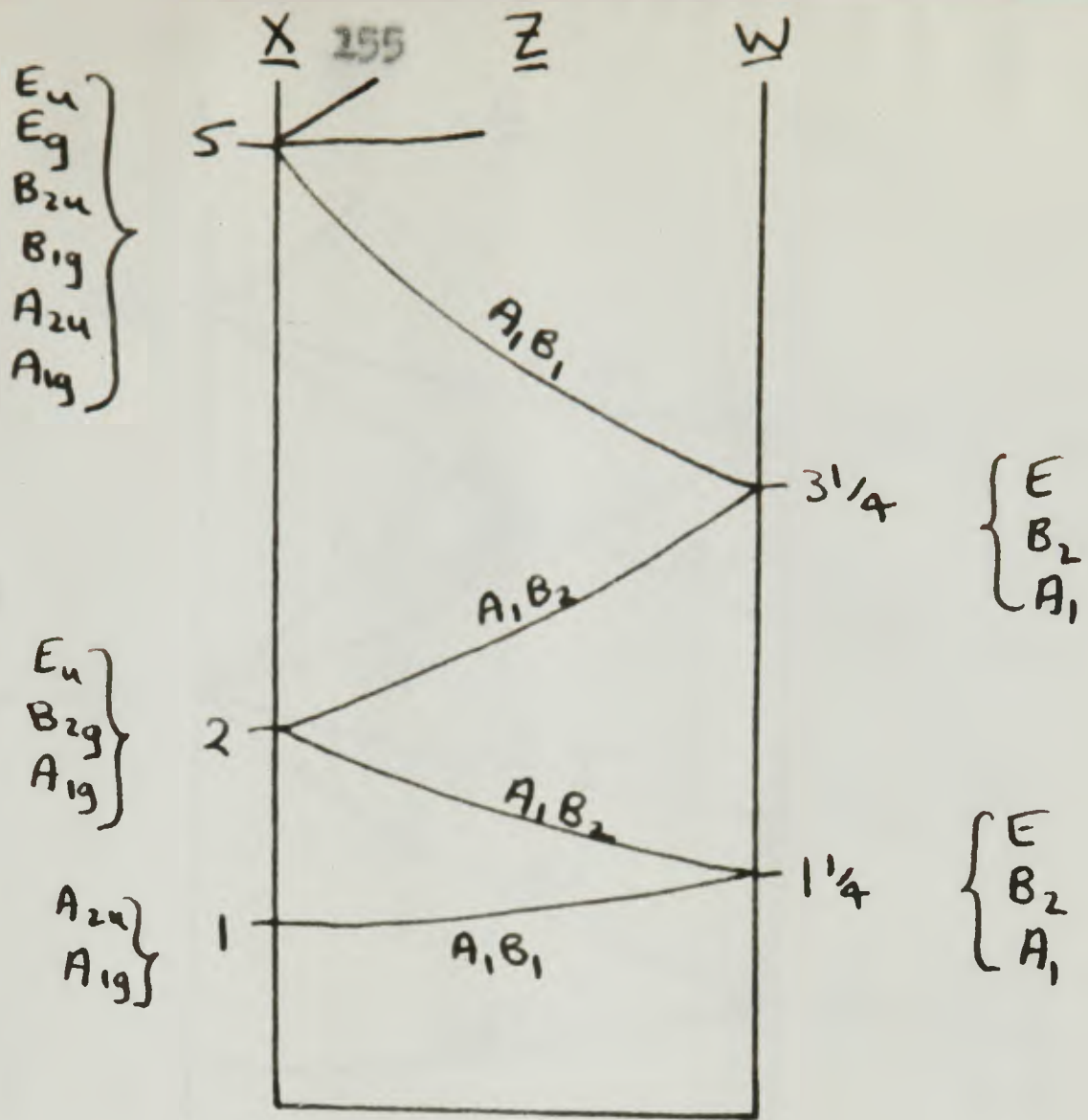
The labelling of the representations along the lines is done by considering the compatibilities of the functions along the lines with those at the points at their ends. The full treatment of the compatibilities is left until the next section.

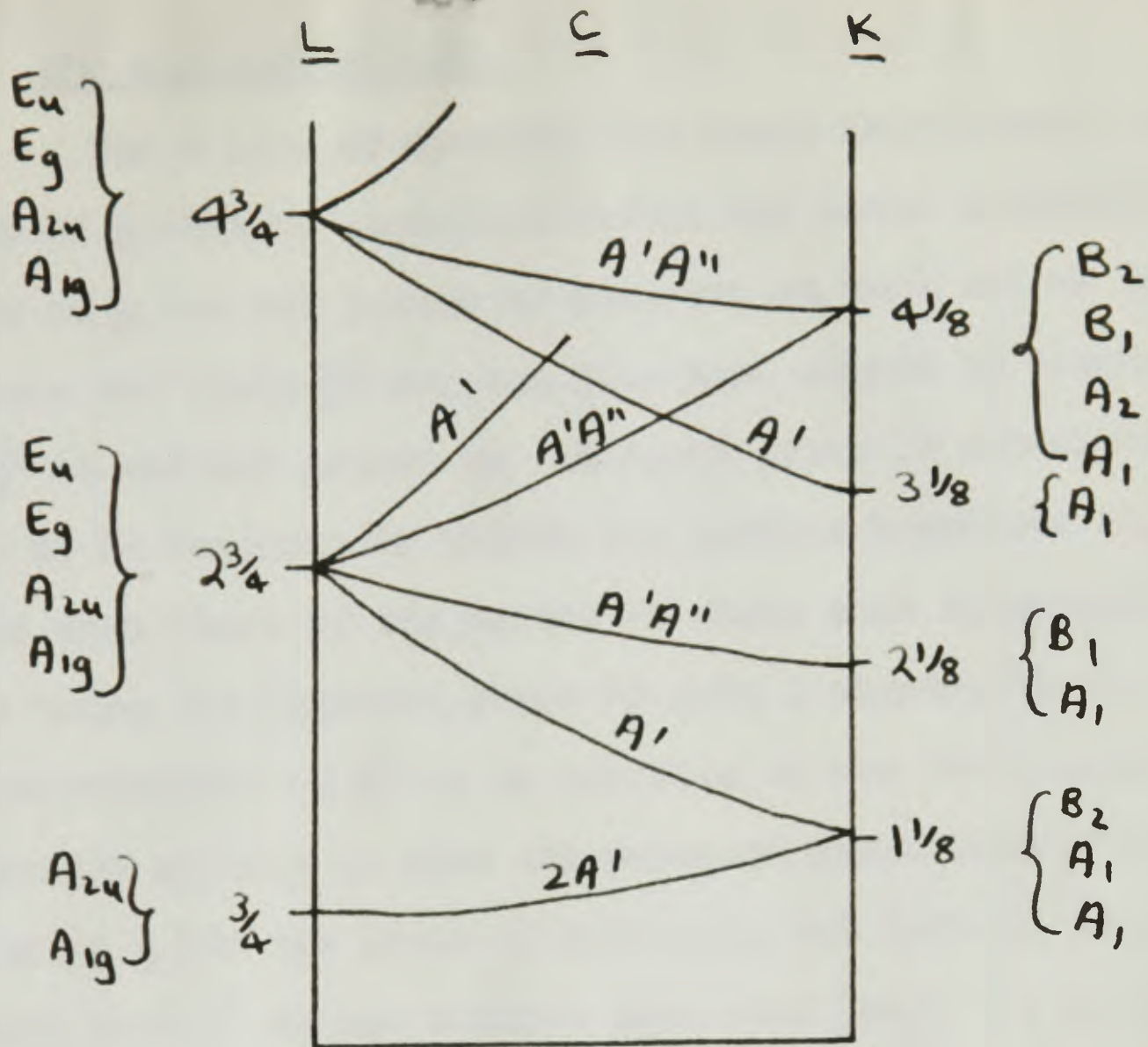
FIGURE 3.1 THE ENERGY BANDS FOR THE EMPTY LATTICE.

Δ 





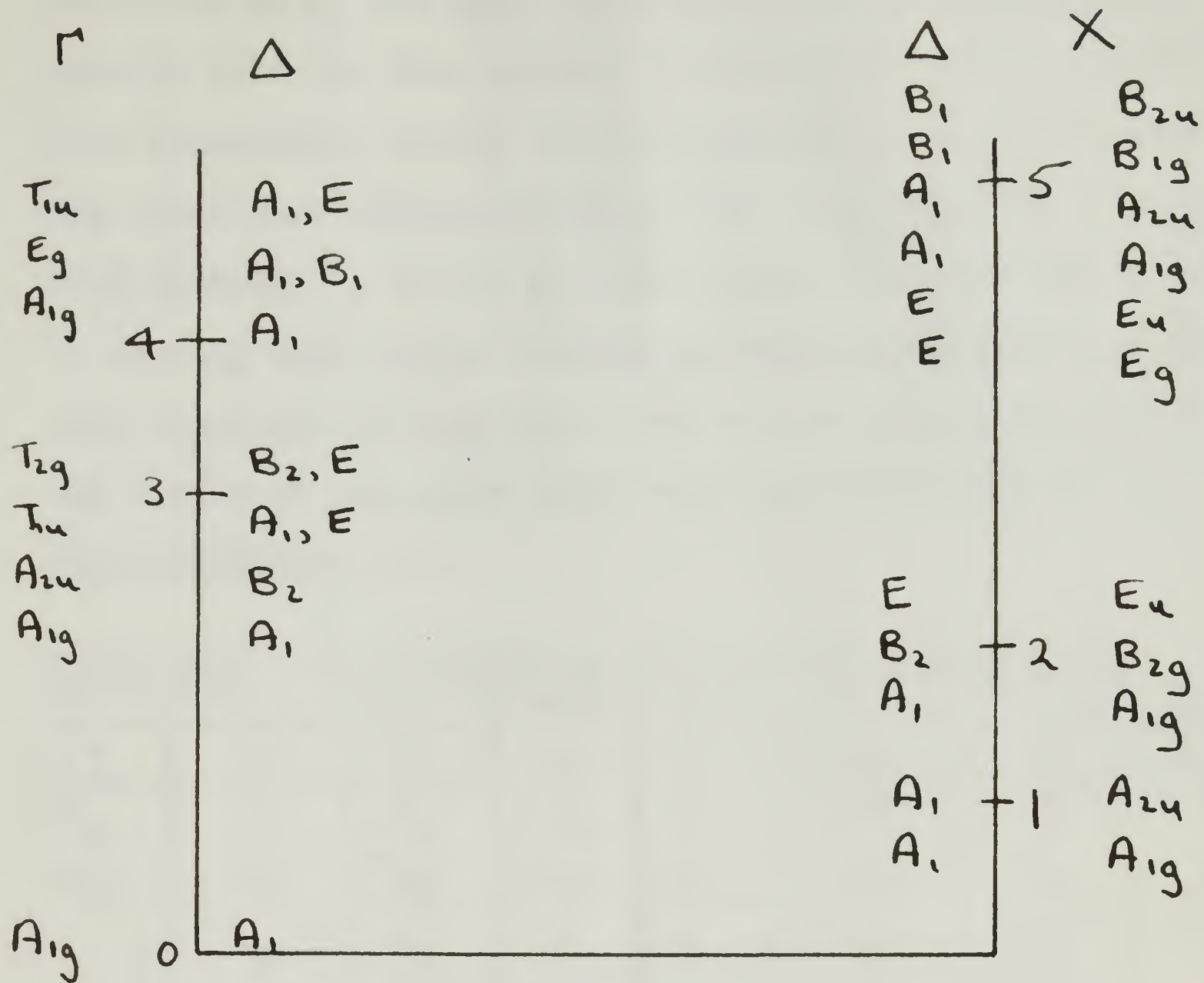




3.7 The Compatibilities.

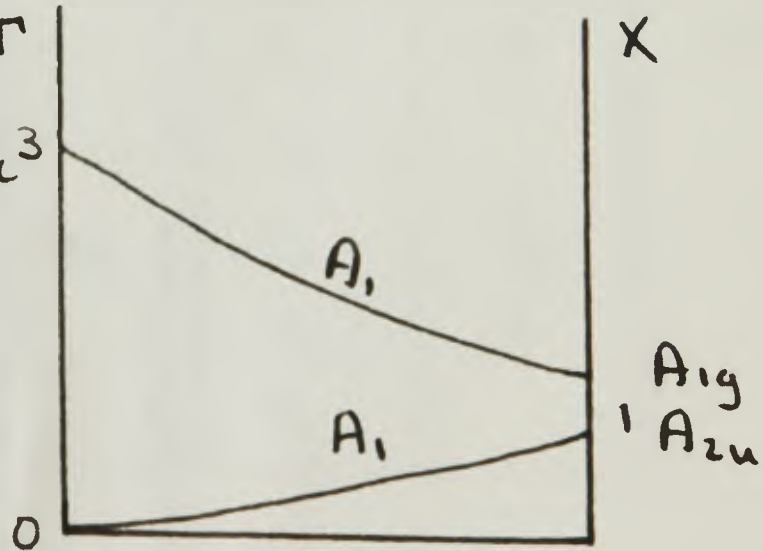
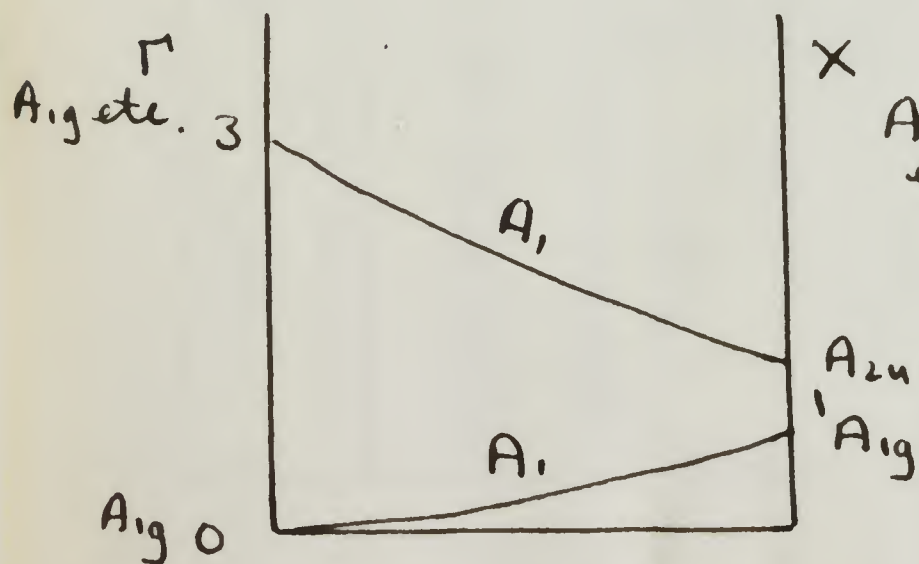
For a line of symmetry the basis functions of the group of $\underline{k}$ must be contained within the basis functions of the group of $\underline{k}$ for the points of symmetry at each end of the line, because the group $\underline{G}^{\underline{k}}$ for the line must always be a subgroup of $\underline{G}^{\underline{k}}$ at the end points as the space group is symmorphic. Thus it is possible to obtain the lattice harmonics for the lines from those of the points at their ends by subduction. Thus using the matrices given in part 1 chapter II for the representations of $\underline{G}^{\underline{k}}$ it is possible to use the process described in S2.3 to find the subduced representations of the group of $\underline{k}$ for the lines of symmetry, but instead of subducing always from Γ we now subduce from each point Γ, K, L, X, W, U , onto those lines passing through that point. The details of the subduction process to obtain the compatibilities is omitted and the results alone are listed below in Table 3.10. Subduction onto planes of symmetry is only included for cases where that plane has actually been used in Figure 3.1.

In sorting out the bands which are shown in Figure 3.1 one has to find, from Table 3.3 how many levels at e.g. Γ , $E=3$ are connected with each of the levels at e.g. X . This is done by taking for each $\underline{n}$ -vector leading to $E=3$ at Γ the energy value which is given by that $\underline{n}$ -vector at X ; in this example four of the levels are connected to X at $E=2$ and four at $E=6$. By writing down the representations of Δ compatible with those at Γ , $E=3$ as in Figure 3.2 one sees that there

FIGURE 3.2 THE COMPATIBILITIES FOR Γ - Δ -X.

(a)

(b)



must be $2\Delta A_1, 2\Delta B_2, 2\Delta E$ representations coming into Γ , $E=3$. Similarly at X , $E=2$ there must be representations $\Delta A_1, \Delta B_2, \Delta E$, so that the band joining Γ , $E=3$ to X , $E=2$ has four-fold degeneracy, having the representations $\Delta A_1, \Delta B_2, \Delta E$; the other four representations, also $\Delta A_1, \Delta B_2, \Delta E$, are in a band joining Γ , $E=3$ to X , $E=6$. Figure 3.1 has been built up in exactly this way by finding how many representations of each line there are joining each level at one point with each of the levels at the other point and then satisfying the compatibilities too.

TABLE 3.10 COMPATIBILITIES FOR BANDS IN F.C.C. METAL.
 $\Gamma \rightarrow \Sigma, \Delta, \Lambda$

Γ	Σ	Δ	Λ	Γ	Σ	Δ	Λ
A_{1g}	A_1	A_1	A_1	A_{1u}	A_2	A_2	A_2
A_{2g}	B_1	B_1	A_2	A_{2u}	B_2	B_2	A_1
E_g {	A_1	A_1	E	E_u {	A_2	A_2	E
	B_1	B_1			B_2	B_2	
T_{2g} {	B_2	B_2	A_1	T_{2u} {	B_1	B_1	A_2
	A_1	E	E		A_2	E	E
	A_2				A_1		
T_{1g} {	A_2	A_2	A_2	T_{1u} {	A_1	A_1	A_1
	B_1	E	E		B_2	E	E
	B_2				B_1		

$$X^{60} \rightarrow \Delta, Z, S.$$

X	Δ	Z	S	X	Δ	Z	S
A_{1g}	A_1	A_1	A_1	A_{1u}	A_2	A_2	A_2
A_{2g}	A_2	B_2	B_2	A_{2u}	A_1	B_1	B_1
B_{1g}	B_1	A_1	B_2	B_{1u}	B_2	A_2	B_1
B_{2g}	B_2	B_2	A_1	B_{2u}	B_1	B_1	A_2
E_g }	E	A_2	A_2	E_u }	E	A_1	A_1
		B_1	B_1			B_2	B_2

$$L \rightarrow \Lambda, Q, C, J.$$

L	Λ	Q	C	J
A_{1g}	A_1	A	A'	A'
A_{2g}	A_2	B	A''	A''
A_{1u}	A_2	A	A''	A'
A_{2u}	A_1	B	A'	A''
E_g }	E	A	A'	A'
		B	A''	A''
E_u }	E	A	A'	A'
		B	A''	A''

$$u \rightarrow S, J.$$

u	S	J
A_1	A_1	A'
A_2	A_2	A''
B_1	B_1	A'
B_2	B_2	A''

$$W \rightarrow Z, O, B, Q.$$

W	Z	O	B	Q
A_1	A_1	A'	A'	A
A_2	A_2	A''	A''	B
B_1	A_2	A''	A''	A
B_2	A_1	A'	A'	B
E }	B_1	A'	A'	A
	B_2	A''	A''	B

$$K \rightarrow \Sigma, O, C^{101}$$

K	Σ	O	C
A ₁	A ₁	A'	A'
A ₂	A ₂	A''	A''
B ₁	B ₁	A'	A''
B ₂	B ₂	A''	A'

3.8 Empty Lattice Results.

The programme was tested for all the lower levels at the six points of symmetry in the Brillouin Zone. The results are listed in Table 3.11. Both absolute and percentage errors are listed. The results and their accuracy are discussed later.

TABLE 3.11 EMPTY LATTICE TESTS, RESULTS.

Point of BZ.	Repn.	Energy. (theory)	Energy. (calc)	Error.	% error.
Γ	A _{1g}	0.0	+10 ⁻⁶	+10 ⁻⁶	-
		3.0	3.002	0.002	+0.07
		4.0	3.956	0.044	-1.1
	A _{2u}	3.0	2.994	0.006	-0.2
	E _{1g}	4.0	4.052	0.052	+1.3
	E _{2g}	4.0	4.041	0.041	+1.0
	E _{1u}	3.0	2.987	0.013	-0.4
	T _{2g} ¹	3.0	2.994	0.006	-0.2
	T _{2g} ²	3.0	2.996	0.004	-0.1
	T _{2g} ³	3.0	3.036	0.036	+1.2
	T _{1u} ¹	3.0	3.009	0.009	+0.4
	T _{1u} ²	3.0	3.046	0.046	+1.5
	T _{1u} ³				

Point of BZ.	Repn.	Energy. (theory)	Energy. (calc)	Error.	% error.
L	A_{1g}	0.75	0.7499	0.0001	-0.01
		2.75	2.7497	0.0003	-0.01
		4.75	4.6803	0.0697	-1.4
	A_{2u}	0.75	0.7503	0.0003	+0.05
		2.75	2.7346	0.0154	-0.54
		4.75	4.6818	0.0687	-1.5
	E_1^1	2.75	2.689	0.061	-2.2
	E_{u2}^1	2.75	2.759	0.009	+0.3
	E_u^1	2.75	2.770	0.020	+0.7
K	A_1	1.125	1.127	0.002	+0.16
	A_2	4.125	4.011	0.114	-2.8
	B_1	2.125	2.044	0.081	-3.9
	B_2	1.125	1.122	0.003	-0.25
W	A_1	1.25	1.251	0.001	+0.1
		3.25	3.209	0.041	-1.3
		5.25	5.202	0.048	-0.9
	A_2	5.25	5.017	0.233	-4.5
	B_1	5.25	5.237	0.013	-0.2
	B_2	1.25	1.254	0.004	+0.32
		3.25	3.213	0.037	-1.1
		5.25	5.269	0.019	+1.8
	E^1	1.25	1.252	0.002	+0.2
		3.25	3.102	0.148	-5.0
		5.25	5.269	0.019	+1.8
	E^2	1.25	1.244	0.006	-0.5
		3.25	3.093	0.157	-5.0
		5.25	5.177	0.073	-1.5

Point of BZ	Repn.	Energy. (theory)	Energy. (calc)	Error.	% error.
X	A_{1g}	1.0	1.0001	0.0001	+0.01
		2.0	2.0014	0.0014	+0.07
		5.0	4.9617	0.0383	-0.76
	B_{2g}	2.0	2.0008	0.0008	+0.04
	B_{1g}	5.0	5.0550	0.0550	+1.1
	A_{2u}	1.0	0.999986	0.000014	-10 ⁻³
		5.0	4.9452	0.0548	-1.1
	B_{2u}	5.0	5.0036	0.0036	+0.06
	E_1	5.0	4.8440	0.1560	-4.0
	E_2	5.0	4.8490	0.1510	-3.2
	E_u	2.0	2.0059	0.0059	+0.29
		5.0	4.720	0.28	-5.6
	T_u^2	2.0	2.0064	0.0064	+0.3
		5.0	4.74	0.26	-5.0
U	A_1	1.125	1.138	0.013	+1.1
	A_2	4.125	4.019	0.006	-0.2
	B_1	1.125	1.127	0.002	+0.17
		4.125	3.804	0.321	-8
	B_2	2.125	2.076	0.049	-2.5

For some higher levels not listed here there is an inflexion but not a minimum.

Energies are listed in rydbergs throughout.

A discussion of these results appears later.

CHAPTER IV. CALCULATIONS ON REAL METALS.

4.1 Accuracy of Calculations.

There are two sources of errors in this cellular programme; firstly there are the accumulation of arithmetical errors and errors due to the use of an insufficient number of terms in the expansion of ψ , and secondly there are the uncertainties introduced by the fact that the potential field in a metal is being approximated to by the potential field due to a free ion of the metallic element in question. Programming blunders need not be considered since they are assumed to have been removed because the empty lattice tests work. The two sources of error are considered separately in the next few sections.

4.2 Errors in Empty Lattice Results.

If one considers the results given in Chapter III, Table 3.11 the discrepancies between the theoretical energies and the energies calculated by the programme can be said to be due to all sources of error other than a faulty choice of the potential field and the fact that the actual potential field in the metal is not spherically symmetrical; that is to items (i), (ii), (iv), and (v) below, item (iii) is not relevant to the empty lattice because the potential is then trivially spherical symmetrical. The sources of error are the following:

- (i) Numerical errors in computing functions such as $F_1^n(\cos\theta)$ and the radial functions $G_1(E, \rho)$.
- (ii) The fact that the expansion of ψ is cut off at some arbitrary l -value.
- (iii) The fact that the potential is not spherically symmetrical (in real metals) around the outer regions of the cell.
- (iv) The functions are only fitted at a small and certainly finite number of points on the surface of the Wigner-Seitz cell, this is $96 \times p$, where p = the number of elements in the group of k with diagonal matrix representatives, and with the matrix representative, or for degenerate representations the appropriate element of the matrix representative, equal to $+1$ rather than -1 .
- (v) A faulty location of the minimum of the residual curve, caused for instance by two minima close together coalescing to give one spurious minimum.

Since the results of the empty lattice tests are, on the whole, very good and they shew that except for (iii) which does not occur in the empty lattice and (v) which is either zero or very large ($\sim 50\%$) the errors are small. One case of a spurious minimum, the second level UB_1 , is included in Table 3.11 to demonstrate the effect of errors of type (v). The empty lattice test errors are analysed in Table 4.1.

TABLE 4.1 ANALYSIS OF EMPTY LATTICE RESULTS.

Range of errors (ry)			No. of levels.
0	-	0.005	17
0.005	-	0.01	8
0.01	-	0.05	15
0.05	-	0.1	9
0.1	-	∞	8

It will be noticed from Table 3.11 that the large errors (both absolute and as % errors) are always associated with large energies; this is due to errors of type (i) for when E is large the radial functions become much less accurate than before. In real metals it is never necessary to go to energies as high as 5 ry since the Fermi energy is usually at about 0.5 ry. The empty lattice tests cover errors of types (i), (ii) and (iv). Errors of type (iii) are considered in the next section.

4.3 The Convergence of the Expansions, and the non-spherical potential.

Many attacks on the cellular method have been based on arguments that the answers are sensitive to the choice of points on the cell over which the wave functions are made to satisfy the boundary conditions and that the expansions used may either not converge sufficiently rapidly in practice or not converge

at all due to the non-spherical potential. Bradley (1962) shewed quite conclusively by comparing two fittings, one using only points on the edges of the cell and the other using points very near the centres of the faces of the cell, that the answers obtained were completely independent of the points used to fit the boundary conditions. No more of this need be said here.

The second criticism, namely that the expansions are slow to converge and may even, some authors suggest, be asymptotic expansions is more difficult to refute. Indeed Saffren (1959) was able to shew that the non-sphericity of the potential in a metal does invalidate the expansions, though he did not demonstrate the extent of this. The only thing which can really be said is that in every case of the large number of cellular calculations we have performed, either the wave function has converged (usually for representations where the cut-off l -values of 6 or 7 are possible), or that (for representations with large numbers of terms when cut-offs have had to be made at $l = 3$ or 4) on increasing the number of l -values considered the convergence has improved. Never have any signs been seen of the onset of a divergence in the expansion even for d -type bands, though it is essential always to include all the spherical harmonics of the largest l -value chosen. As a loose estimate it seems to be the case that if it is possible to do a cellular calculation for l -values up to $l = 6$ then the wave function expansion converges

well and the answer is quite reliable. The limiting factor in the cases for $\underline{k}$ -vectors of low symmetry, and for general points in the Brillouin Zone is the lack of storage space in the "Mercury" computer used and the time required for each calculation as the expansions become larger. Energies found using expansions which are cut off before $l = 6$ are to be viewed with suspicion.

For practical purposes in computation it may be asserted therefore that the wave function expansions used in the cellular method are sufficiently rapidly convergent to enable good band structures to be calculated, and since any alleged non convergence of the expansions was shown to be due to the non-spherical nature of the potential it follows that the errors due to source (iii) must be small.

This concludes our review of the sources of error listed as (i) - (iv) in S4.2. The last of those sources of error, number (v), will now be considered.

4.4 The General Point in the Brillouin Zone.

With a point of symmetry the expansion of ψ only needs a few terms before quite high l -values are reached but as one moves to the consideration of planes of symmetry the group of $\underline{k}$ becomes reduced to only about two elements and the expansions include many more terms. For a general point all the spherical harmonics must be used so that with the storage space available in the computer it is only possible to go up

to $l = 2$. It was found to be possible to run the programme for a general point so long as there are no other minima in the residual curve near the one in question.

As an example it was attempted to compute empty lattice energies for the point $\underline{k} = 2\pi/a(0.1, 0.2, 0.3)$ which is near Γ and might be expected to be fairly favourable, the special value of $a = 2\pi$, for convenience, is used. The empty lattice energies are $|\underline{k} + \underline{K}|^2$ where $\underline{K}$ = any reciprocal lattice vector. The first few energies are shown in Figure 4.1. When it is remembered that the actual number of levels below the energy of 5 ry for any given representation of a point of symmetry is usually only one, and never more than four (for UA_1) it is clear that the residual curve for a general point A will be much more complicated than for some representation of one of the points. This problem of the close approach of two minima and the possibility of the two minima coalescing to form one spurious minimum was mentioned in chapter II.

For the first level at $\underline{k} = (0.1, 0.2, 0.3)$ the programme gave the result $E = 0.140019\text{ry}$, the correct answer being 0.14ry , which represents an error of 0.000019ry or 0.015% . By most standards this is quite satisfactory, but to try to identify the higher levels is fairly difficult as Figure 4.2 shows. From this Figure 4.2 it is clear that a certain amount of luck is involved in finding the higher levels; thus 2.34 is fairly obvious from the curve while 2.14 is not

FIGURE 4.1: THE FIRST 15 EMPTY LATTICE LEVELS AT

$$k = (0.1, 0.2, 0.3).$$

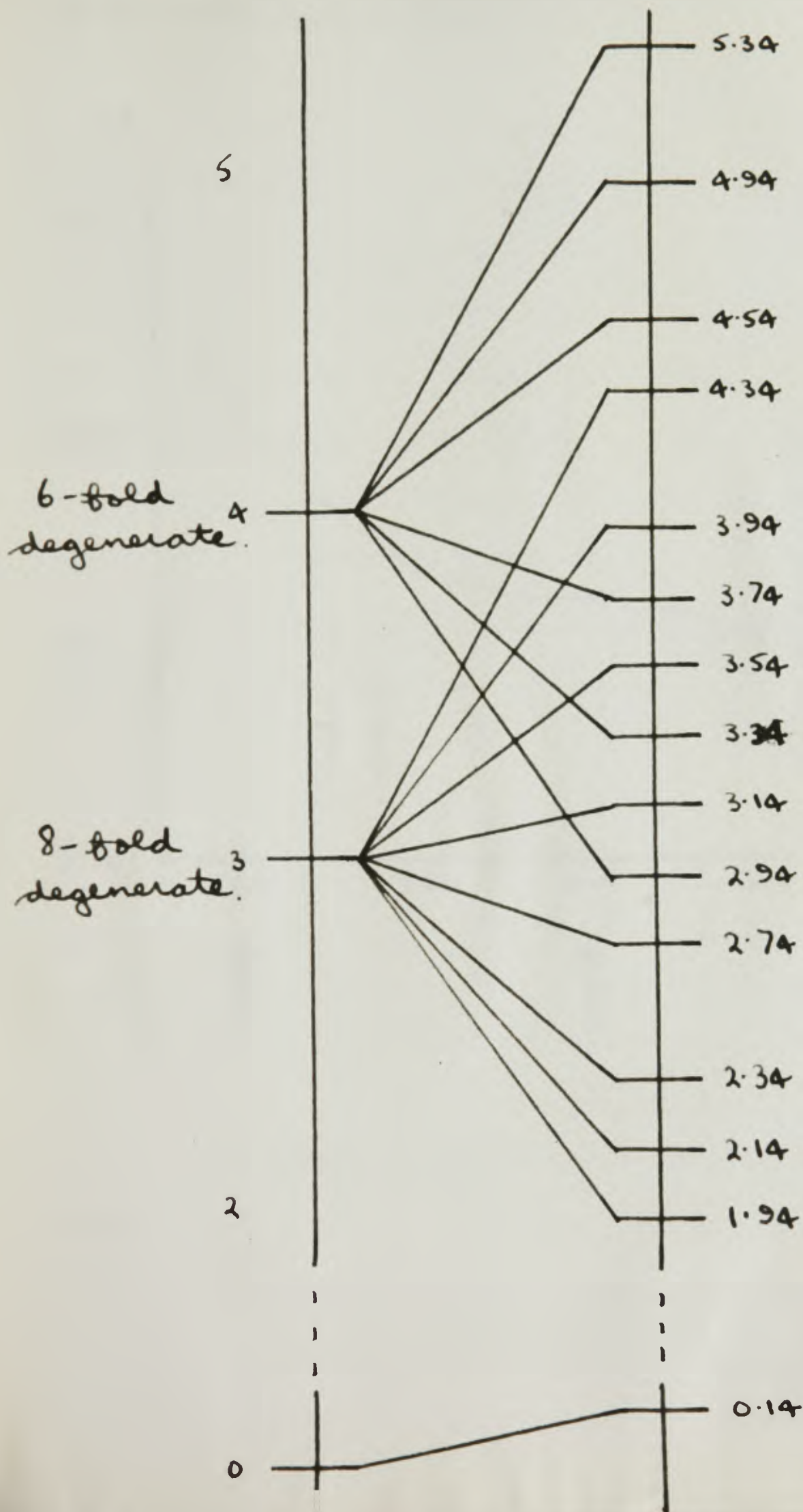
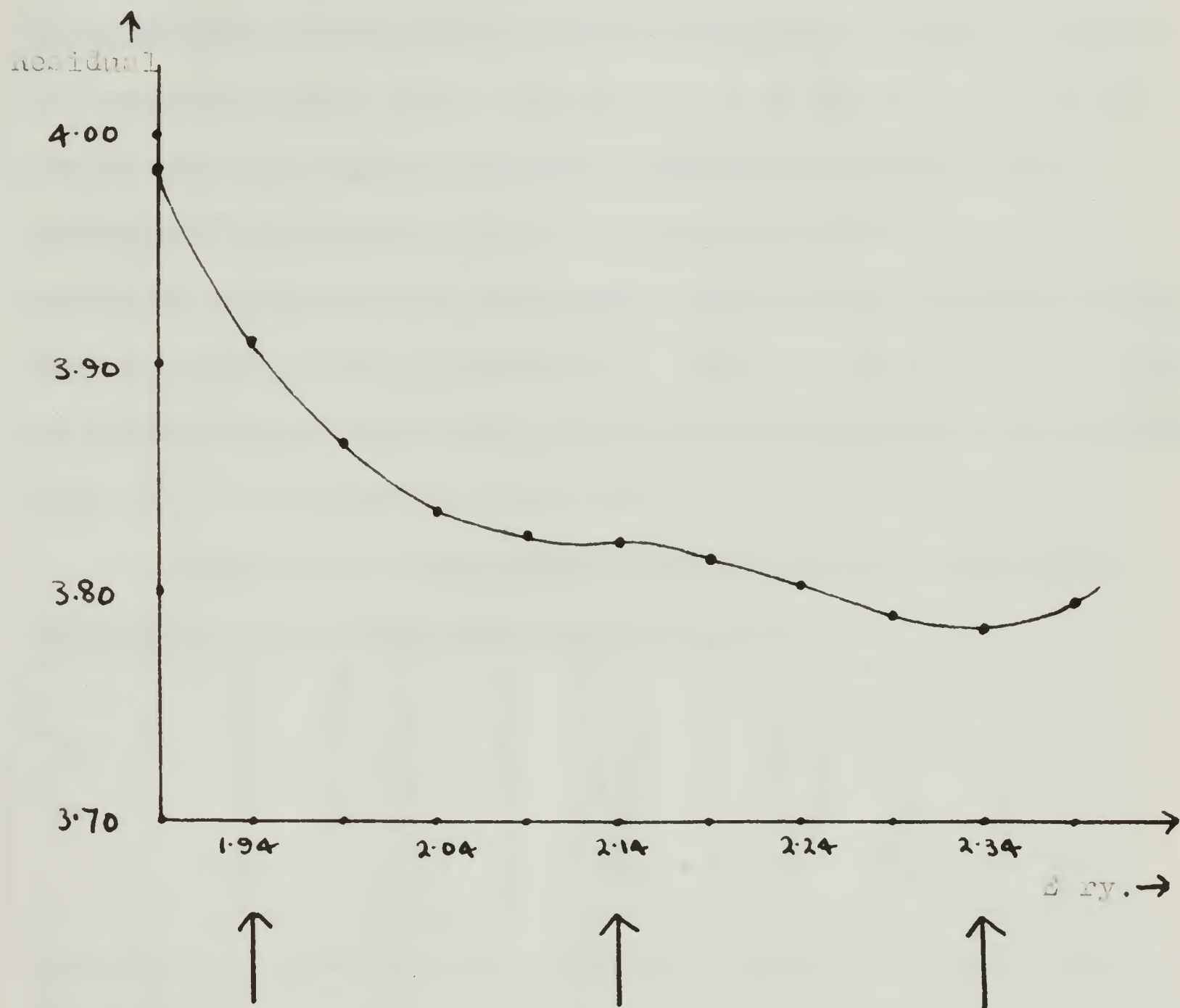


FIGURE 4.2: CURVE OF RESIDUAL AND ENERGY FOR
THREE LEVELS AT $k = (0.1, 0.2, 0.5)$.



The arrows indicate the theoretical positions of the minima.

entirely obvious and 1.94 has just vanished.

Thus it is clear that in some cases at least the source of error listed as (v) in S4.2 can lead either to serious errors or to the complete disappearance of a level. However this is only serious when there are several minima of the residual curve close together. Because some of the 15 levels for $k = (0.1, 0.2, 0.3)$ become degenerate and then distribute themselves among various representations at the points of symmetry this difficulty will only be important when the group of k has low symmetry. Thus the levels at Γ present no difficulty of this sort, they divide among the representations of Γ as listed in Table 4.2.

TABLE 4.2 THE DISTRIBUTION OF THE 15 LEVELS JUST CONSIDERED AMONG THE REPRESENTATIONS OF Γ .

A_{1g}	3	E_g^1	1	T_{2g}^1	1	T_{1u}^1	2
A_{2u}	1	E_g^2	1	T_{2g}^2	1	T_{1u}^2	2
				T_{2g}^3	1	T_{1u}^3	2

Even for A_{1g} which has three levels the minima appear quite distinctly. For most representations of most of the other points of symmetry this difficulty was not encountered, though for KA_1 and UA_1 which each have four minima for E below 5ry both did have minima which vanished or coalesced with the next one to give a completely spurious answer. Thus for KA_1 with theoretical empty lattice energies at $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$, $4\frac{1}{2}$, the actual answers were 1.128ry (error of 0.27%) and one completely

spurious level which was found in between the $3\frac{1}{2}$ and $4\frac{1}{2}$ levels (at 3.775ry) instead of the other three levels.

This effect can therefore be very serious, but, provided one has an independent way of detecting that it is present, it is so large as to be considered not as an error but as a blunder leading one to conclude that without using more points to fit the boundary conditions certain levels are not computable. In view of the fact that the next development of cellular programmes will probably be to consider only general points and rely solely on k to force the functions to have the correct symmetry by fitting the boundary conditions at a very large number of points, it is absolutely crucial to ensure that this effect will not sabotage entirely the possibility of the advance in cellular calculations. In comparison with the errors considered in the next section all these errors are quite small as will be seen shortly.

4.5 Errors due to Faulty Choice of the Potential Field.

The results quoted from the empty lattice tests show that if the potential field is given correctly and expansions up to $l = 6$ are used the energies computed using this cellular programme have a very high order of accuracy. This is of course always within the limitations of the model, i.e. with the electrons' motions over-correlated, and ignoring exchange interactions between the conduction electrons and the core electrons, and between the various conduction electrons. And it is quite possible (on the basis of the

empty lattice results) to assign quite narrow limits of error to each of the energy levels computed for a real metal. But there are errors of another sort which contribute much more significantly to the uncertainties of the computations. These arise from the lack of knowledge about the potential field $V(\underline{r})$ which exists in the metal. And this difficulty is not peculiar to the cellular method but is common to all methods employed in calculating band structures.

In the computations described here the field used is that due to an ion assumed to be at the centre of the Wigner-Seitz cell together with the potential due to the conduction electrons. For example in calcium there are two conduction electrons per atom and so the potential field used for each conduction electron is that of a Hartree-Fock self-consistent potential field for the Ca^{2+} ion, together with the potential field due to the other conduction electron which is assumed to be perfectly free. Actually of course the other conduction electron is not perfectly free but the discrepancy is slight, (see chapter VII). In the case of some other metal e.g. scandium the potential field is the potential due to some suitable ion core and a number of free electrons equal to one less than the valency of the ion, in the case of scandium it is Sc^{3+} and two free electrons.

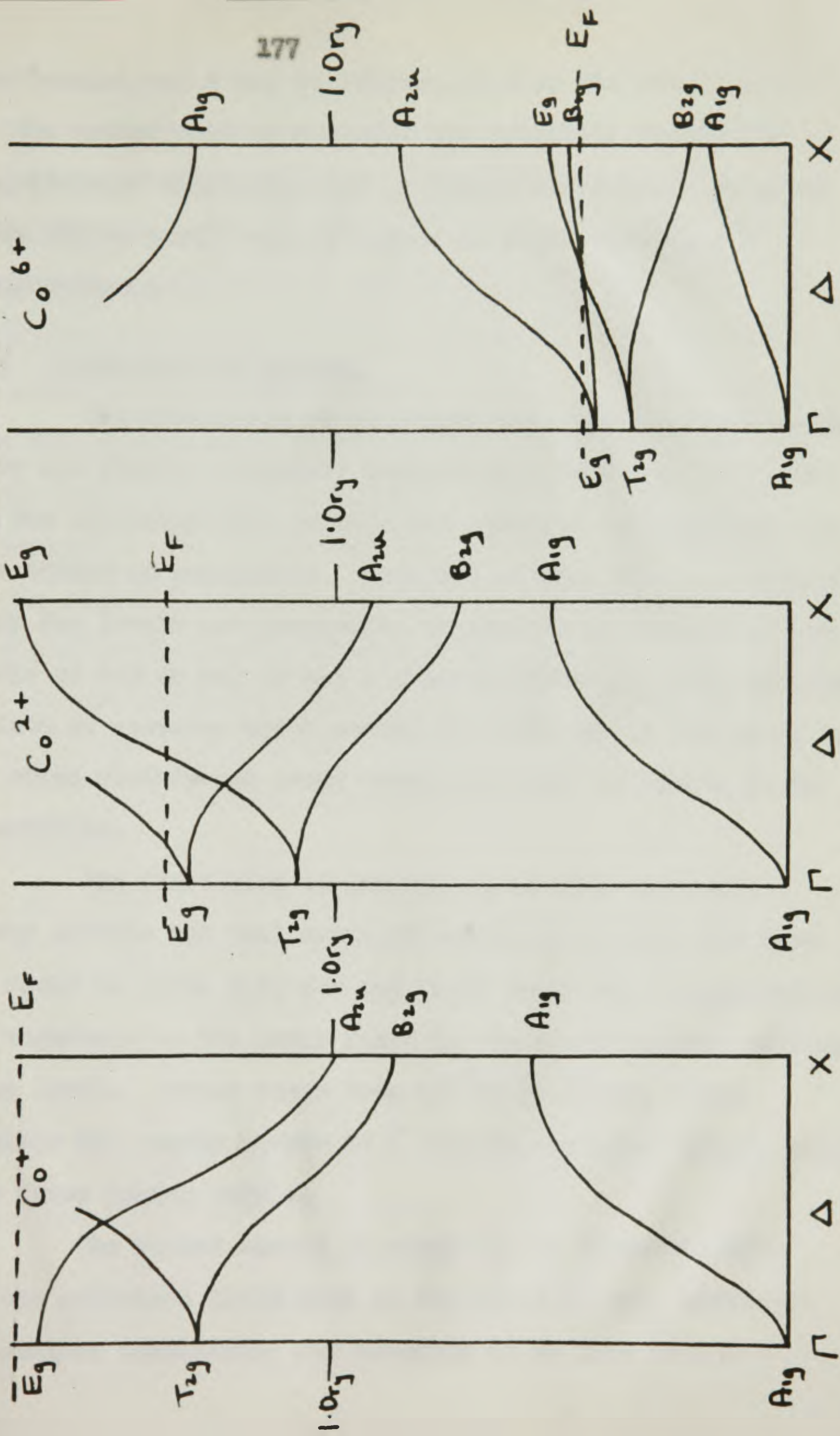
Let us consider this method of choice of potential critically: firstly, within the ion core potentials used exchange between the electrons is included in the fields

supplied to us and correlation effects are well known to be over-allowed for in the Wigner-Seitz method since when an electron moves out of one cell into the next, some other electron is assumed suddenly to appear and move into the first cell keeping strictly the same fixed number of electrons in each cell all the time. Thus correlation effects are not considered separately. Exchange between the conduction electrons and between conduction electrons and core electrons is not considered; both are small as Heine (1957) showed and they have not been considered because there seem to be larger effects to consider. The choice of an ion with valency equal to the number of conduction electrons would seem the least unrealistic ion to choose for the ion-core potential. In the cases of calcium or aluminium this choice is fairly obvious anyway, but for metals with variable valency such as cobalt the choice of ion core is not so immediately obvious, from considerations of the valency at any rate. However the number of conduction electrons is fairly obvious from the structure of the atom of cobalt. If there is any doubt about the number of conduction electrons any very rough ionic field for the metal can be used to locate the highest ion core levels (which will be k -independent) and then put the rest of the electrons into the conduction band. Thus for cobalt the number of conduction electrons is nine since all the electrons $3d^7 4s^2$ in the cobalt atom are very close together in energy and in the metal become spread out into overlapping

bands, whereas the usual chemical valencies are 2 and 3. It is not unreasonable to try to see whether a lower state of ionisation than Co^{9+} might in fact give a more realistic field to compensate for the fact that the conduction electrons are not perfectly free. The effects on the bands achieved by using the potentials due to various states of ionisation of cobalt and the appropriate number of free electrons are shown in Figure 4.3. The effect of the various ionisations is a gradual change of the width of the bands and a consequent change in the Fermi energy, though not necessarily in the shapes of the bands, in their connectivities or in the Fermi surface, although these may be affected. The higher the state of ionisation used the narrower are the bands and consequently the lower is the Fermi energy.

The assumption behind taking ion core potentials in this way is that if an ion of e.g. cobalt, say Co^{3+} is taken with 9 free electrons and put with a lot of similar ions to make up a metal with the 9 free electrons per ion going into the conduction band, then the ion-cores are approximately unaltered; but in reality the effect of compressing the free electrons to be contained in the volume of the equivalent sphere and adding all the extra ions is to cause an alteration in the ion-core levels, so that the problem of the potential field is really a massive problem in self-consistency. In view of the complexity of this its consideration is left until chapter VII. It is enough to say at this stage that a

FIGURE 4.2 BANDS ALONG Γ - Δ -X FOR POTENTIALS USING ION CORES Co^+ , Co^{2+} , and Co^{6+} .



E_F = approx. Fermi energy.

substantial error may be introduced into the calculations by the method used in choosing the potential field, the magnitude of this will also be considered later; it is in fact the most substantial source of error left in the computations.

4.6 Assessment of Errors.

The discussion above limits the errors to two sources, they are firstly numerical inaccuracies of types (i) - (iv) in the classification of S4.2 and secondly uncertainties in the choice of potential. Item (v) of S4.2 though making a very few levels not computable or grossly in error (of the order of 50% or so) is not a general source of error for the points of symmetry which enable the outlines of the bands to be fixed clearly and gross errors on lines or planes to be identified.

The first kind of errors are equally present in empty lattice and real metal calculations so that for them it would be quite fair for any level to claim an accuracy equal in magnitude to the error found in the empty lattice test on that level. These range from 10^{-6} ry to 0.3ry, being smaller for points nearer to Γ and at any given point, smaller for lower energy levels.

The second source of error due to "uncertainties" in the potential field used in the metal is very difficult to analyse completely, and moreover it is less important in

some aspects of the calculations than in others. For example the actual ordering of the levels at a point is relatively insensitive to the choice of potential whereas the scale of the whole scheme of the bands, i.e. the separation of the levels, and also the location of the whole band scheme on the energy scale is very sensitive to the choice of potential. In spite of this however, since the Fermi energy rises as the band scheme becomes widened out, the Fermi surface may well be topologically unchanged by large changes in the potential. The extent to which our fields approach reality is to be judged by the comparison of the calculated results for physically observable quantities, and the whole question of the potential field will be discussed again in chapter VII.

CHAPTER V. RESULTS: Al, Ca, Sc, Co.5.1 The Metals Computed.

There are in all about 25 metals which exist at some reasonable temperature in the cubic close packed (face centred cubic) structure. In the calculations for which results are presented here a selection from these has been made to cover several various types of metal which occur. Those chosen were aluminium, calcium, scandium and cobalt.

Aluminium was computed because it is an example of a nearly free electron like metal and because there is available a very good potential field for it, due to Heine (1957), which allows for most corrections which must be made to the field due to a free ion to produce the field in a real metal.

The group IIA metals of the periodic table are particularly interesting because there have, until very recently, e.g. Harrison (1963), been hardly any reliable calculations of the band structures of these metals, and so calcium was computed in an attempt to help fill this gap especially as experimental work is also under way on calcium by Condon and Marcus (1961), (1964).

Because of the interest which currently exists in the effect on the density of states and Fermi surface of a metal when it undergoes a phase change, and because a similar calculation on scandium in the hexagonal close packed structure has just been completed by Bradley (1964) it was

decided to compute the band structure of scandium in the f.c.c. form to study the effects of the transition $\text{Sc (hcp)} \rightleftharpoons \text{Sc (fcc)}$ on the Fermi surface. Because the hcp results for scandium mentioned are not yet published the study of the phase transition is omitted and the results for scandium are presented here for the fcc structure alone.

And finally, because the transition elements present the greatest challenge for any band calculations, one transition metal has also been computed and the one chosen was cobalt.

5.2 Data for the Computations.

The data necessary for the computation of the band structure of a metal consists of the lattice constant and the potential field. The lattice constants used are taken from Smithell's (1962), and are given in Table 5.1 in Angström units and in atomic units. The lattice constants are given to three figures only, their temperature variation is very small and is only likely to alter the scale of the band scheme and the Fermi energy, and not affect the general shapes of the bands.

The potential fields used are given, in condensed form, in Table 5.2; they are given as Z_p , the effective nuclear charge for the electrostatic potential at equal logarithmic increments of r , and include the contributions due to the other conduction electrons.

TABLE 5.2 $Z_p(r)$ FOR METALS COMPUTED.

r (a.u.)	Al	Ca	Sc	Co
0.002639	12.885	19.789	20.775	26.682
0.003388	12.853	19.730	20.711	26.593
0.004350	12.811	19.653	20.629	26.478
0.005586	12.757	19.555	20.525	26.331
0.007173	12.685	19.431	20.391	26.144
0.009210	12.600	19.272	20.222	25.907
0.01183	12.489	19.070	20.007	25.608
0.01518	12.348	18.816	19.736	25.236
0.01950	12.166	18.499	19.399	24.776
0.02503	11.943	18.109	18.985	24.216
0.03214	11.663	17.635	18.483	23.547
0.04127	11.323	17.071	17.888	22.758
0.05300	10.919	16.412	17.193	21.841
0.06805	10.444	15.652	16.392	20.777
0.08738	9.905	14.784	15.475	19.543
0.1122	9.298	13.791	14.423	18.120
0.1441	8.626	12.655	13.220	16.521
0.1850	7.875	11.381	11.880	14.816
0.2375	7.022	10.022	10.469	13.098
0.3050	6.070	8.683	9.095	11.407
0.3916	5.058	7.453	7.825	9.678
0.5028	4.086	6.324	6.623	7.865
0.6456	3.272	5.207	5.394	6.076
0.8290	2.638	4.029	4.142	4.547
1.064	2.193	2.904	3.024	3.390
1.367	1.844	2.079	2.199	2.500
1.755	1.497	1.573	1.663	1.737
2.254	1.182	1.295	1.301	1.142
2.894	1.004	1.122	1.055	0.997
3.715	1.000	1.014	0.999	1.000
4.771	1.000	1.000	1.000	1.000
6.126	1.000	1.000	1.000	1.000

TABLE 5.1. THE LATTICE CONSTANT, a .

Metal	$a(\text{\AA})$	$a(\text{atomic units})$
Al	4.04	7.69
Ca	5.57	10.5
Sc	4.53	8.56
Co	3.54	6.69

n.b. the definition of a is given in section 3.1.

5.3 The Computed Bands.

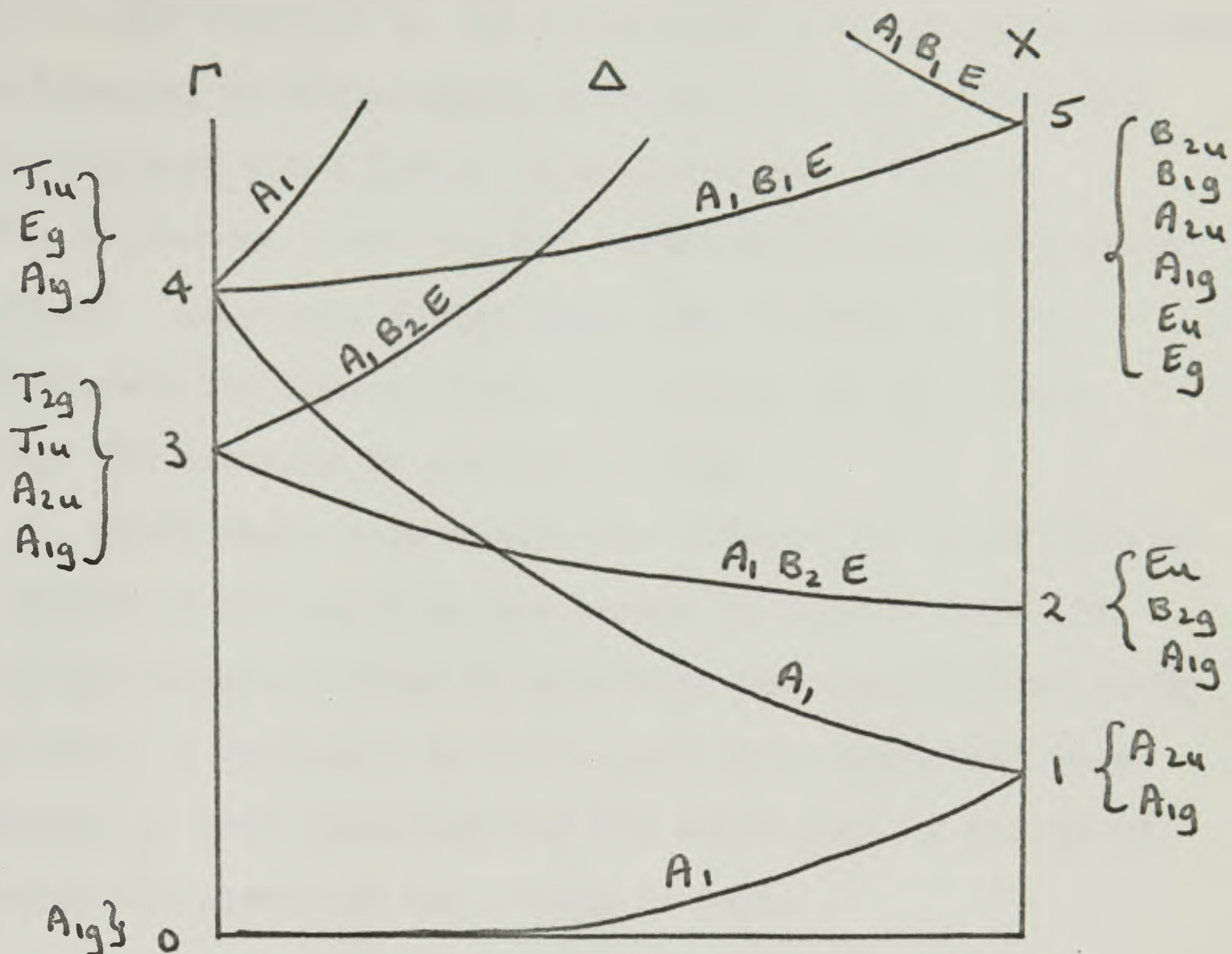
From the cellular programme it is possible to obtain for each metal the energy levels and wave functions at the points of symmetry and along the lines of symmetry. As was mentioned in the previous chapter it is only possible to get reliable results when it is possible to handle expansions up to $l = 6$, and this means that results on planes of symmetry or for general points are not sufficiently reliable to be of use.

Where no computed values exist for a plane of symmetry, one is faced with the problem of connecting the levels at the various points to form bands. This is only a problem of inadequate knowledge; if it were possible to use the large expansions required to compute the energy values on the planes in question this difficulty would not arise.

The rule which must be obeyed is that the compatibilities which were listed in Chapter III, Table 3.10 must be

satisfied when going onto the planes from the points or lines at the edges of the plane. And in addition to this, it must be possible since $E(\underline{k})$ is a continuous function of $\underline{k}$ to start from a certain level at some point of symmetry, to follow a closed path back to the starting point and arrive back at the same level at which one started; this will always be possible by staying in the same band all the way round, provided the scheme of labelling the bands used by, for example, Wannier (1960) p 145 is adopted, where the bands are labelled by an index $q = 1, 2, 3, 4, \dots$ and where $q' > q$ if $E_{q'}(\underline{k}) > E_q(\underline{k})$. The bands of this notation will not necessarily have $\text{grad}_{\underline{k}} E(\underline{k})$ continuous because two "bands" characterised by having both $E(\underline{k})$ and $\text{grad}_{\underline{k}} E(\underline{k})$ continuous may cross. This crossing of bands can occur both for bands of the same symmetry type and different symmetry types, see Herring (1937), though these crossings will in general be just curves and not surfaces in space. An example of the crossing of two bands of the same symmetry is in $\Gamma - \Delta - X$ for the free electron case considered in chapter III; the $\underline{n}$ -vectors and the energies of the two bands at $2\pi/a(0, \delta, 0)$ where $0 \leq \delta \leq 1$ are as shown in Figure 5.1, which shows that the two bands have an accidental degeneracy at $\delta = \frac{1}{2}$. By imposing a small perturbation having only the translational symmetry of the lattice the degeneracy is lifted along the original curve of intersection and replaced by a curve of intersection near to the original one.

FIGURE 5.1 FREE ELECTRON BANDS FOR Γ - Δ -X.



ENERGIES.

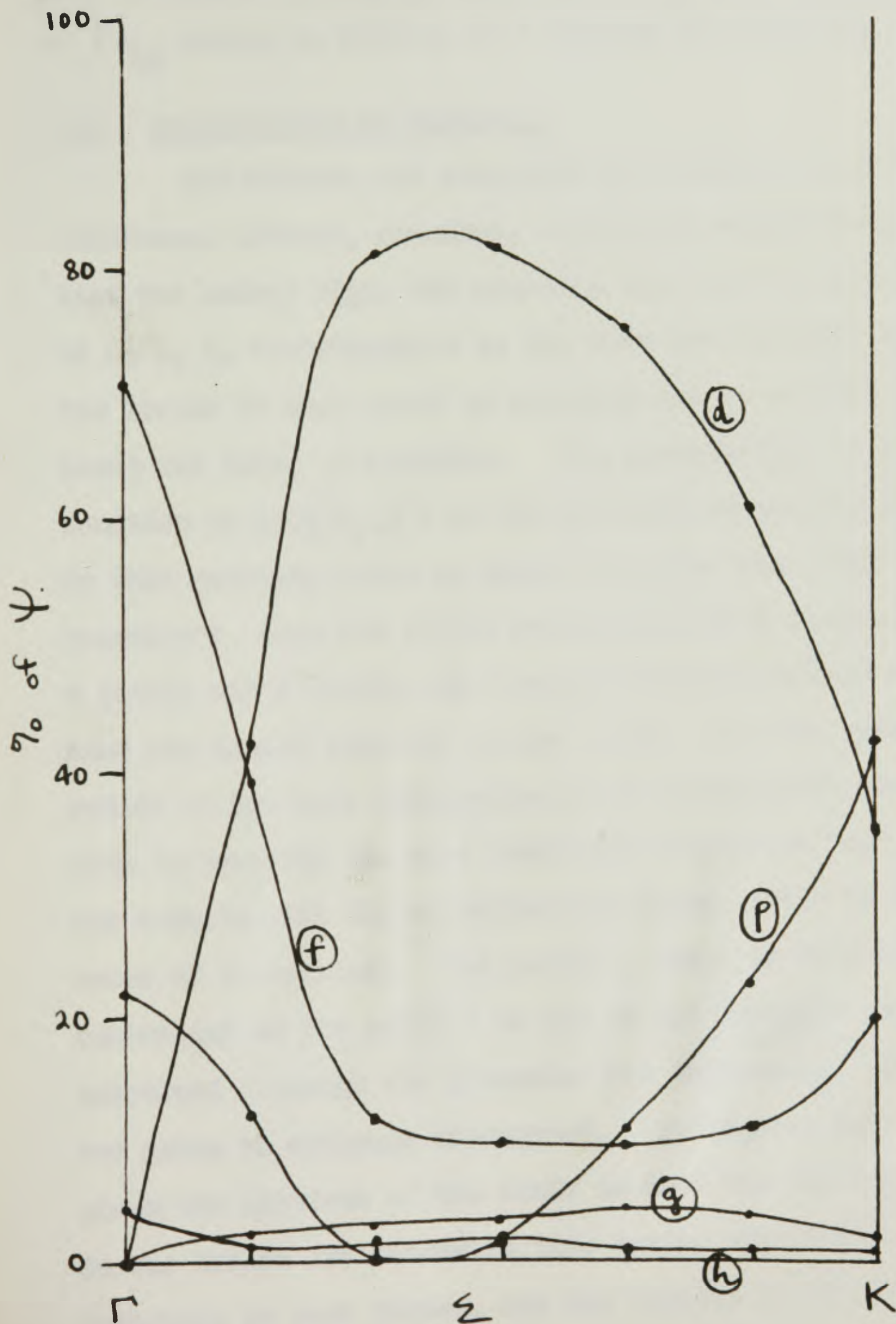
	Γ				X
$\underline{n}$	$\delta=0$	$\delta=\frac{1}{4}$	$\delta=\frac{1}{2}$	$\delta=\frac{3}{4}$	$\delta=1$
0 2 0	4	$3\frac{1}{16}$	$2\frac{1}{4}$	$1\frac{9}{16}$	1
$\bar{1}$ 1 1	3	$2\frac{9}{16}$	$2\frac{1}{4}$	$2\frac{1}{16}$	2
1 1 $\bar{1}$					
$\bar{1}$ 1 $\bar{1}$					
1 1 1					

It is a feature of the cellular method that it is particularly unsuited to the investigation of crossings of this type because, as mentioned in section 2.12, the method may cause two very close levels to coalesce and produce a spurious crossing where the two bands really only come close together. Moreover, if two bands are observed to cross according to the calculations, one has no way of telling whether the crossing is genuine or not.

Where there does remain doubt about the connection of the levels at one point to the levels at another point it has to be resolved either by improving the computations or by guesswork; fortunately in the calculations described here guesswork is only necessary for the connection of points of symmetry via planes of the Brillouin Zone.

5.4 An Analysis of the Wave Functions.

Many workers seem to think of bands in metals as only slightly perturbed atomic energy levels and hence talk of, in the case of the transition metals, the 4s and 3d bands as forming the conduction band. It will be seen from Tables 5.3-5.6 that though a band may be largely s-type there are always, in some parts of the Brillouin Zone at least, substantial contributions arising from other l-values. For example, Figure 5.2 well illustrates that for the fairly typical band $\leq B_1$ the other l-values are present in substantial proportions in what is essentially a d-band. For certain levels at certain

FIGURE 5.2 ANALYSIS OF THE TMS FUNCTION OF Σ .

points of symmetry it is still true in the metal that a band may be 100% s or 100% d, for example the lowest level at Γ , a $\Gamma_{A_{1g}}$ level, is 100% s, to 4 figures of accuracy.

5.5 Presentation of Results.

The results are tabulated in Tables 5.3-5.6 for aluminium, calcium, scandium, and cobalt respectively. We list the energy $E(\underline{k})$, the symmetry type and the percentage of s, p, d, contributions to the wave function for the lowest few levels at each point of symmetry and at several points along the lines of symmetry. The contribution to the wave function is $100 \sum |B_l|^2 \%$ in the notation of section 1.2, and it is this quantity which is tabulated under the entry "wave function"; they are listed separately for s ($l=0$), p ($l=1$), d ($l=2$), and f ($l=3$), and then the higher l -values' contributions are lumped together in one entry. It was felt to be better to put this information on a quantitative basis rather than to describe the wave functions roughly as "sp" or "pdf" for example with the contributions being listed in decreasing order of importance. The point U, which is in fact equivalent to the point K as far as the energies are concerned although the harmonics are different^{is omitted}. Energies are given in rydbergs throughout. In Figures 5.3-5.6 are given the pictures of the bands to show how the levels listed in the Tables are connected into bands, the energy scale is indicated in each figure, and the lengths in the Brillouin

Zone are drawn on the scale $2\pi/a = 5$ cm.

Zone		Frequency (MHz)	a	b	c	d	e
Γ	A_{1g}	0.20497	300.0	*	*	*	1
A_1	A_1	0.20518	299.7	300	*	0.1	2
A_2	A_2	0.20537	299.3	300	300	0.1	3
A_3	A_3	0.20558	298.9	299.5	300	0.1	4
A_4	A_4	0.20579	298.5	299.1	299.7	0.1	5
A_5	A_5	0.20600	298.1	298.7	299.3	0.1	6
A_6	A_6	0.20621	297.7	298.3	298.9	0.1	7
A_7	A_7	0.20642	297.3	297.9	298.5	0.1	8
A_8	A_8	0.20663	296.9	297.5	298.1	0.1	9
A_9	A_9	0.20684	296.5	297.1	297.7	0.1	10
A_{10}	A_{10}	0.20705	296.1	296.7	297.3	0.1	11
A_{11}	A_{11}	0.20726	295.7	296.3	296.9	0.1	12
A_{12}	A_{12}	0.20747	295.3	295.9	296.5	0.1	13
A_{13}	A_{13}	0.20768	294.9	295.5	296.1	0.1	14
A_{14}	A_{14}	0.20789	294.5	295.1	295.7	0.1	15
A_{15}	A_{15}	0.20810	294.1	294.7	295.3	0.1	16
A_{16}	A_{16}	0.20831	293.7	294.3	294.9	0.1	17
A_{17}	A_{17}	0.20852	293.3	293.9	294.5	0.1	18
A_{18}	A_{18}	0.20873	292.9	293.5	294.1	0.1	19
A_{19}	A_{19}	0.20894	292.5	293.1	293.7	0.1	20
A_{20}	A_{20}	0.20915	292.1	292.7	293.3	0.1	21
A_{21}	A_{21}	0.20936	291.7	292.3	292.9	0.1	22
A_{22}	A_{22}	0.20957	291.3	291.9	292.5	0.1	23
A_{23}	A_{23}	0.20978	290.9	291.5	292.1	0.1	24
A_{24}	A_{24}	0.20999	290.5	291.1	291.7	0.1	25
A_{25}	A_{25}	0.21020	290.1	290.7	291.3	0.1	26
A_{26}	A_{26}	0.21041	289.7	290.3	290.9	0.1	27
A_{27}	A_{27}	0.21062	289.3	289.9	290.5	0.1	28
A_{28}	A_{28}	0.21083	288.9	289.5	290.1	0.1	29
A_{29}	A_{29}	0.21104	288.5	289.1	289.7	0.1	30
A_{30}	A_{30}	0.21125	288.1	288.7	289.3	0.1	31
A_{31}	A_{31}	0.21146	287.7	288.3	288.9	0.1	32
A_{32}	A_{32}	0.21167	287.3	287.9	288.5	0.1	33
A_{33}	A_{33}	0.21188	286.9	287.5	288.1	0.1	34
A_{34}	A_{34}	0.21209	286.5	287.1	287.7	0.1	35
A_{35}	A_{35}	0.21230	286.1	286.7	287.3	0.1	36
A_{36}	A_{36}	0.21251	285.7	286.3	286.9	0.1	37
A_{37}	A_{37}	0.21272	285.3	285.9	286.5	0.1	38
A_{38}	A_{38}	0.21293	284.9	285.5	286.1	0.1	39
A_{39}	A_{39}	0.21314	284.5	285.1	285.7	0.1	40
A_{40}	A_{40}	0.21335	284.1	284.7	285.3	0.1	41
A_{41}	A_{41}	0.21356	283.7	284.3	284.9	0.1	42
A_{42}	A_{42}	0.21377	283.3	283.9	284.5	0.1	43
A_{43}	A_{43}	0.21398	282.9	283.5	284.1	0.1	44
A_{44}	A_{44}	0.21419	282.5	283.1	283.7	0.1	45
A_{45}	A_{45}	0.21440	282.1	282.7	283.3	0.1	46
A_{46}	A_{46}	0.21461	281.7	282.3	282.9	0.1	47
A_{47}	A_{47}	0.21482	281.3	281.9	282.5	0.1	48
A_{48}	A_{48}	0.21503	280.9	281.5	282.1	0.1	49
A_{49}	A_{49}	0.21524	280.5	281.1	281.7	0.1	50
A_{50}	A_{50}	0.21545	280.1	280.7	281.3	0.1	51
A_{51}	A_{51}	0.21566	279.7	280.3	280.9	0.1	52
A_{52}	A_{52}	0.21587	279.3	279.9	280.5	0.1	53
A_{53}	A_{53}	0.21608	278.9	279.5	280.1	0.1	54
A_{54}	A_{54}	0.21629	278.5	279.1	279.7	0.1	55
A_{55}	A_{55}	0.21650	278.1	278.7	279.3	0.1	56
A_{56}	A_{56}	0.21671	277.7	278.3	278.9	0.1	57
A_{57}	A_{57}	0.21692	277.3	277.9	278.5	0.1	58
A_{58}	A_{58}	0.21713	276.9	277.5	278.1	0.1	59
A_{59}	A_{59}	0.21734	276.5	277.1	277.7	0.1	60
A_{60}	A_{60}	0.21755	276.1	276.7	277.3	0.1	61
A_{61}	A_{61}	0.21776	275.7	276.3	276.9	0.1	62
A_{62}	A_{62}	0.21797	275.3	275.9	276.5	0.1	63
A_{63}	A_{63}	0.21818	274.9	275.5	276.1	0.1	64
A_{64}	A_{64}	0.21839	274.5	275.1	275.7	0.1	65
A_{65}	A_{65}	0.21860	274.1	274.7	275.3	0.1	66
A_{66}	A_{66}	0.21881	273.7	274.3	274.9	0.1	67
A_{67}	A_{67}	0.21902	273.3	273.9	274.5	0.1	68
A_{68}	A_{68}	0.21923	272.9	273.5	274.1	0.1	69
A_{69}	A_{69}	0.21944	272.5	273.1	273.7	0.1	70
A_{70}	A_{70}	0.21965	272.1	272.7	273.3	0.1	71
A_{71}	A_{71}	0.21986	271.7	272.3	272.9	0.1	72
A_{72}	A_{72}	0.22007	271.3	271.9	272.5	0.1	73
A_{73}	A_{73}	0.22028	270.9	271.5	272.1	0.1	74
A_{74}	A_{74}	0.22049	270.5	271.1	271.7	0.1	75
A_{75}	A_{75}	0.22070	270.1	270.7	271.3	0.1	76
A_{76}	A_{76}	0.22091	269.7	270.3	270.9	0.1	77
A_{77}	A_{77}	0.22112	269.3	269.9	270.5	0.1	78
A_{78}	A_{78}	0.22133	268.9	269.5	270.1	0.1	79
A_{79}	A_{79}	0.22154	268.5	269.1	269.7	0.1	80
A_{80}	A_{80}	0.22175	268.1	268.7	269.3	0.1	81
A_{81}	A_{81}	0.22196	267.7	268.3	268.9	0.1	82
A_{82}	A_{82}	0.22217	267.3	267.9	268.5	0.1	83
A_{83}	A_{83}	0.22238	266.9	267.5	268.1	0.1	84
A_{84}	A_{84}	0.22259	266.5	267.1	267.7	0.1	85
A_{85}	A_{85}	0.22280	266.1	266.7	267.3	0.1	86
A_{86}	A_{86}	0.22301	265.7	266.3	266.9	0.1	87
A_{87}	A_{87}	0.22322	265.3	265.9	266.5	0.1	88
A_{88}	A_{88}	0.22343	264.9	265.5	266.1	0.1	89
A_{89}	A_{89}	0.22364	264.5	265.1	265.7	0.1	90
A_{90}	A_{90}	0.22385	264.1	264.7	265.3	0.1	91
A_{91}	A_{91}	0.22406	263.7	264.3	264.9	0.1	92
A_{92}	A_{92}	0.22427	263.3	263.9	264.5	0.1	93
A_{93}	A_{93}	0.22448	262.9	263.5	264.1	0.1	94
A_{94}	A_{94}	0.22469	262.5	263.1	263.7	0.1	95
A_{95}	A_{95}	0.22490	262.1	262.7	263.3	0.1	96
A_{96}	A_{96}	0.22511	261.7	262.3	262.9	0.1	97
A_{97}	A_{97}	0.22532	261.3	261.9	262.5	0.1	98
A_{98}	A_{98}	0.22553	260.9	261.5	262.1	0.1	99
A_{99}	A_{99}	0.22574	260.5	261.1	261.7	0.1	100

TABLE 5.3 RESULTS: BANDS FOR ALUMINIUM.

		<u>Band 1.</u>				
Point & repn.	Energy (ry)	Wave function. (%)				
		s	p	d	f	rest.
Γ A_{1g}	0.0000	100.0	.	.	.	.
Λ_1 A_1	0.0110	97.7	2.3	.	.	.
Λ_2 A_1	0.0556	91.1	8.7	0.2	.	.
Λ_3 A_1	0.1285	80.9	17.9	1.2	.	.
Λ_4 A_1	0.2279	66.5	28.1	3.3	0.1	.
Λ_5 A_1	0.3522	55.3	37.1	7.2	0.3	0.1
L A_{1g}	0.4981	76.1	.	25.8	.	0.1
Γ A_{1g}	0.0000	100.0	.	.	.	.
Σ_1 A_1	0.0135	96.6	3.3	0.1	.	.
Σ_2 A_1	0.0338	86.9	12.5	0.5	0.1	.
Σ_3 A_1	0.1906	72.7	25.1	2.1	0.1	.
Σ_4 A_1	0.3385	56.0	37.8	5.8	0.3	0.1
Σ_5 A_1	0.5186	39.3	47.5	12.2	0.1	0.9
K B_2	0.7063	.	86.7	10.8	2.3	0.2
Γ A_{1g}	0.0000	100.0	.	.	.	.
Δ_1 A_1	0.0420	93.2	6.7	0.1	.	.
Δ_2 A_1	0.1717	74.8	23.6	1.6	.	.
Δ_3 A_1	0.3782	50.0	42.7	6.8	0.5	.
X A_{2u}	0.6367	.	96.5	.	3.5	.
W E	0.7770	.	78.0	19.9	1.8	0.3

Band 2.

Point & repn.	Energy (ry)	Wave function (%)				
		s	p	d	f	rest.
Γ T_{2g}	1.5719	.	.	94.3	.	5.7
Λ_1 A_1	1.5800	2.4	55.3	32.4	6.7	3.2
Λ_2 A_1	1.3138	5.0	42.5	43.6	7.2	1.7
Λ_3 A_1	1.0796	10.3	46.2	37.2	5.5	0.8
Λ_4 A_1	0.8650	17.9	49.6	28.6	3.5	0.4
Λ_5 A_1	0.6720	27.8	50.3	19.9	1.9	0.1
L A_{2u}	0.5139	.	98.9	.	1.1	.
Γ T_{2g}	1.5719	.	.	94.3	.	5.7
Σ_1 B_2	1.5848	.	53.6	30.3	12.5	3.6
Σ_2 B_2	1.3838	.	36.9	50.4	11.5	1.2
Σ_3 B_2	1.0766	.	44.1	48.1	7.1	0.7
Σ_4 B_2	0.9162	.	57.6	38.2	3.7	0.5
Σ_5 B_2	0.7691	.	72.1	24.9	2.4	0.6
π A_1	0.7658	70.4	1.3	24.4	3.7	0.4
Γ T_{2g}	1.6719	.	.	94.3	.	5.7
Δ_1 B_2	1.5181	.	.	84.5	14.1	1.4
Δ_2 A_1	1.4071	0.2	16.2	67.4	14.3	1.9
Δ_3 A_1	0.9987	11.9	42.0	40.1	5.5	0.5
χ A_{1g}	0.6875	56.5	.	43.2	.	0.3
ψ B	0.7770	.	78.0	19.9	1.8	0.3

Band 3.

Point & repn.	Energy (ry)	Wave function.				
		s	p	d	f	rest.
Γ T_{2g}	1.6719	.	.	94.3	.	5.7
Λ_1 E	1.4187	.	3.1	95.9	.	1.0
Λ_2 E	1.4523	.	11.4	84.5	2.5	1.6
Λ_3 E	1.4818	.	26.1	67.9	3.6	2.4
Λ_4 E	1.5153	.	51.3	40.6	5.2	2.9
Λ_5 E	1.5287	.	76.7	13.4	5.2	4.7
L E_g	1.5574	.	.	94.7	.	5.3
Γ T_{2g}	1.6719	.	.	94.3	.	5.7
Σ_1 A_1	1.7090	0.6	17.8	75.4	2.0	4.2
Σ_2 A_1	1.4515	8.2	36.6	41.6	11.0	2.6
Σ_3 A_1	1.2293	18.4	35.1	34.6	10.5	0.4
Σ_4 A_1	1.0354	30.6	29.5	31.0	8.3	0.6
Σ_5 A_1	0.8765	46.4	17.7	30.0	5.6	0.3
K A_1	0.8172	55.2	8.1	33.7	2.3	0.7
Γ T_{2g}	1.6719	.	.	94.3	.	5.7
Δ_1 A_1	1.7718	.	.	84.5	14.1	1.4
Δ_2 B_2	1.3243	.	.	89.3	10.4	0.3
Δ_3 B_2	1.2002	.	.	96.0	3.2	0.8
X B_{2g}	1.1575	.	.	98.7	.	1.3
W B_2	0.8052	.	50.6	46.4	2.9	0.1

TABLE 5.4 RESULTS: BANDS FOR CALCIUM.

		Band 1.				
Point & repn.	Energy (ry).	Wave function (%)				
		s	p	d	f	rest
Γ A_{1g}	0.0000	100.0	.	.	.	.
Λ_1 A_1	0.0154	96.6	3.4	.	.	.
Λ_2 A_1	0.0532	87.9	11.5	0.6	.	.
Λ_3 A_1	0.1211	75.3	21.0	3.5	0.1	0.1
Λ_4 A_1	0.1791	62.7	24.2	12.5	0.6	.
Λ_5 A_1	0.2177	58.7	11.1	19.2	.	.
E A_{1g}	0.2348	52.4	.	47.4	.	0.2
Γ A_{1g}	0.0000	100.0	.	.	.	.
Σ_1 A_1	0.0220	95.0	5.0	.	.	.
Σ_2 A_1	0.0767	82.3	16.5	1.1	0.1	.
Σ_3 A_1	0.1446	66.4	28.4	4.8	0.4	.
Σ_4 A_1	0.2245	48.0	38.9	11.8	1.1	0.2
Σ_5 A_1	0.3123	22.4	50.4	25.4	1.1	0.7
K A_1	0.3838	10.6	29.0	57.9	1.3	1.2
Γ A_{1g}	0.0000	100.0	.	.	.	.
Δ_1 A_1	0.0403	90.3	9.4	0.3	.	.
Δ_2 A_1	0.1358	67.3	27.0	5.6	.	0.1
Δ_3 A_1	0.2233	39.5	23.4	36.9	0.1	0.1
X A_{1g}	0.2577	21.9	.	77.6	.	0.5
W B_2	0.3360	.	30.2	65.1	3.7	1.0

Point & repn.	Energy (ry).	Wave function. (%)				
		s	p	d	f	rest
Γ T_{2g}	0.6329	.	.	94.0	.	6.0
Λ_1 A_1	0.6314	.	4.7	79.8	11.8	3.7
Λ_2 A_1	0.5520	0.2	12.5	73.8	12.2	1.3
Λ_3 A_1	0.4708	.	25.5	64.3	9.6	0.6
Λ_4 A_1	0.4336	0.4	45.2	46.6	7.6	0.2
Λ_5 A_1	0.3781	.	80.3	14.9	4.5	0.3
L A_{2u}	0.3673	.	95.9	.	3.9	0.2
Γ A_{1g}	0.6329	.	.	94.0	.	6.0
Σ_1 B_2	0.6349	.	9.3	67.1	20.5	3.1
Σ_2 B_2	0.5348	.	14.5	68.5	16.2	0.8
Σ_3 B_2	0.4691	.	22.9	65.7	11.3	0.1
Σ_4 B_2	0.4356	.	35.3	57.8	6.1	0.8
Σ_5 B_2	0.4303	.	51.9	42.7	4.5	0.9
K B_2	0.4479	.	71.6	23.2	4.6	0.6
Γ A_{1g}	0.6329	.	.	94.0	.	6.0
Δ_1 B_2	0.5735	.	.	86.8	11.3	1.9
Δ_2 B_2	0.4797	.	.	89.9	9.8	0.3
Δ_3 B_2	0.4180	.	.	95.9	3.2	0.9
X B_{2g}	0.3964	.	.	98.6	.	1.4
W A_1	0.5566	49.8	.	29.2	20.6	0.4

TABLE 5.5 RESULTS: BANDS FOR SCANDIUM.

Band 1.

Point & repn.	Energy (ry).	Wave function (%)				
		s	p	d	f	rest
Γ A_{1g}	0.0000	100.0	.	.	.	.
Λ_1 A_1	0.0238	96.5	3.5	.	.	.
Λ_2 A_1	0.0761	87.4	11.8	0.8	.	.
Λ_3 A_1	0.1456	75.1	19.6	5.3	.	.
Λ_4 A_1	0.2101	60.7	18.6	20.5	0.2	.
Λ_5 A_1	0.2460	47.5	6.7	45.5	0.2	0.1
L A_{1g}	0.2726	42.8	.	57.0	.	0.2
Γ A_{1g}	0.0000	100.0	.	.	.	.
Σ_1 A_1	0.0333	94.7	5.2	0.1	.	.
Σ_2 A_1	0.1086	81.6	16.8	1.5	.	0.1
Σ_3 A_1	0.2055	64.6	28.7	6.2	0.5	.
Σ_4 A_1	0.3145	43.3	39.7	15.7	1.0	0.3
Σ_5 A_1	0.4062	14.3	48.2	35.8	0.9	0.8
K A_1	0.4343	2.0	30.6	66.4	0.1	0.9
Γ A_{1g}	0.0000	100.0	.	.	.	.
Δ_1 A_1	0.0575	90.0	9.6	0.4	.	.
Δ_2 A_1	0.1824	64.1	26.2	9.5	.	0.2
Δ_3 A_1	0.2496	30.7	14.6	54.2	0.4	0.1
X A_{1g}	0.2609	15.6	.	84.0	.	0.4
W B_2	0.3701	.	25.1	71.3	2.7	0.9

Point & repn.	Energy (ry).	Wave function (%)				
		s	p	d	f	rest
Γ T_{2g}	0.7040	.	.	96.6	.	3.4
Λ_1 E	0.5841	.	0.9	98.5	0.6	.
Λ_2 A_1	0.6314	.	8.7	83.2	7.2	0.9
Λ_3 A_1	0.5539	.	20.4	71.8	7.4	0.4
Λ_4 A_1	0.5036	0.2	44.3	49.4	5.7	0.4
Λ_5 A_1	0.4926	0.5	79.2	15.7	4.3	0.3
L A_{2u}	0.4962	.	95.8	4.1	.	0.1
Γ T_{2g}	0.7040	.	.	96.6	.	3.4
Σ_1 B_2	0.6930	.	4.7	86.8	6.6	1.9
Σ_2 B_2	0.6023	.	9.7	80.5	9.3	0.5
Σ_3 B_2	0.5321	.	16.3	76.0	7.3	0.4
Σ_4 B_2	0.5064	.	26.8	67.8	4.7	0.7
Σ_5 B_2	0.5214	.	41.2	54.2	3.7	0.9
K B_2	0.5695	.	59.7	35.3	4.3	0.7
Γ T_{2g}	0.7040	.	.	96.6	.	3.4
Δ_1 B_2	0.6433	.	.	92.7	2.0	5.3
Δ_2 B_2	0.5234	.	.	93.5	5.5	1.0
Δ_3 B_2	0.4396	.	.	97.3	2.2	0.5
X B_{2g}	0.4100	.	.	99.1	.	0.9
W E	0.5224	.	34.3	62.5	1.5	1.7

Band 3.

Point & repn.	Energy (ry).	Wave function (%)				
		s	p	d	f	rest
Γ E_g	0.9321	.	.	97.5	.	2.5
Λ_1 A_1	0.7049	.	2.4	91.6	3.7	2.3
Λ_2 E_g	0.6462	.	3.2	94.6	2.2	.
Λ_3 E_g	0.7465	.	8.4	87.1	4.5	.
Λ_4 E_g	0.8540	.	16.5	78.1	5.2	0.1
Λ_5 E_g	0.5579	.	0.3	99.1	0.5	0.1
L E_g	0.6580	.	.	96.8	.	3.2
Γ T_{2g}	0.7040	.	.	96.6	.	3.4
ξ_1 A_2	0.7268	.	.	96.1	0.7	3.2
ξ_2 A_2	0.7619	.	.	94.9	2.6	2.5
ξ_3 A_2	0.8154	.	.	93.3	4.9	1.8
ξ_4 A_2	0.8859	.	.	92.1	6.7	1.2
ξ_5 A_2	0.9663	.	.	92.2	6.6	1.2
K A_2	1.0451	.	.	94.4	4.2	1.4
Γ E_g	0.9321	.	.	97.5	.	2.5
Δ_1 A_1	0.8397	0.5	0.1	91.2	6.4	1.8
Δ_2 A_1	0.6547	5.0	7.8	76.2	10.2	0.8
Δ_3 A_1	0.6091	9.5	59.2	23.7	7.5	0.1
X A_{2u}	0.6569	.	93.2	.	6.7	0.1
W E_g	0.5224	.	34.3	62.5	1.5	1.7

TABLE 5.6 RESULTS: BANDS FOR COBAIT.

Band 1.

Point & repn.	Energy (ry)	Wave function.				
		s	p	d	f	rest
Γ A_{1g}	0.0000	100.0	.	.	.	.
Δ_1 A_1	0.0585	91.7	7.4	0.9	.	.
Δ_2 A_1	0.1781	54.5	17.2	28.3	.	.
Δ_3 A_1	0.1761	13.1	4.1	82.6	0.2	.
X A_{1g}	0.1771	4.8	.	95.1	.	0.1

Band 2.

Point & repn.	Energy (ry)	Wave function.				
		s	p	d	f	rest
Γ T_{2g}	0.3419	.	.	99.3	.	0.7
Δ_1 B_2	0.3310	.	.	99.2	0.4	0.4
Δ_2 B_2	0.2794	.	.	99.1	0.8	0.1
Δ_3 B_2	0.2311	.	.	99.5	0.4	0.1
X B_{2g}	0.2123	.	.	99.8	.	0.2

Band 3.

Point & repn.	Energy (ry)	Wave function.				
		s	p	d	f	rest
Γ T_{2g}	0.3419	.	.	99.3	.	0.7
Δ_1 E	0.3363	.	0.7	99.3	.	.
Δ_2 E	0.3761	.	1.8	97.1	1.0	0.1
Δ_3 E	0.4552	.	1.2	97.8	0.8	0.2
X E_g	0.5140	.	.	99.8	.	0.2

Band 4 is degenerate with Band 3 along $\Gamma - \Delta - X$.

Band 5.

Point & repn.	Energy (ry)	Wave function.				
		s	p	d	f	rest.
Γ E_g	0.4314	.	.	99.6	.	.
Δ_1 A_1	0.4016	0.3	.	99.2	0.2	0.3
Δ_2 A_1	0.4172	20.8	11.5	66.7	0.9	0.1
Δ_3 A_1	0.6368	28.0	53.5	16.5	2.0	.
X A_{2u}	0.8567	.	95.3	.	4.7	.

Band 6.

Point & repn.	Energy (ry)	Wave function.				
		s	p	d	f	rest.
Γ E_g	0.4314	.	.	99.6	.	0.4
Δ_1 B_1	0.4393	.	.	99.6	0.1	0.3
Δ_2 B_1	0.4582	.	.	99.5	0.3	0.2
Δ_3 B_1	0.4762	.	.	99.7	0.2	0.1
X B_{1g}	0.4840	.	.	99.9	.	0.1

The rest of the points in the Brillouin Zone are not included in this Table for the reason given in the note to Figure 5.6.

FIGURE 5.4 THE BANDS FOR CALCIUM.

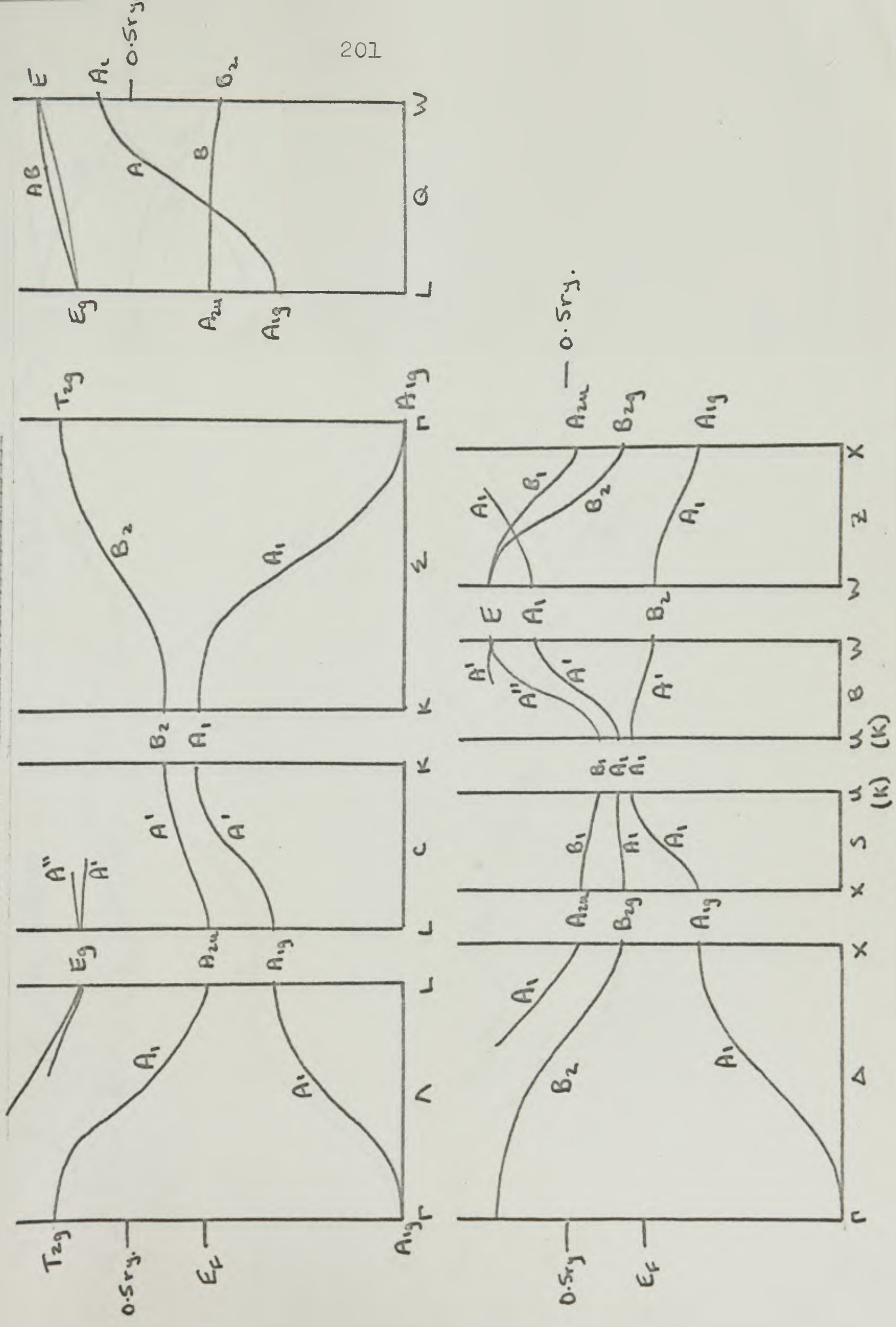


FIGURE 5.5 THE BANDS FOR SCANDIUM.

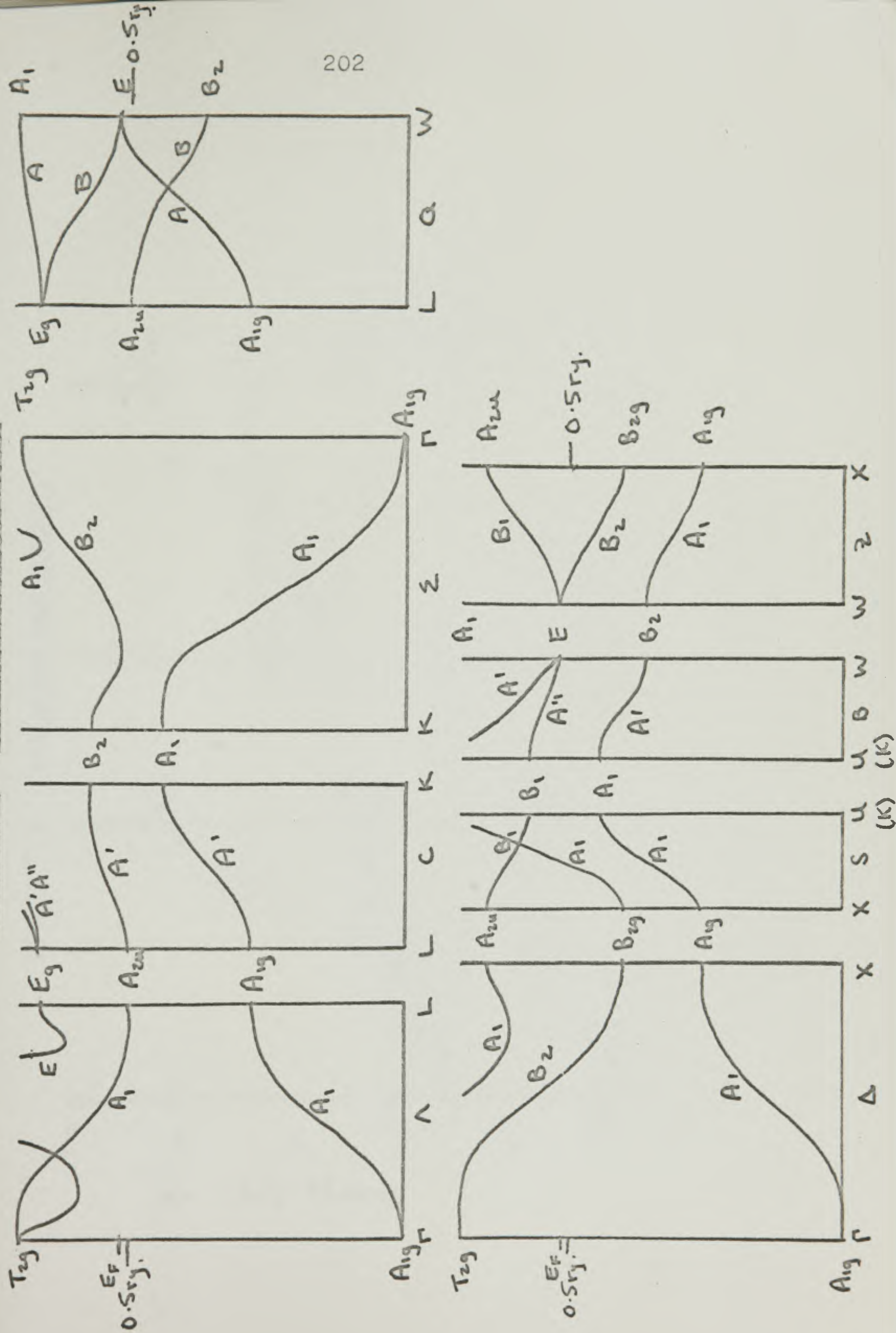
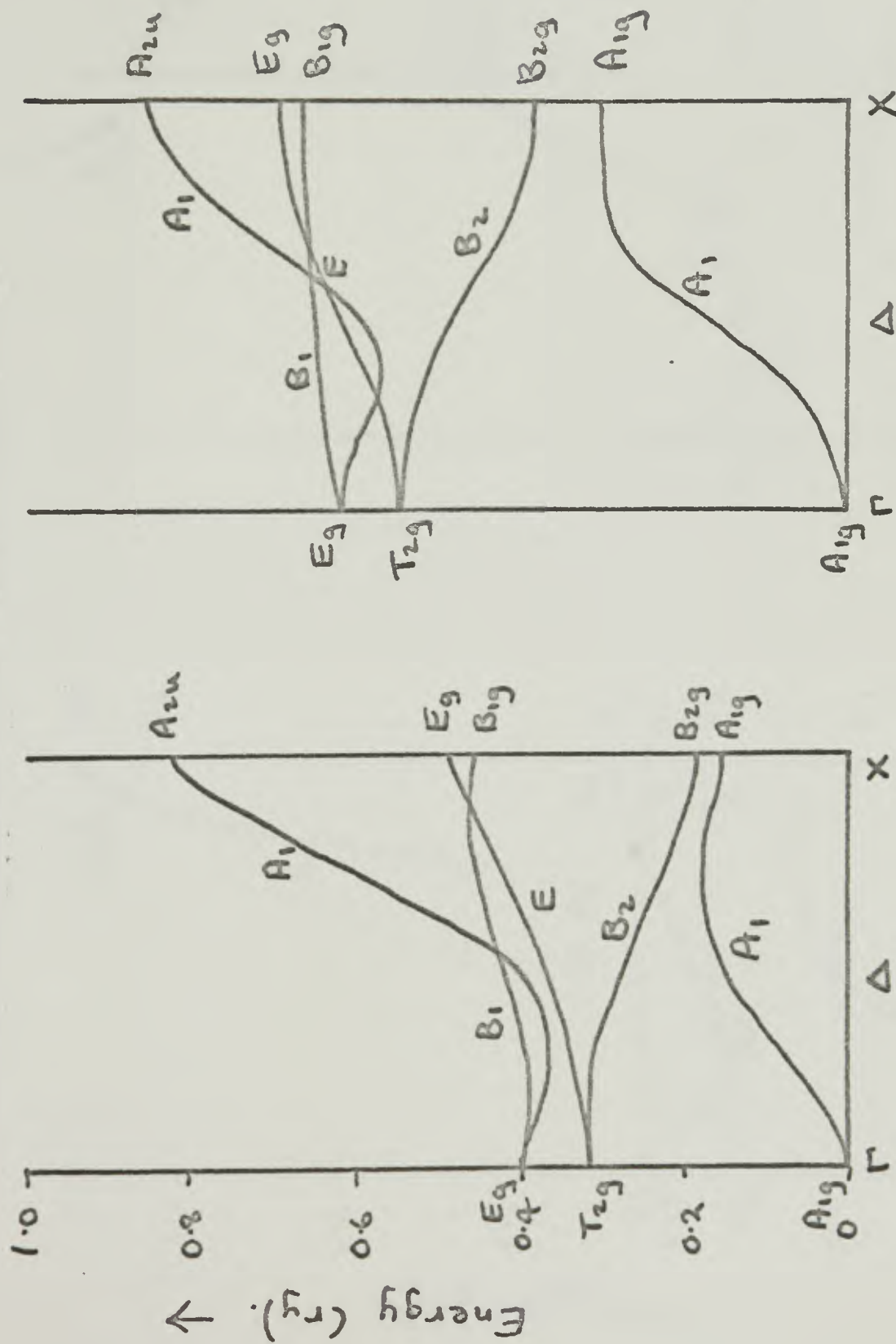
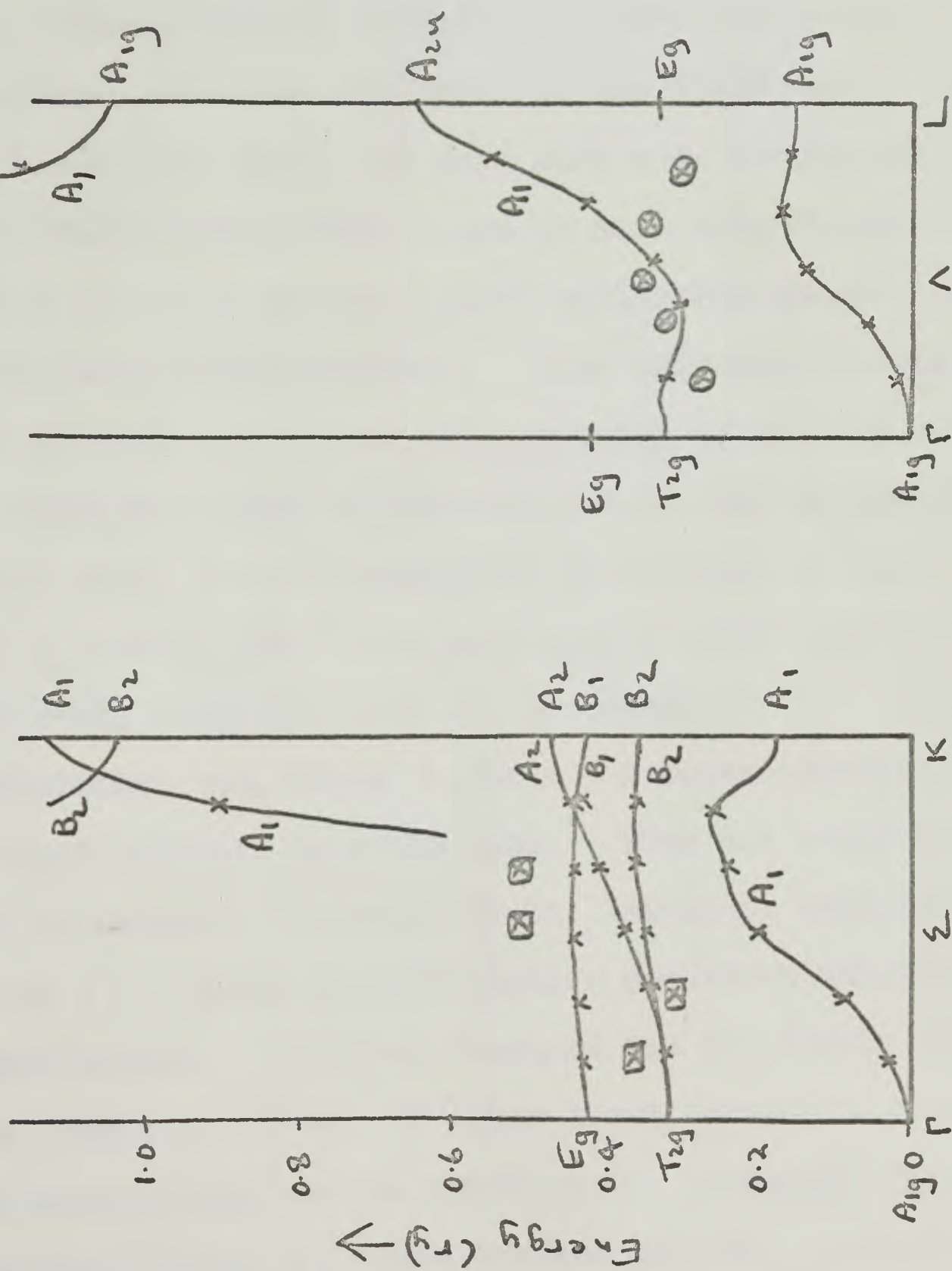


FIGURE 5.6 THE BANDS FOR COBALT.



- (a) Present calculation. (b) Mattheiss (1963).
 The bands for the lines Γ - Λ -L and Γ - Σ -K are shown on the next page.

FIGURE 5.6 (continued).



Note on Figure see over.

Note on Figure 5.6.

The bands along $\Gamma-\Delta-X$ have been found satisfactorily and they are shown in Figure 5.6. They can be seen to agree fairly closely in shape with those of Mattheiss (1963) for the same line $\Gamma-\Delta-X$ which is also shown in Figure 5.6. But in other directions the computations have encountered difficulties which did not occur in the three metals Al, Ca, and Sc. Because the bands are very much more compressed in cobalt than in these other metals there is much more danger of two minima on the same residual curve coalescing simply because they are much nearer together. This only occurs when the levels are less than about 0.03 ry apart so that it does not occur along the lines of symmetry for Al, Ca, or Sc, nor does it occur along Δ for cobalt, but it does for Σ and Λ . The levels E_g and T_{2g} at Γ are only 0.09 ry apart and both levels must, along the line Σ , be connected to a ΣA_1 representation and, along Λ , to a ΛE representation, from the compatibilities in Table 3.10. Thus the programme trying to compute ΛE levels or ΣA_1 levels to connect up with ΓE_g and ΓT_{2g} finds a false minimum somewhere between the two true levels. This has happened for the levels marked $\otimes$ in the Figure for ΛE . No other level between 0.2 ry and 0.6 ry can be found by the programme. A similar thing has happened along Σ , where instead of the A_1 levels marked $\boxtimes$ there should be two levels, one to connect up with ΓE_g and one with ΓT_{2g} . If the $\bar{G}^k$ for the lines Σ and Λ contained

more symmetry elements, so that each representation had fewer harmonics, larger l values could be used and there would be fewer minima to find on each curve as is the case along Δ .

As mentioned already in section 4.4 this problem of the "lost minimum" is felt to be by far the most serious problem standing in the way of future development of the cellular method.

CHAPTER VI. APPLICATIONS OF RESULTS.

6.1 The Electronic Properties of Metals.

In this chapter an attempt is made to compare the results of the calculations described in the previous chapter with the results of certain physical experiments. The density of states curve is computed, and from this are found, the Fermi energy, the electronic specific heat and the Pauli spin paramagnetic susceptibility of the electrons. The Fermi surface is also deduced as well as possible from the calculations and the de Haas-van Alphen effect periods are considered. The other item of importance is the Knight shift which can be calculated from the quantities already mentioned together with a knowledge of the wave functions of the electrons. Quantities involving interaction of the electrons with the lattice vibrations or phonons are not considered here in detail.

Many of the results of the theory of the properties of electrons in metals are here only quoted; good detailed discussions are given by Pippard (1960), Rosenberg (1963) and Ziman (1960)*. Other references are given as necessary.

6.2 The Interpolation to Find $E(k)$.

The cellular calculations which have been described already in considerable detail give results which consist of the energy levels and the corresponding wave functions for electrons at each point of symmetry and at selected points

*also Callaway(1964).

along the lines of symmetry, Σ , Δ , Λ , S , and Z in the Brillouin Zone. We have seen already that though it would be possible to compute some (but not all) of the levels for planes of symmetry and even for general points in the zone this is very time consuming and since only low order expansions ($l \leq 2$ or $l \leq 3$) are able to be used the accuracy is very poor.

Therefore, from the levels determined it is necessary to determine $E(\underline{k})$, the energy, and $\Psi_{\underline{k}}(\underline{r})$, the wave function, for an electron with a completely arbitrary $\underline{k}$ -vector. In Figure 6.1 are shown the points and lines where $E(\underline{k})$ and $\Psi_{\underline{k}}(\underline{r})$ are known for each band. Since nothing is known about the form of the function $E(\underline{k})$ except that it is continuous the interpolation to find $E(\underline{k})$ is bound to be somewhat arbitrary; one could try to do the interpolation by fitting "slightly distorted" free-electron bands with the known values to give the parameters in a general expression for $E(\underline{k})$. But this is not guaranteed to be the best method because the bands in real metals are very seriously distorted from the free-electron bands. In view of this a result which will not be much worse than that found by the method adopted could be obtained by using any reasonable numerical interpolation procedure assuming, what is in fact nearly true, that there is no "inside" physical information available as to the shapes of the bands.

The interpolation procedure adopted was the following:
In Figure 6.1 imagine 5 planes parallel to the plane of

LUWK, and with equations $k_x + k_y + k_z = \frac{2n\pi}{4a}$, ($1 \leq n \leq 5$).

These all intersect Σ , and Λ , but only three of them intersect Δ , the fourth passes through X and the fifth intersects S and Z instead of Δ . The cellular calculation was performed to yield $E(\underline{k})$ and $\psi_{\underline{k}}(\underline{r})$ for each band at the points on Σ , Δ , Λ , S, and Z where these five planes and the lines intersect. Thus to find the interpolated value $E(\underline{k})$ at any given value of $\underline{k} = 2\pi/a(\xi, \eta, \zeta)$ the (111) plane through the point $\underline{k}$ is considered; its equation is

$k_x + k_y + k_z = 2\pi/a(\xi + \eta + \zeta)$, and it therefore intersects the lines Σ , Δ , and Λ at

$$\Sigma_1 = (\xi + \eta + \zeta)2\pi/a(\frac{1}{3}, \frac{1}{3}, 0)$$

$$\Delta_1 = (\xi + \eta + \zeta)2\pi/a(0, 1, 0)$$

$$\Lambda_1 = (\xi + \eta + \zeta)2\pi/a(1/3, 1/3, 1/3),$$

or if $(\xi + \eta + \zeta) > 1$, it cuts Σ , Λ , S and Z at

$$\Sigma_1 = (\xi + \eta + \zeta)2\pi/a(\frac{1}{3}, \frac{1}{3}, 0)$$

$$\Lambda_1 = (\xi + \eta + \zeta)2\pi/a(1/3, 1/3, 1/3)$$

$$S_1 = 2\pi/a(\frac{1}{3}(\xi + \eta + \zeta - 1), 1, \frac{1}{3}(\xi + \eta + \zeta - 1))$$

$$Z_1 = 2\pi/a((\xi + \eta + \zeta - 1), 1, 0).$$

The values of $E(\underline{k})$ at the points Σ_1 , Δ_1 , and Λ_1

or at Σ_1 , Λ_1 , S_1 , and Z_1 are found by a Lagrange's 3, 5, or 7 point interpolation formula, using the known values for the appropriate numbers of points on those lines. This gives $E(\underline{k})$ at the vertices of the triangle or quadrilateral through $\underline{k}$ and parallel to the hexagonal face of the Brillouin Zone (see Figure 6.2). The weighted mean of these, weighted inversely

FIGURE 5.1 THE REPRESENTATIVE PORTION OF THE
BRILLOUIN ZONE.

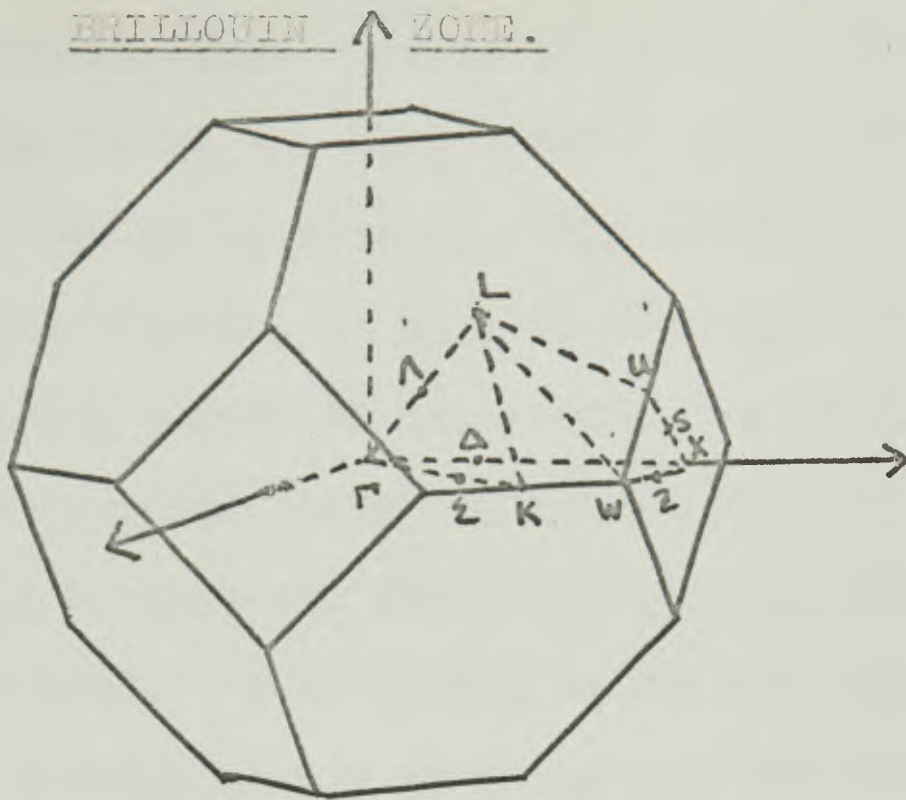
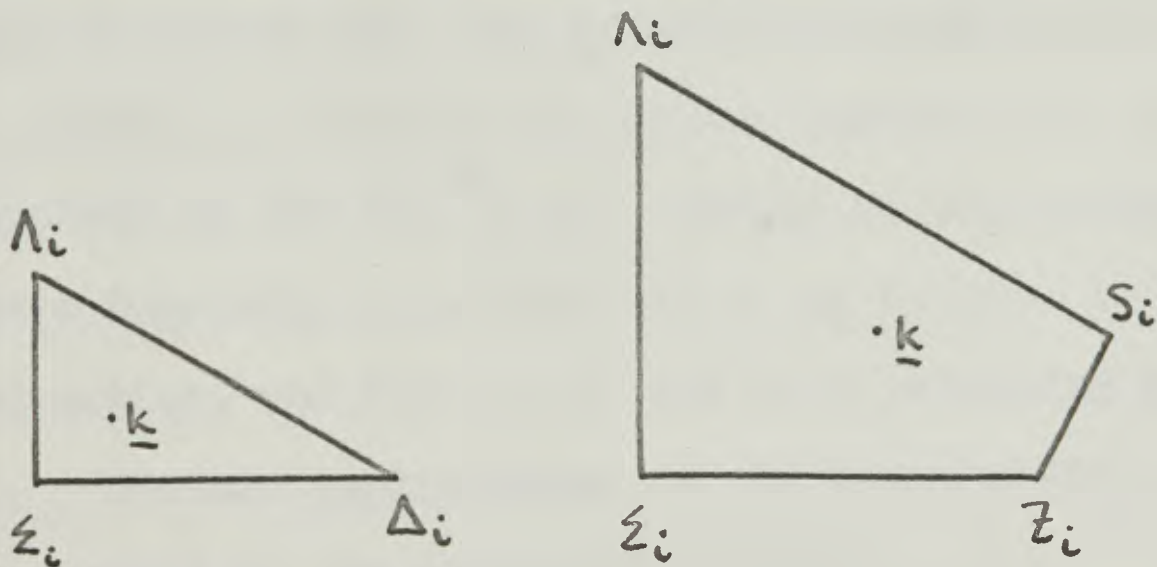


FIGURE 6.2 INTERNAL (111) PLANES.



as $\underline{r}^2$, where $\underline{r}$ is the vector from $\underline{k}$ to the point $\underline{z}_1$ etc., is taken as the value of $E(\underline{k})$. There are various ways of using this routine which has been programmed for the "Mercury" computer, one is to evaluate $E(\underline{k})$ over a grid of values for $\underline{k}$. Alternatively, to find the density of states curve, $n(E)$, a random $\underline{k}$ vector is generated; it is then forced to be in the representative section of the zone in which one has chosen to work and the corresponding $E(\underline{k})$ is calculated for each band. A histogram is constructed by repeating this for a large number of $\underline{k}$ -vectors and this enables $n(E)$, the density of states curve to be constructed, and the Fermi energy found. Alternatively, with the Fermi energy found, the programme can generate random $\underline{k}$ -vectors, find $E(\underline{k})$ and if they are sufficiently near to E_F , the Fermi energy, it prints $E(\underline{k})$ and $\underline{k}$, thus enabling one to draw the Fermi surface. Another use of the programme is to interpolate on the $|\underline{b}_1|^2$, the squares of the coefficients in the wave function, i.e. the % of s, p, d, etc. type in the wave function, and this is of use in calculating the Knight shift. Various applications of the interpolation routine are discussed in the following sections.

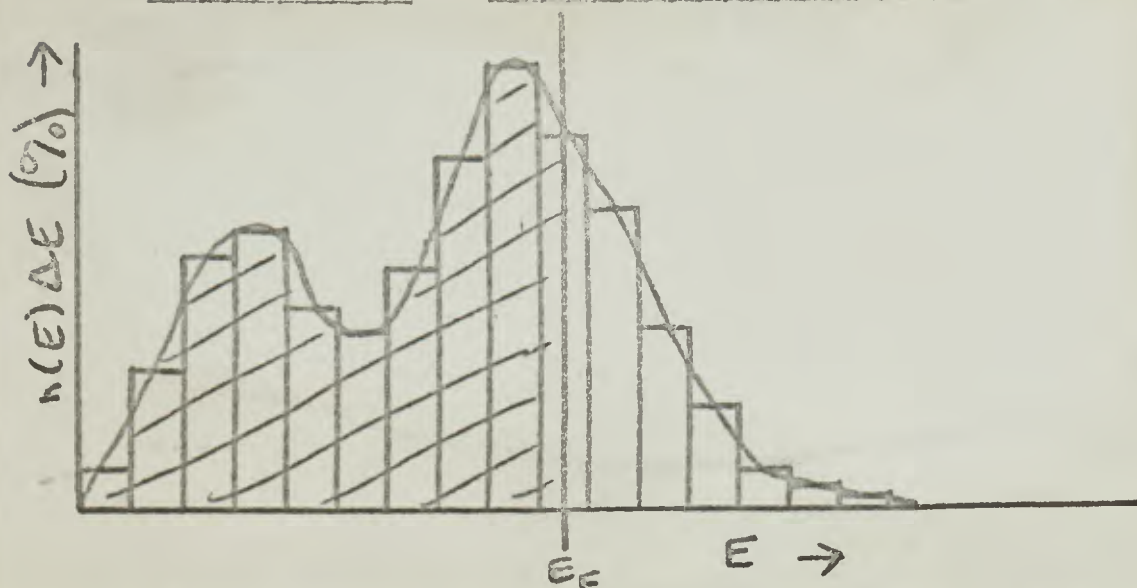
For the empty lattice energies, where the $E(\underline{k})$ are known analytically all over the zone it is possible to test the accuracy of the programme and this is found to be of the order of a few per cent or so. However, for a real metal

one has no external evidence to test the interpolation with since, though it would be possible to do a cellular calculation for a general point in the zone its accuracy would be so low as not to provide a very good test of the accuracy of the interpolation. Thus in a real metal one must say that the individual interpolated energies are subject to errors of at least a few per cent and possibly as much as 10%. The interpolated function $E(\underline{k})$ is of course still a continuous function of $\underline{k}$, so that the errors are by no means random, and interpolated values depending on the derivatives of $E(\underline{k})$, such as the electronic velocity, or the effective mass may not be completely meaningless.

6.3 The Density of States and the Fermi Energy.

Using the programme described in the previous section it is possible for any given $\underline{k}$ -vector to find by interpolation the corresponding energy for each band. This programme can also be modified to generate $\underline{k}$ -vectors at random in the representative portion of the Brillouin Zone, to evaluate $E(\underline{k})$ for that point in each band, and to store in a histogram form the number of energies appearing in each of a number of small energy intervals. After doing this for a large number of points in the zone, say several thousand, the histogram can be used to give a good idea of the density of states curve, and thence the Fermi energy. An example is shown sketched below in Figure 6.3.

FIGURE 6.3 DENSITY OF STATES CURVE.

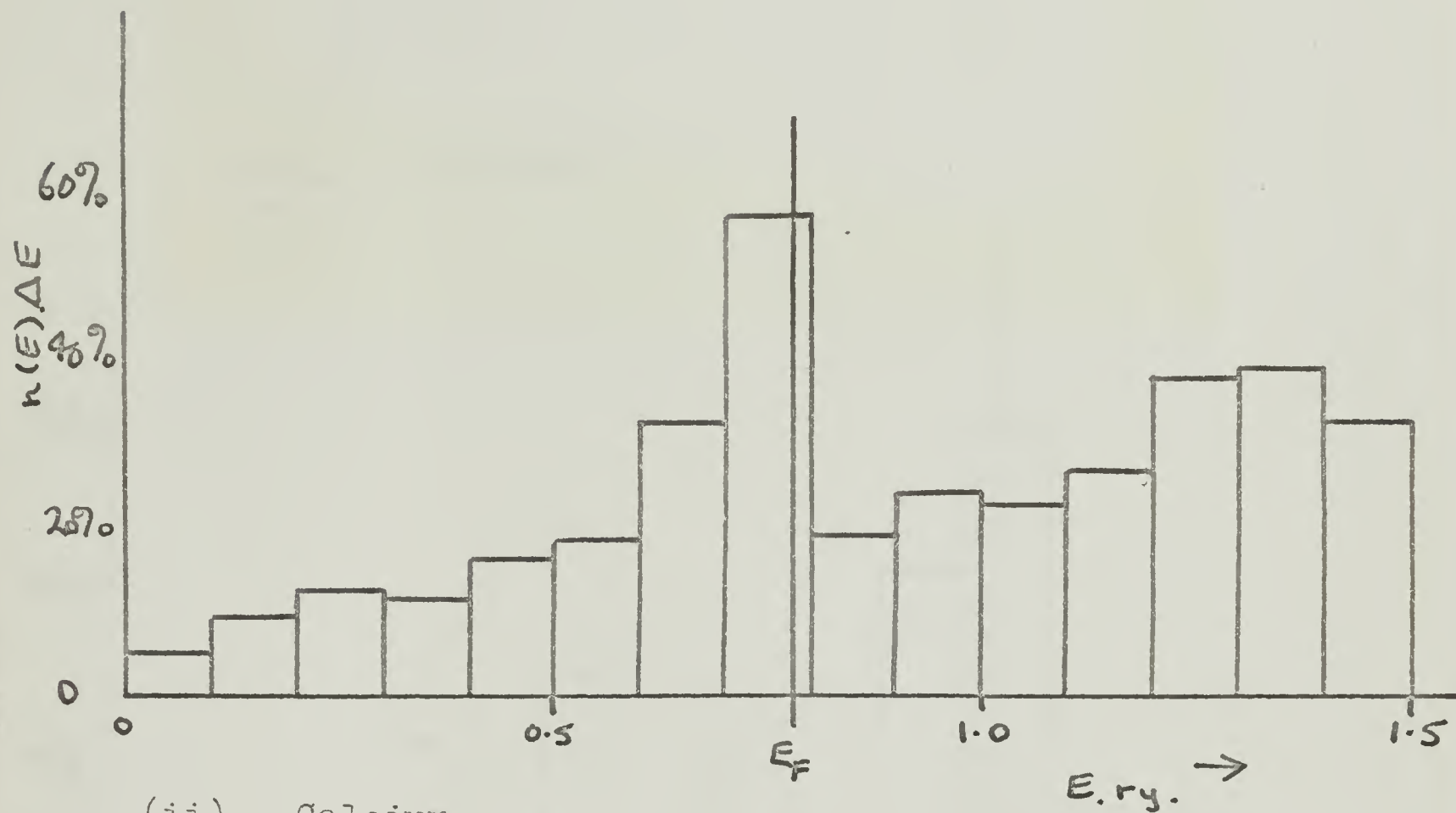


Any band contains $2N$ states and the $n(E)$ given as $p\%$ for a certain range of energy, ΔE , means that there are $2Np/100$ states in that energy range, with spin taken into account. If the total number of conduction electrons per atom is s then there are sN electronic states to be occupied and the Fermi energy must occupy so that the area shaded in Figure 6.3 is equal to sN , thus:

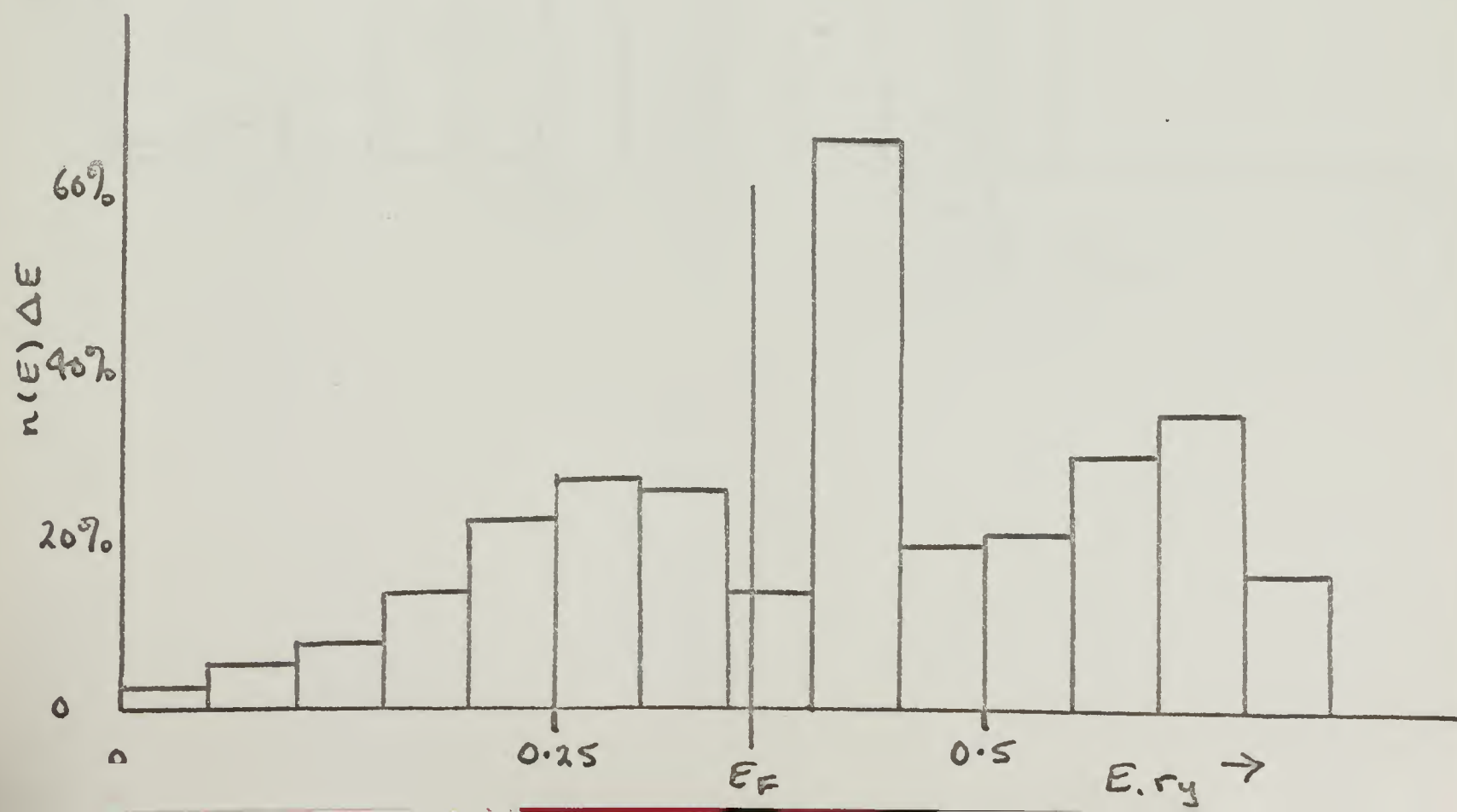
$\sum_i P_i = 100s/2$, and the Fermi energy is found by satisfying this condition.

In Figure 6.4 are shown the $n(E)$ curves computed for Al, Ca, Sc, and Co. The curve for Co is a little speculative for the reasons given in the note on Figure 5.6. It can be seen to be fairly similar to the $n(E)$ curve of the simple model due to Mott (1935) which appears to be believed in implicitly at least by metallurgists, see e.g. Hume-Rothery (1963) p.93, and which is also shown in Figure 6.4. The four metals all possess the pronounced double peak common to most theoretical $n(E)$ curves. It will be noticed that the $n(E)$

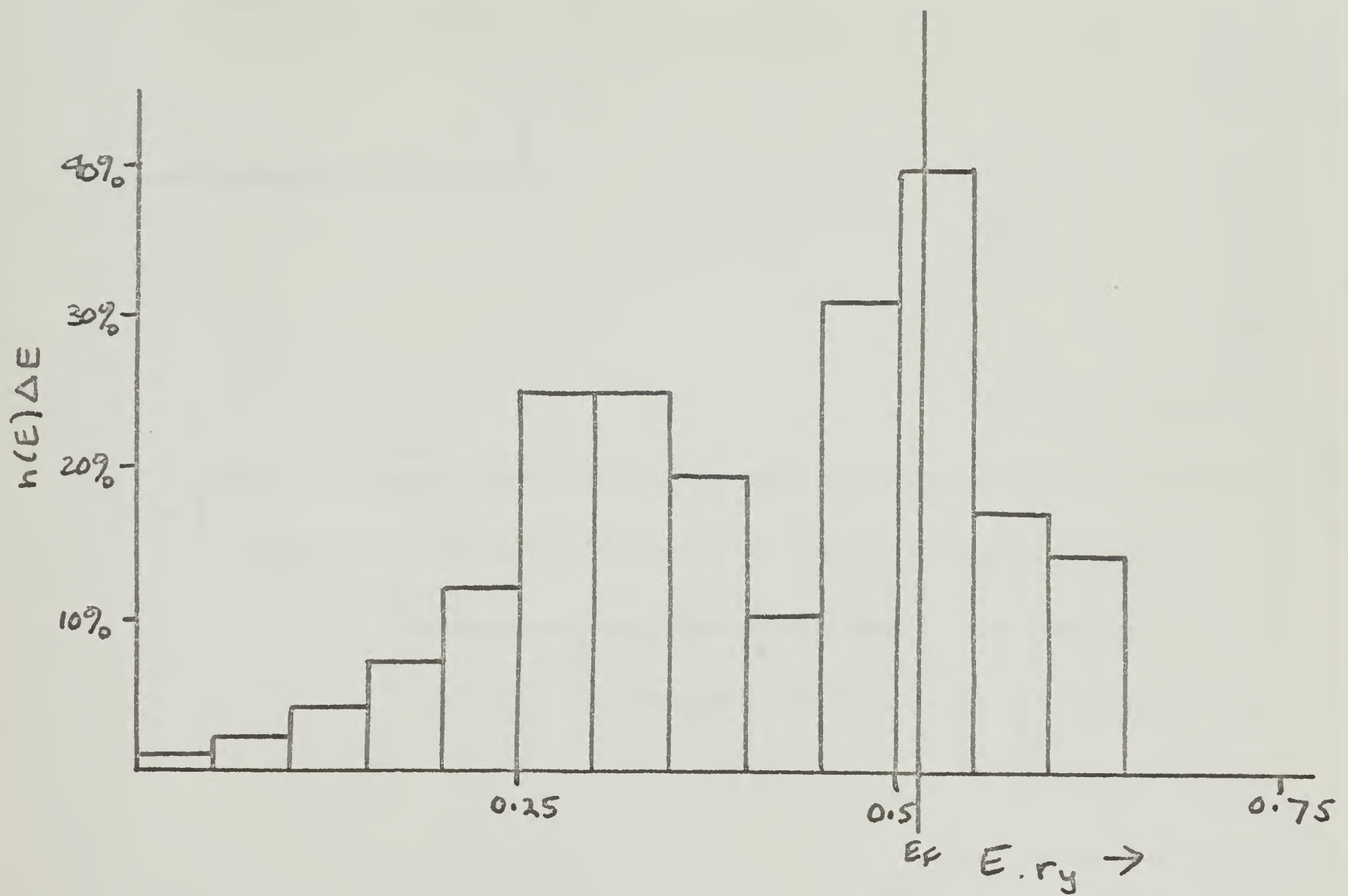
(i) Aluminium.

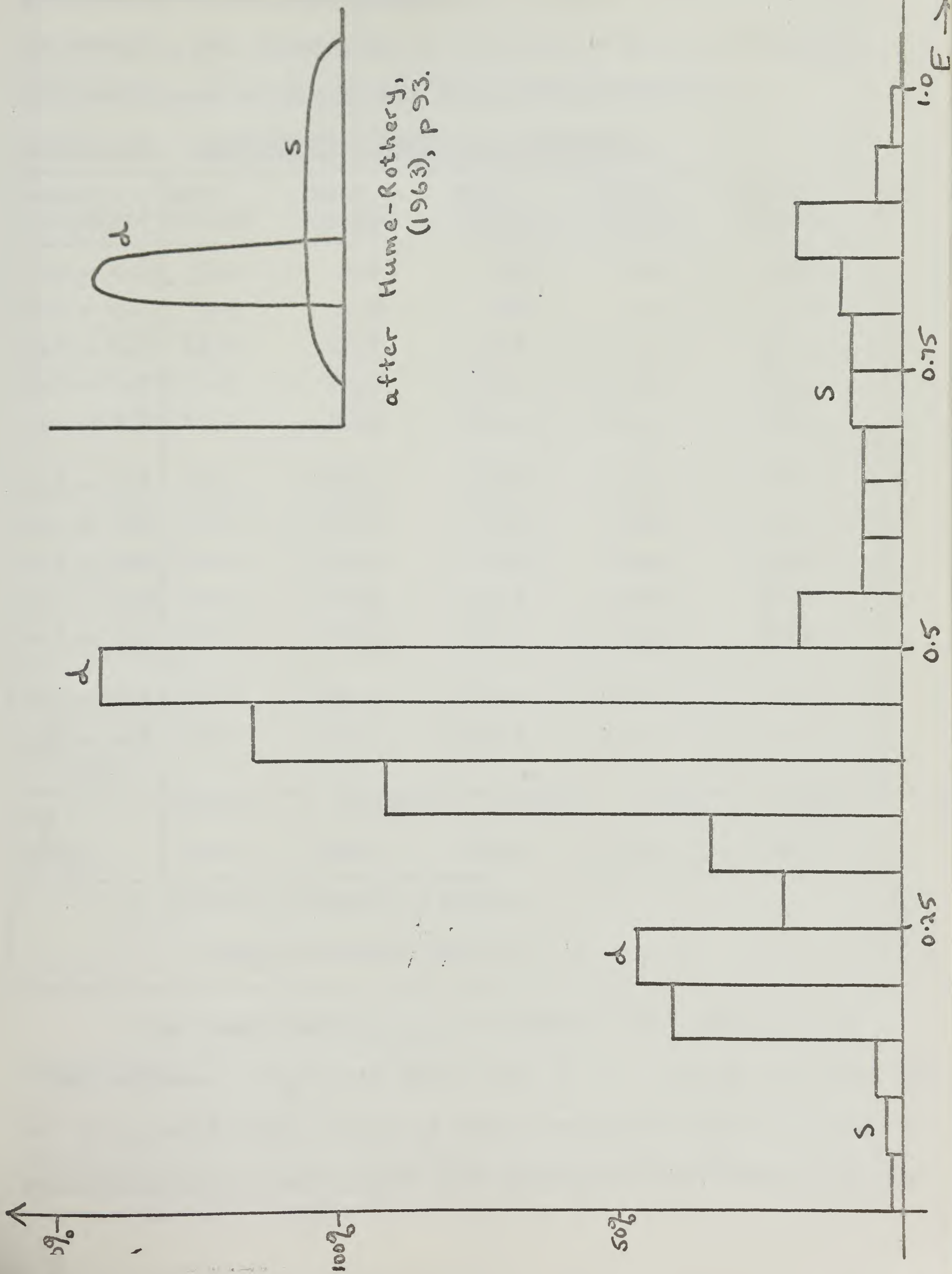


(ii) Calcium.



(iii) Scandium.





curve for calcium does not possess the very narrow d band postulated in the calculation of Manning and Krutter (1937). An example, for aluminium, of the data used in constructing the histograms of Figure 6.4 is given in Table 6.1.

TABLE 6.1 DENSITY OF STATES FOR ALUMINIUM.

Energy range(ry)	1000 points	2000 points	3000 points	4000 points	5000 points
0.0 - 0.1	5.0	4.7	4.6	4.9	4.9
0.1 - 0.2	7.8	8.6	8.9	9.1	9.1
0.2 - 0.3	11.4	11.7	12.2	11.9	12.0
0.3 - 0.4	11.8	10.8	11.1	10.8	11.1
0.4 - 0.5	14.2	15.0	15.2	15.3	15.6
0.5 - 0.6	19.5	18.9	18.3	18.6	18.1
0.6 - 0.7	31.5	32.6	31.8	31.9	31.6
0.7 - 0.8	59.0	57.3	57.6	56.4	55.8
0.8 - 0.9	16.7	17.3	18.3	18.3	18.7
0.9 - 1.0	25.9	23.8	23.4	23.3	23.5
1.0 - 1.1	21.8	22.2	21.4	21.8	22.0
1.1 - 1.2	25.2	25.2	25.4	25.6	25.6
etc.					
E_F	0.783	0.783	0.783	0.784	0.785
$p(E_F)$	54.2	52.2	53.3	52.6	52.3
final $E_F = 0.784 \pm 0.001$					
$p(E_F) = 52.9 \pm 0.7 \%$					

The Fermi energy, E_F , and density of states at the Fermi surface, $p(E_F)$, are given for Al, Ca, and Se in Table 6.2. For each metal 5000 points in each band were computed (this is equivalent to 240,000 points per band over the whole zone) and

the errors quoted are the variance found from the separate results for each 1000 points.

TABLE 6.2 FERMI ENERGY AND DENSITY OF STATES FOR

Al, Ca and Sc.

	Al	Ca	Sc
E_F (ry)	0.784	0.375	0.516
error in E_F (ry)	± 0.005	± 0.002	± 0.002
E_F free-elec(ry)	0.85	0.35	0.68
E_F (ev) expt	11.8	7.0(?)	-
E_F (ev) calc	10.7	4.98	7.02
p_F	52.9	20.9	34.2
error in p_F	± 0.7	± 0.1	± 0.2
ΔE (ry)	0.1	0.05	0.05

The experimental values of E_F are taken, for Al from Skinner (1940), and for Ca from Skinner, Bullen and Johnston (1954). It will be noticed that for Al and Sc the Fermi energies computed are less than the free-electron Fermi energies, but for Ca the Fermi energy computed is greater than the free-electron Fermi energy. On the other hand considering the general shapes of the bands as shown in the previous chapter the Al band shapes are much less perturbed from the free-electron band shapes than is the case for Ca or Sc. This all suggests that the bands computed for Ca are not sufficiently compressed and this leads to a Fermi energy which is too large and to a density of states which is too small.

If the interval in energy used in the histogram is ΔE ry then the number of states in the range ΔE is $n(E)\Delta E = 2Np/100$, so that $n(E) = 2Np/100\Delta E$ states ry⁻¹.

Where we use the density of states at the Fermi surface, $n(E_F)$ in the next few sections a formula in terms of $p_F/\Delta E$ will be deduced and the values given in Table 6.2 will be used.

The importance of the $n(E)$ curve is that it enables theoretical values of the temperature coefficient of the electronic specific heat, the Pauli spin paramagnetic susceptibility and, together with the knowledge of the wave functions, the Knight shift to be calculated. These are considered separately in the following sections.

Direct measurement of the Fermi energy of a metal is not easy; in the past great store has been set by the soft X-ray measurements but recently grave doubts have been expressed about much of the X-ray work, e.g. by Hume-Rothery, (1953) p 94, who claims that the samples used in most of the earlier work were spoilt by surface contamination.

6.4 The Electronic Specific Heat.

The electronic specific heat per mole is, Mott and Jones (1936) p 179,

$$C_V = \pi^2 n(E_F) k^2 T/3 = \gamma T, \text{ so that}$$

$$\gamma = \pi^2 n(E_F) k^2/3.$$

Substituting for k and π , and from the previous section for $n(E_F)$ we find that:

$$\gamma = \frac{(3.142)^2 \times (1.380 \times 10^{-16})^2 \times 2 \times 6.023 \times 10^{23}}{5 \times 4.186 \times 10^7 \times 100 \times 2.1796 \times 10^{-11}} \times \frac{p_F}{\Delta E} \text{ cal mole}^{-1} \text{ deg}^{-2}$$

$$= 8.23 \times 10^{-7} \times p_F / \Delta E \text{ cal mole}^{-1} \text{ deg}^{-2},$$

where p_F is in % and ΔE is in rydbergs as in Table 6.2. The values of γ deduced using this formula are given for Al, Ca and Sc in Table 6.3, together with the experimental values, the sources of the experimental values are, for Al and Ca Rosenberg (1963) and for Sc Iomer (1962).

TABLE 6.3 TEMPERATURE COEFFICIENT OF THE ELECTRONIC
SPECIFIC HEAT FOR Al, Ca, and Sc.

	Al	Ca	Sc
γ calc.	4.35	3.44	5.63
γ exp.	3.24	6.5	24.7
γ calc	1.82	1.44	2.36
γ exp	1.36	2.8	10.5

Note: the units in the first two rows are $\text{cal mole}^{-1} \text{ deg}^{-2}$, and in the second two rows are $\text{mJ mole}^{-1} \text{ deg}^{-2}$.

The theoretical values appear to be too high for Al and too low for Ca and Sc. The high value for Al suggests that our band structure is probably slightly too compressed and the Fermi energy too low; the low value for Ca suggests that there should be rather more overlap between the first and second bands to make $n(E_F)$ larger. The value for scandium is inexplicable; it has been suggested that the $n(E)$ curve has a very high and narrow peak near the Fermi energy but this seems unreasonable.

The low value for calcium agrees with the result of the previous section that its band structure is not sufficiently compressed, its Fermi energy is too high, and consequently $n(E)$ is too low. The values for cobalt are not included because the density of states curve in Figure 6.4 (iv) is only tentative.

6.5 The Pauli Spin Paramagnetic Susceptibility.

The Pauli spin paramagnetic susceptibility χ_p is, like χ , directly deducible from the density of states curve and it is given, Mott and Jones (1936) p 186, by:

$$\chi_p = (\mu_B)^2 n(E_F),$$

where μ_B is the Bohr magneton, $= 9.273 \times 10^{-21}$ erg gauss $^{-1}$.

In terms of p_F and ΔE then,

$$\chi_p = \frac{(9.273 \times 10^{-21})^2 \times 2 \times 6.023 \times 10^{23}}{100 \times 2.1796 \times 10^{-11}} \times \frac{p_F}{\Delta E} \text{ e.m.u. mole}^{-1},$$

$$\text{i.e. } \chi_p = 4.75 \times 10^{-8} p_F / \Delta E \text{ e.m.u. mole}^{-1}.$$

The computed and experimental values of χ_p for Al, Ca and Sc are given in Table 6.4, both in e.m.u. mole $^{-1}$ and in e.m.u. gm $^{-1}$. The experimental values are taken from Gussack (1958). Even if the density of states curve for cobalt were completely reliable there would be little point in computing its paramagnetic susceptibility since these values are for absolute zero and the modifications necessary for any other temperature, such as above the Curie point of cobalt, are not considered here; the theory is given by Mott and Jones (1936) p 186.

TABLE 6.4 PARAMAGNETIC SUSCEPTIBILITY OF Al, Ca, and Sc.

	χ_p calc.	χ_p expt.
Al	25.1	17.5
	0.93	0.65
Ca	19.9	44.1
	0.50	1.10
Sc	32.5	315
	0.72	7.0

Note: values are given in units of 10^{-6} e.m.u. mole $^{-1}$ in the first row for each metal and of 10^{-6} e.m.u. gm $^{-1}$ in the second row.

Lomer (1952) points out that the experimental ratio of χ_p/γ is far from the constant $3(\mu_B)^2/\pi^2 k^2 = 5.76 \times 10^{-2}$, where χ_p is in e.m.u. mole $^{-1}$ and γ is in cal mole $^{-1}$ deg $^{-2}$, which it should be from the theory. He attributes it to the fact that there is also a van Vleck temperature independent contribution to the paramagnetism if over a large part of the Brillouin zone there are levels in different bands just below and just above the Fermi level separated by about 1 or 2 ev, i.e. by about 0.1 ry. This contribution, which is by no means easy to calculate, can often be as large as the Pauli contribution. The discrepancy is largest in Sc, and this very large susceptibility is known to be temperature independent, Blumberg et al (1960), so that it seems clear that the Pauli susceptibility which we have calculated is not the only

contribution to the paramagnetic susceptibility, and it is the latter which is measured experimentally and listed in the last column of Table 6.4.

6.6 The Fermi Surface.

Using the interpolation routine described above random $\underline{k}$ -vectors can be generated and $E(\underline{k})$ calculated for each of the bands. If $E(\underline{k})$ is very near the Fermi energy then the programme prints $\underline{k}$, $E(\underline{k})$ and the band number. From these outputs sections of the Fermi surface have been drawn so that the shapes of the Fermi surfaces of Al, Ca and Sc could be deduced. Co is ferromagnetic so that this is an extra complication, in addition to the computational difficulties with Co which have already been mentioned.

(1) Aluminium.

The outlines of the present calculation on aluminium are roughly the same as those of the calculation due to Heine (1956; 1957) since the same field has been used. In this calculation the bands are rather more compressed though the ordering of the levels, especially at W is the same as in Heine's original calculation. At W the lowest level is the degenerate level E ($=W_3$) and the next levels are B_2 ($=W_2'$) and A_1 ($=W_1$) respectively. Heine tried various slight modifications of the potential to see how the levels at W were affected. The interest, in aluminium, centres around the point W because, as shown in Figure 5.3, the first two

levels E and B_2 at W are very close together and very near to the Fermi level. It is clear that, while our results agree with those of Heine very well for the general shape of the bands and the ordering of the levels we have nothing much to add to his results. From the de Haas-van Alphen effect experiments there is, as Heine showed, probably a pocket of electrons in the third band at W and thus the Fermi level is just above the B_2 level at W which makes the first and second bands at W also full. Ashcroft (1963) devoted considerable attention to the study of the levels at W in aluminium, and if we accept the ordering of the levels obtained by Heine originally and now in this calculation it follows that either two, three or four levels at W must be full and to fit the de Haas-van Alphen results described in the next section we must assume the Fermi level to be above the WB_2 level. If the interpolation for the $E(k)$ and hence the Fermi energy were more accurate we could say definitely how many levels at W are occupied according to our calculations. Apart from W there is little doubt about the details of the Fermi surface of Al. The first band is full everywhere, the second band is full all over the surface of the zone but has a very large Fermi surface of holes centred on Γ . The detailed shape of the Fermi surface in the second band is the most useful thing we can deduce from our calculations; this is not very sensitive to the small changes in Fermi energy which are so important at W . The third band

FIGURE 6.5 THE FERMI SURFACE OF ALUMINIUM.

Band 2, sections, with electrons shaded.

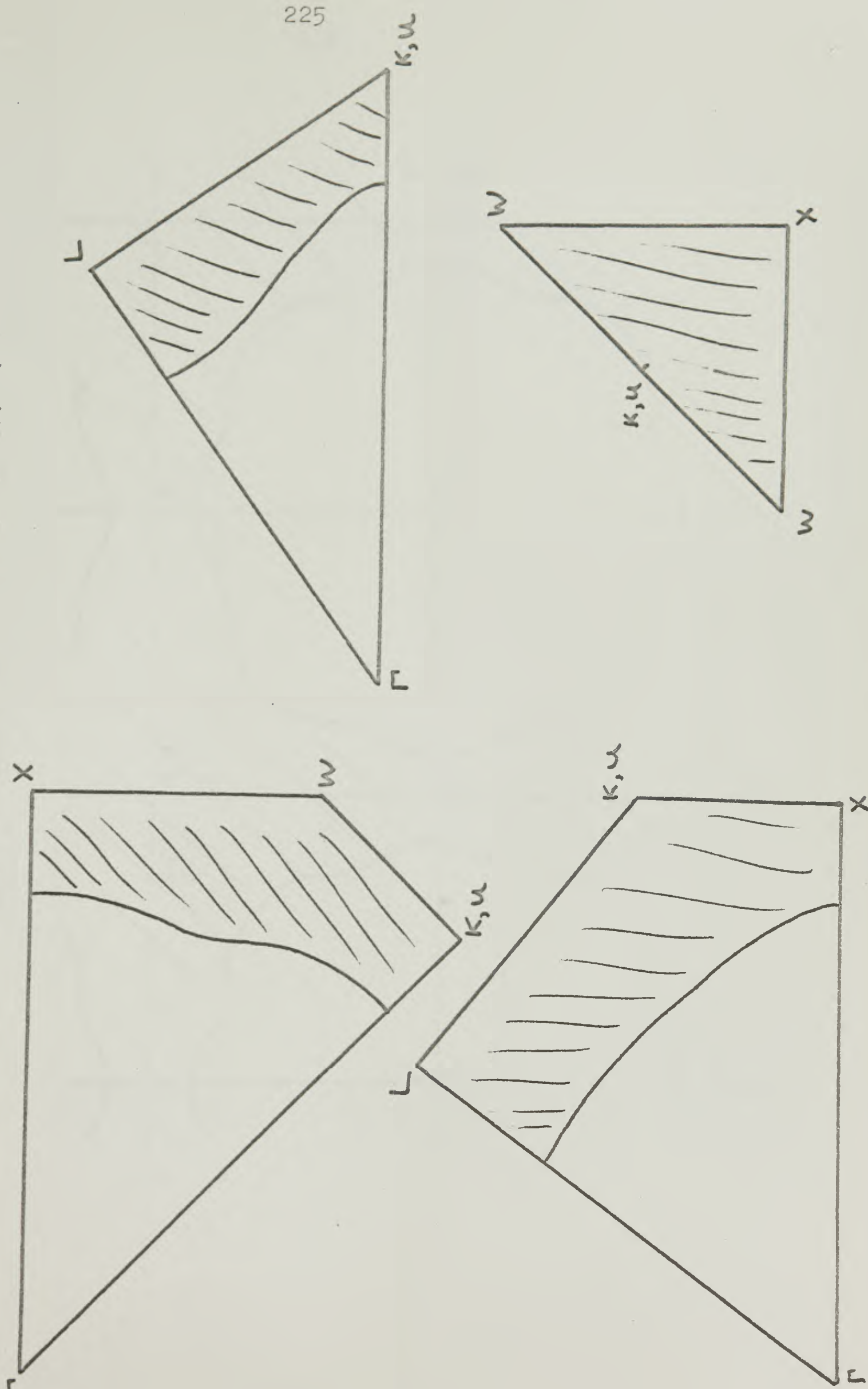


FIGURE 6.5 (contd.)

Band 2. 100 section, with electrons shaded.

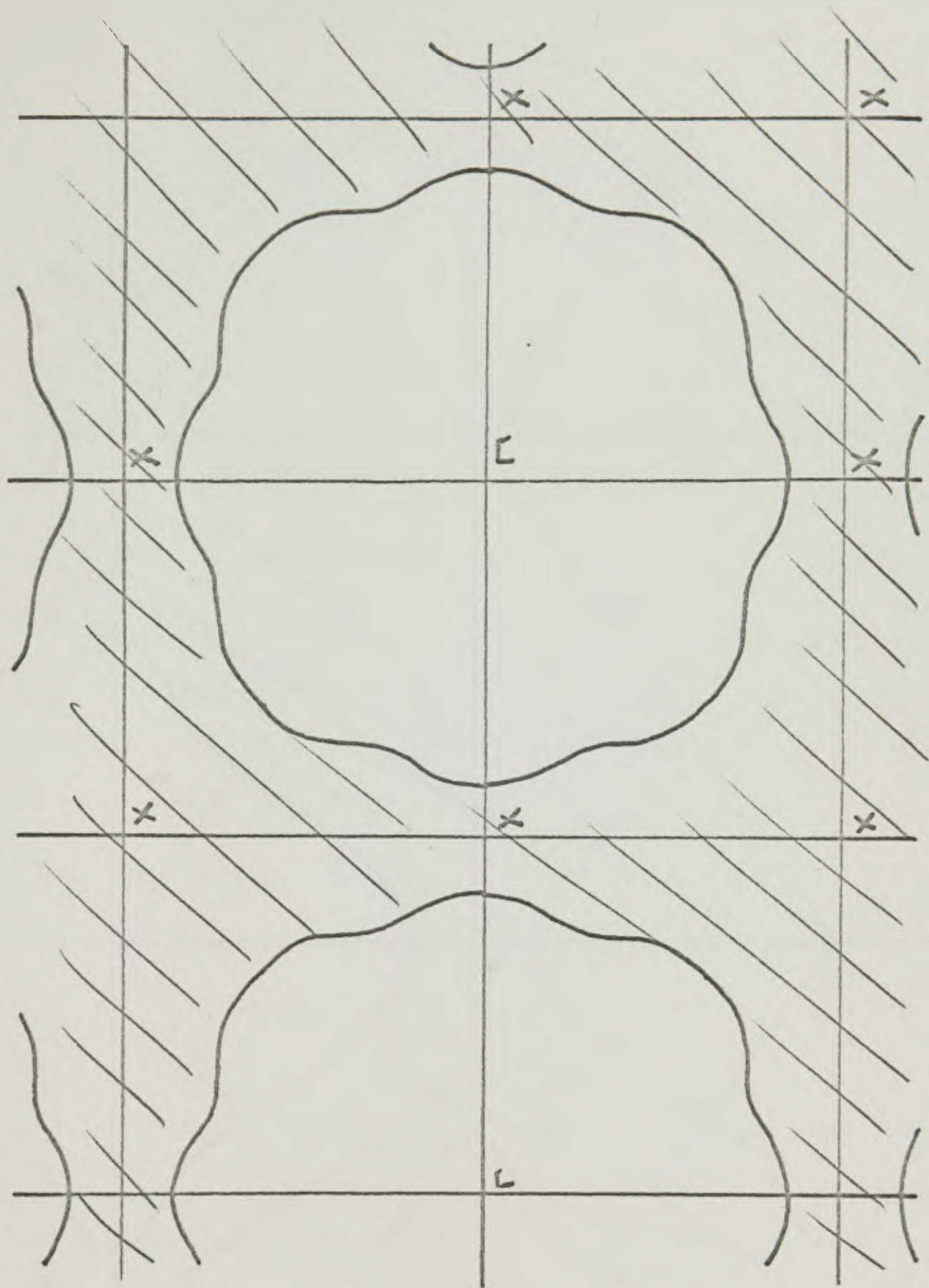
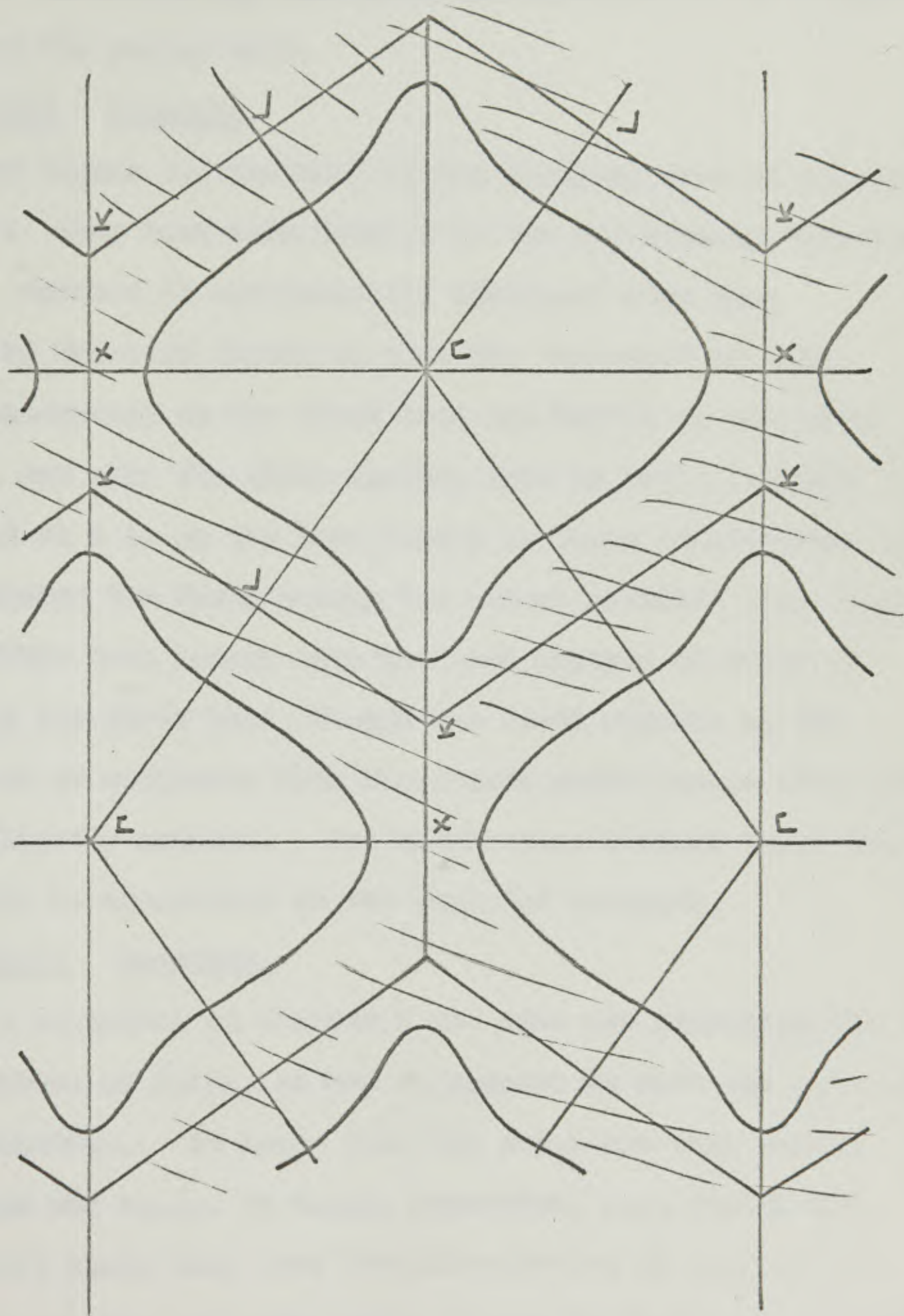


FIGURE 6.5 (contd.)

Band 2, 110 section, with electrons shaded.



contains just a small pocket of holes at W whose size it is best to estimate from the de Haas-van Alphen experimental results. In Figure 6.5 are shown the sections of the Fermi surface in the second band.

(ii) Calcium.

In Figure 6.6 sections of the Fermi surface of calcium are shown; they have been deduced in the way already described. The Fermi surface is substantially different from that proposed by Harrison (1965) in that the "monster" of holes which he suggested in the first band has become in our model dissected and only the limbs remain, this is really because the first band at W is on the band scheme of these calculations a long way below the Fermi energy and cannot possibly have holes there. This then leaves only isolated pockets of holes at K and U in the first band, though the Fermi surface in the second band is unaltered from Harrison's model except that its size is slightly reduced. The differences between these two models will be considered in the next few sections.

(iii) Scandium.

As mentioned in Chapter V the case for computing the band structure of f.c.c. Sc was to compare it with the h.c.p. form of scandium. It seems that the metal can very easily change from the h.c.p. to f.c.c. structure, e.g. Taylor and Kagle (1963) claim that even the introduction of 0.4% Si and 0.4% Fe impurities can cause Sc to change to the f.c.c. structure

FIGURE 6.6 THE FERMAT SURFACE OF CALCULI

Band 1, sections, with holes shaded.

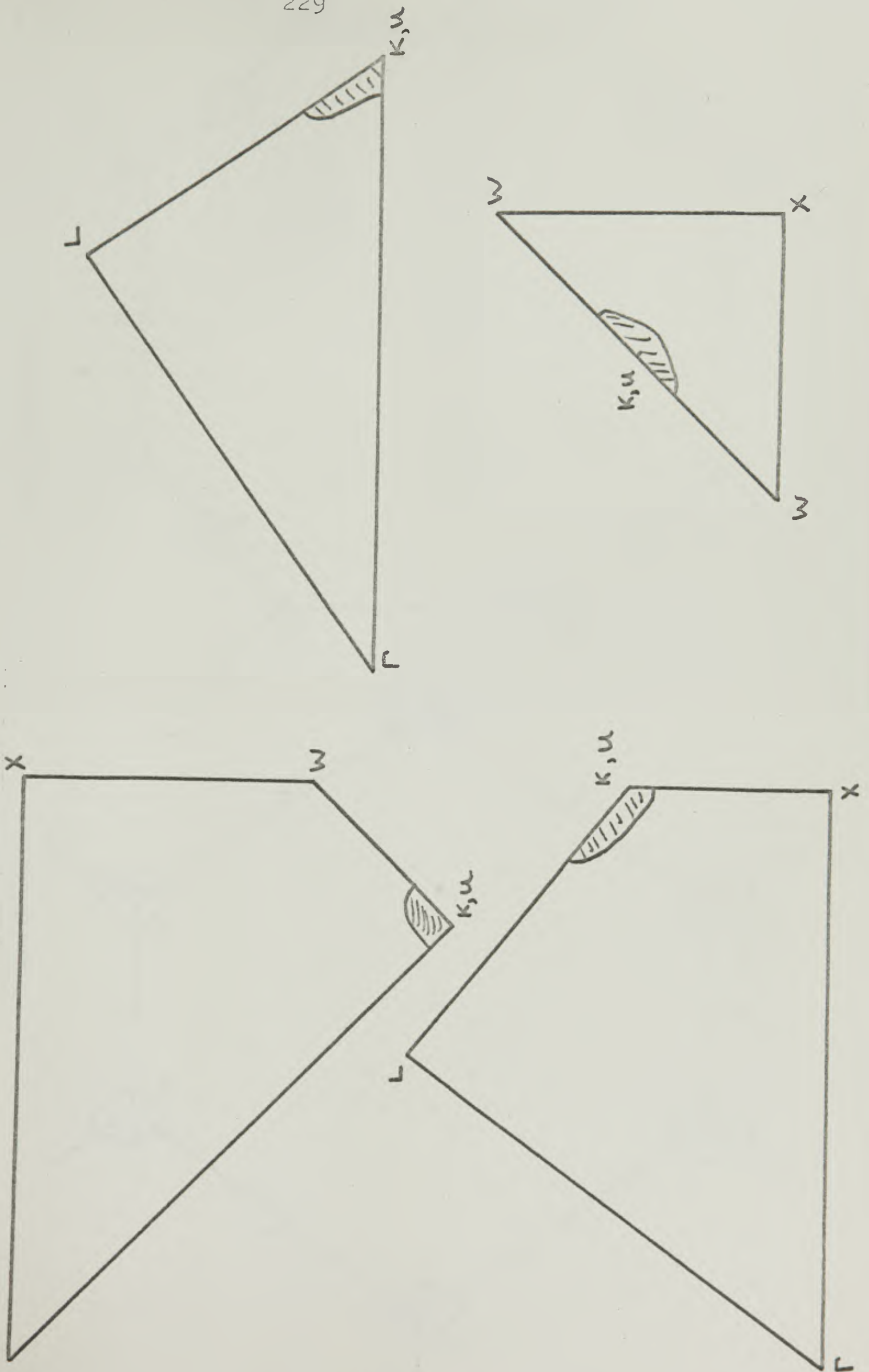
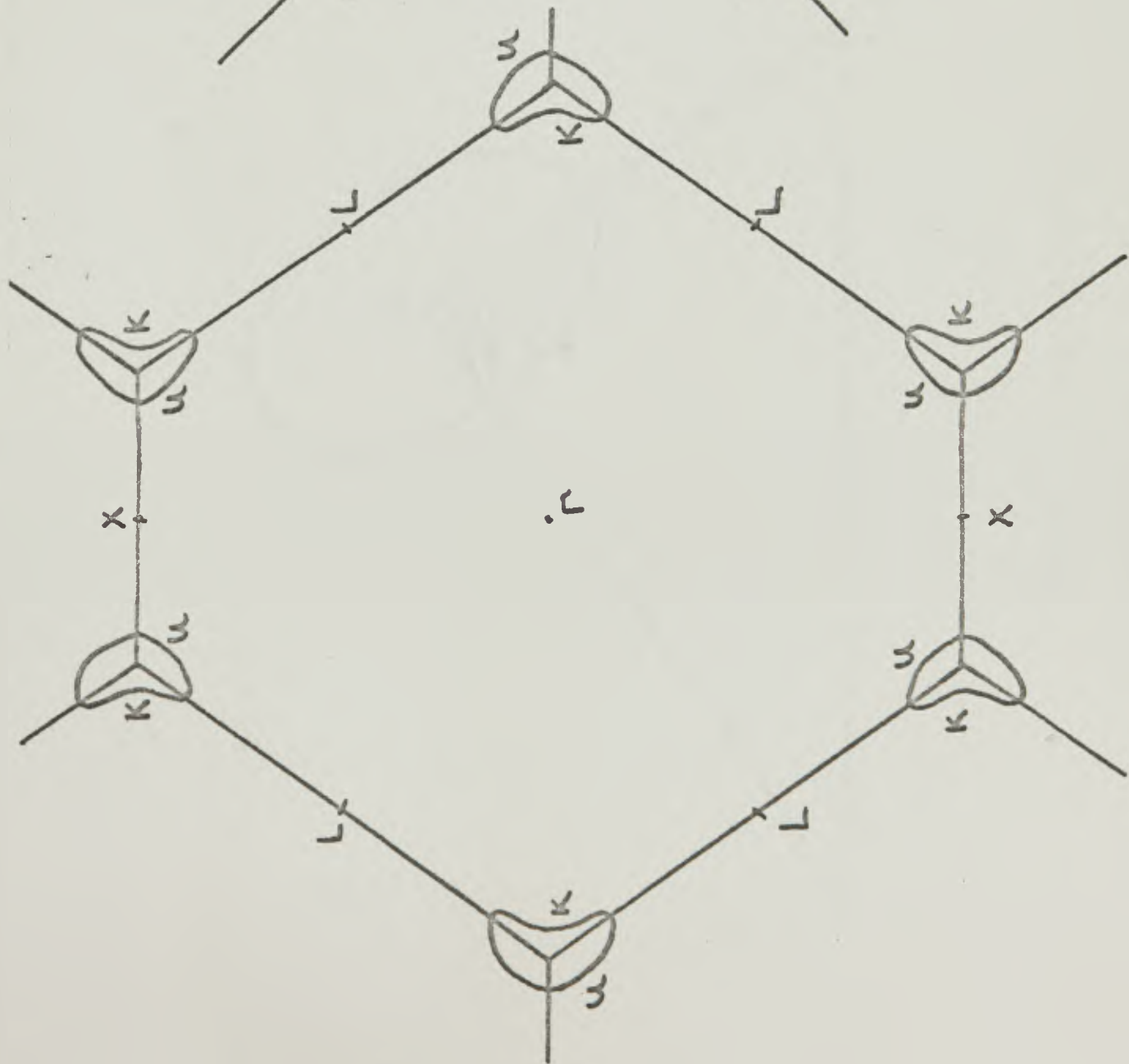


FIGURE 6.6 (contd.) Band 1.

110 section.



100 section.

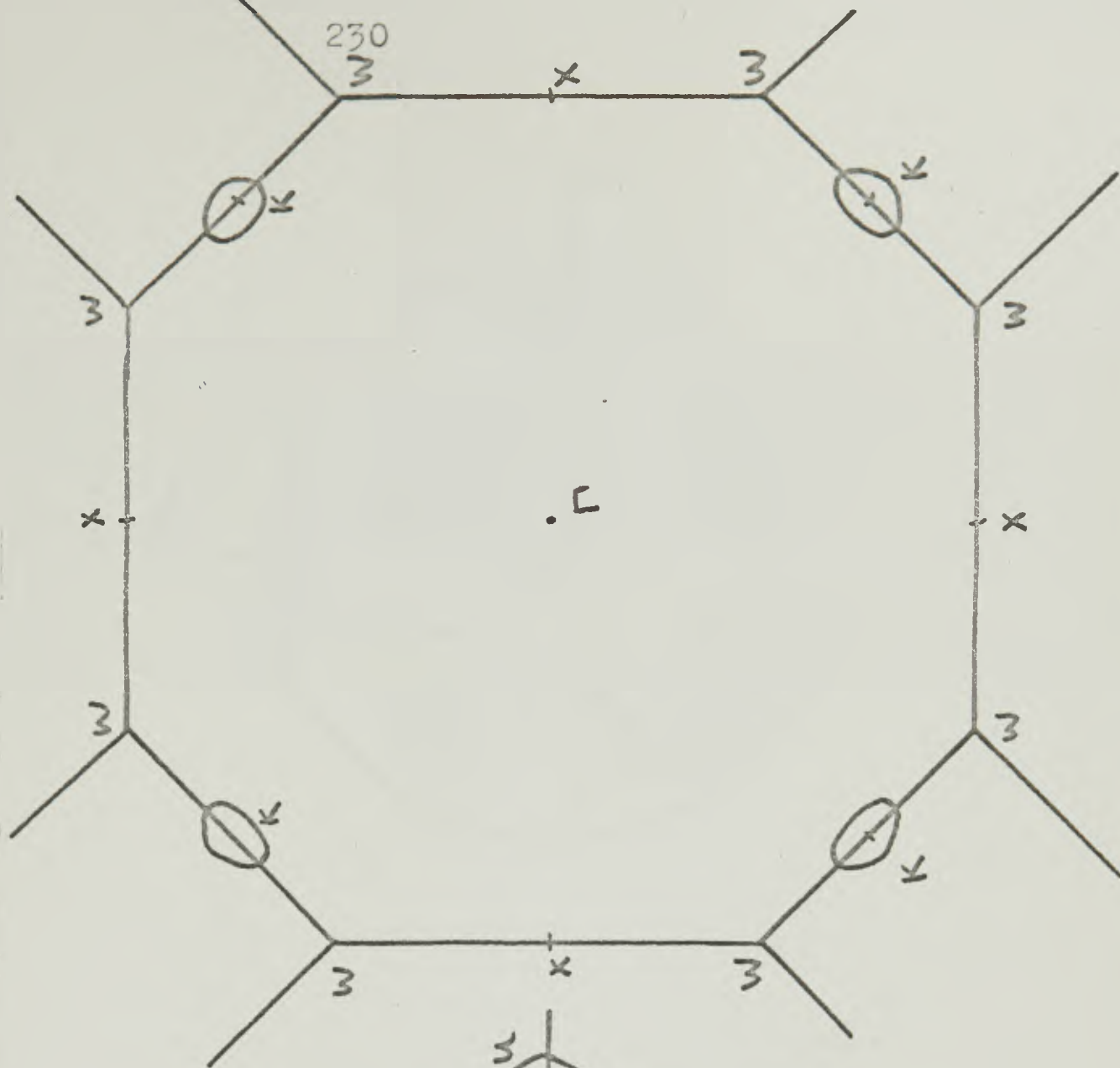
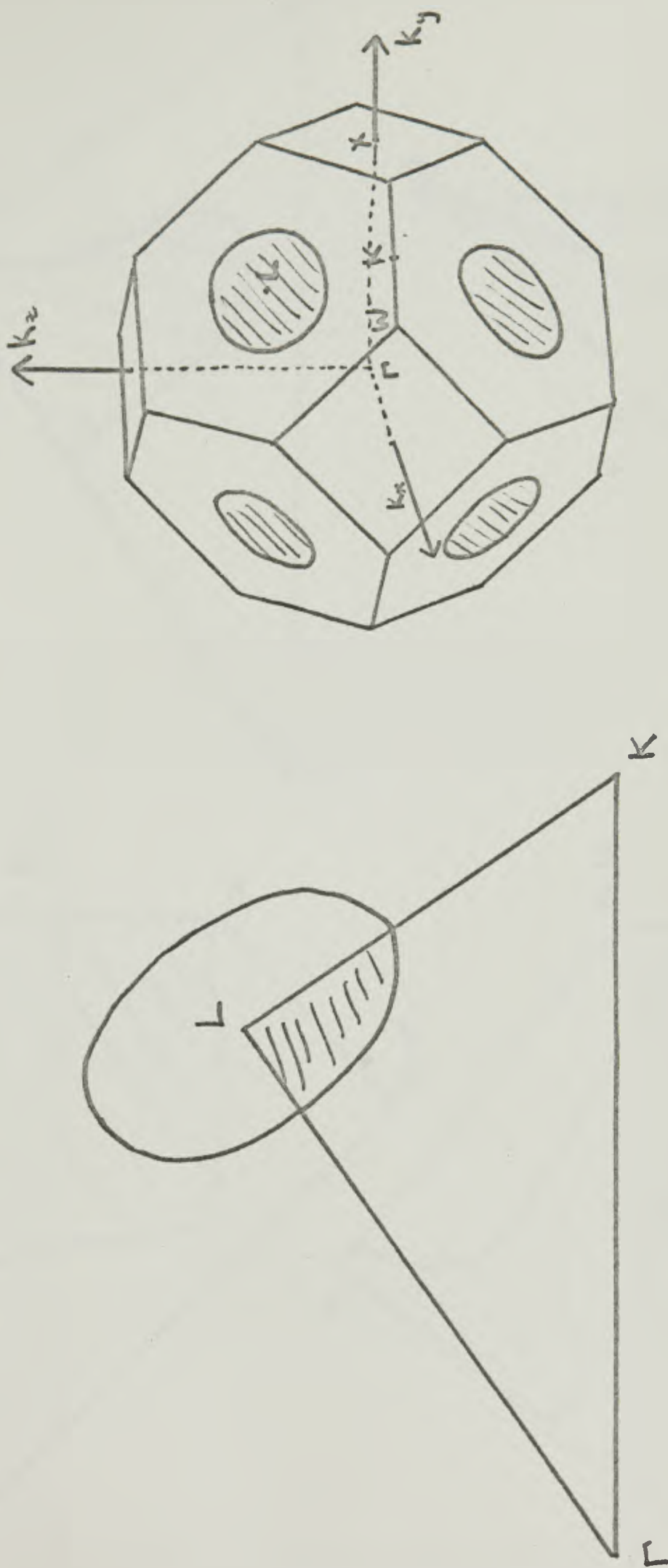


FIGURE 6.6 (contd.) Band 2, electrons shaded.



The Fermi surface in the second band consists of discs in the $l\bar{l}l$ planes and with the section normal to these planes shown in the diagram on the left.

FIGURE 6.7 THE FERMII SURFACE OF SCANDIUM.

Band 2, sections, with electrons shaded.

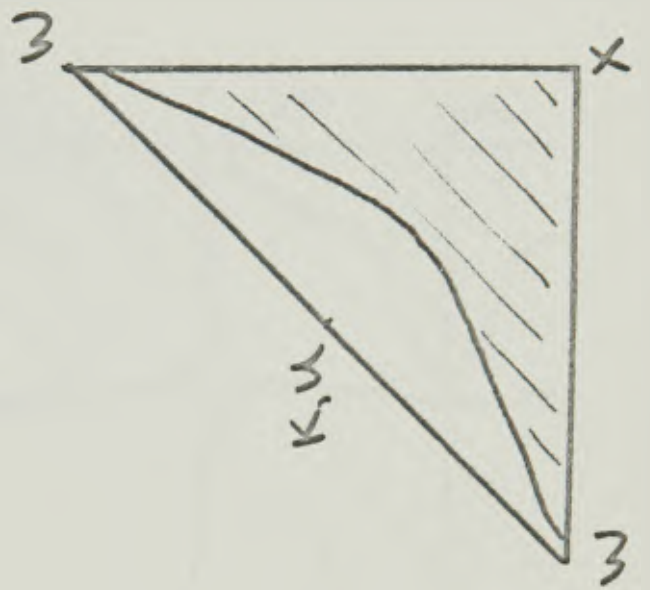
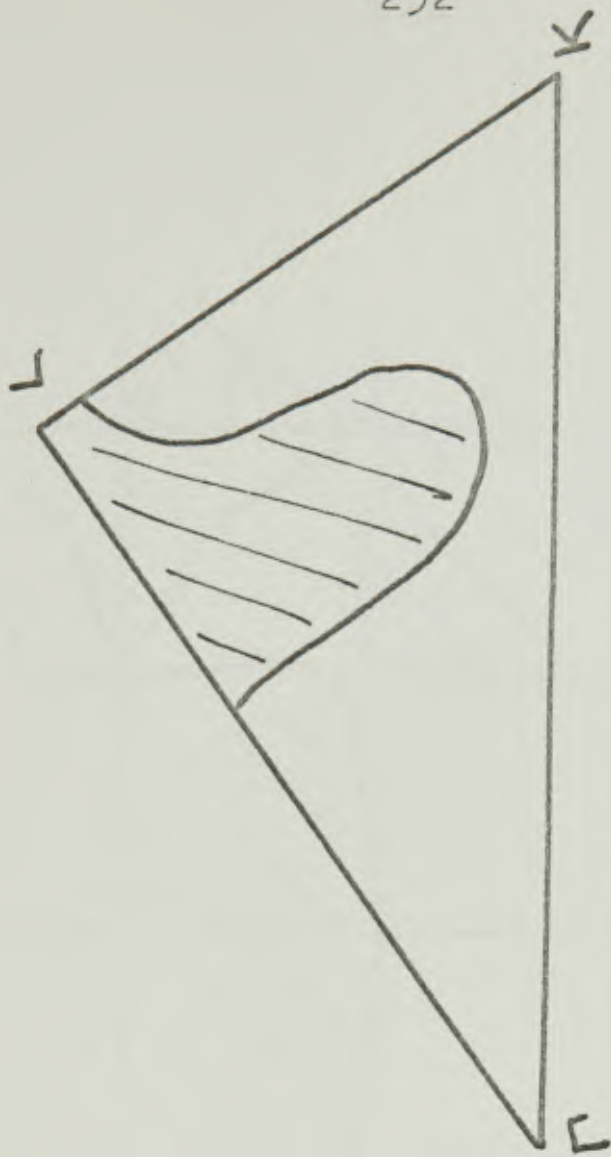
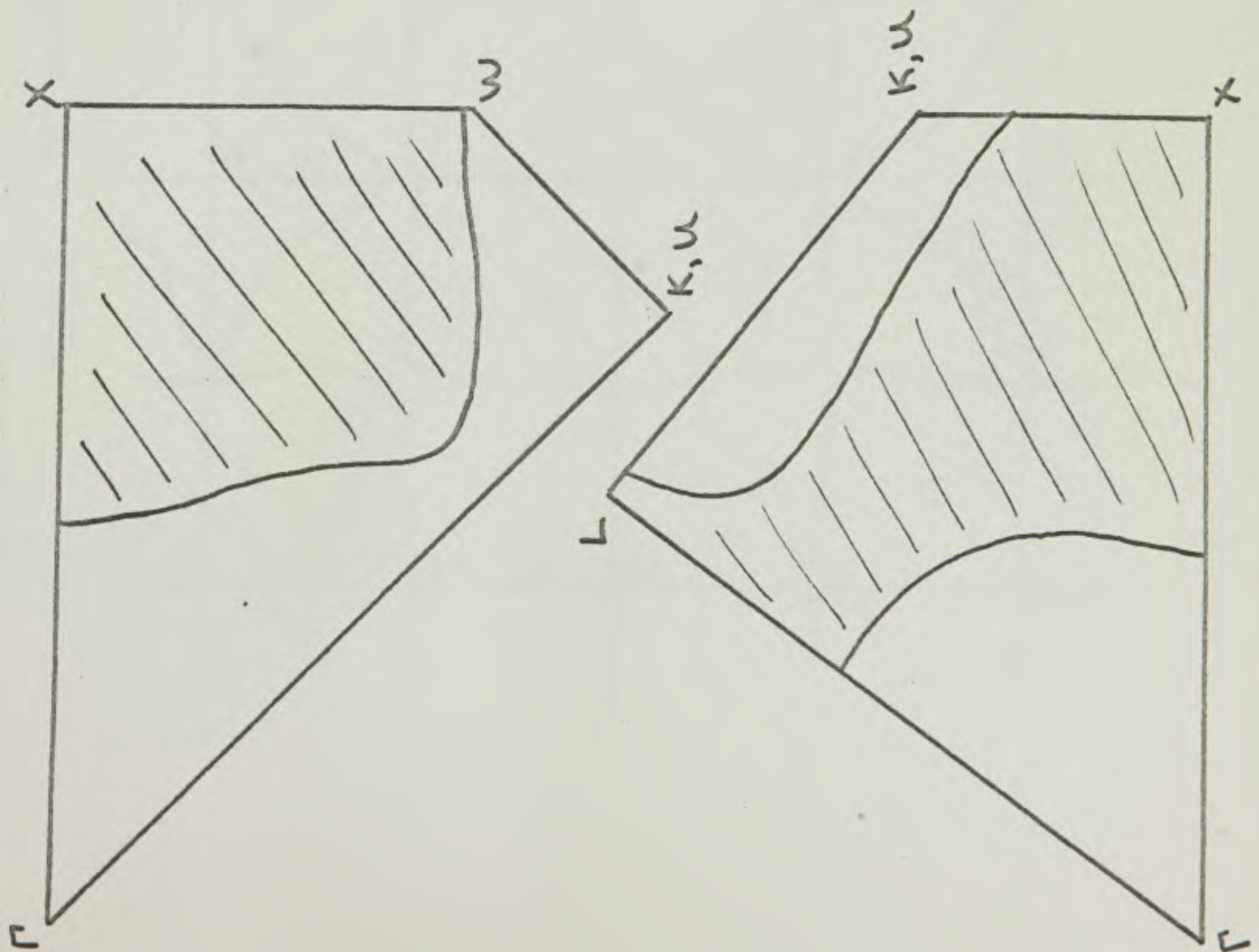


FIGURE 6.7 (contd.)

Band 2. 100 section, with electrons shaded.

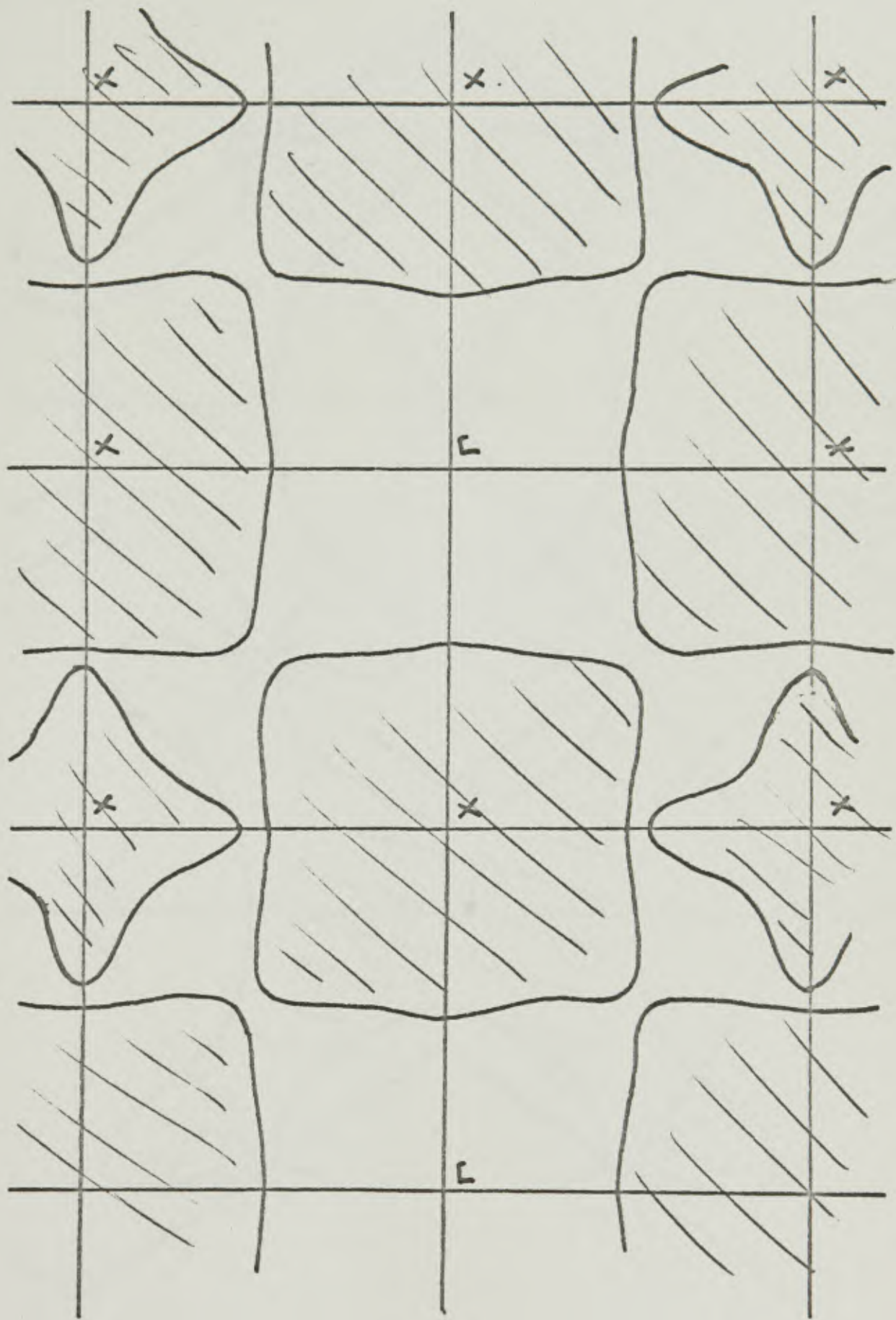


FIGURE 6.7 (contd.)

Band 2. 110 section, with electrons shaded.

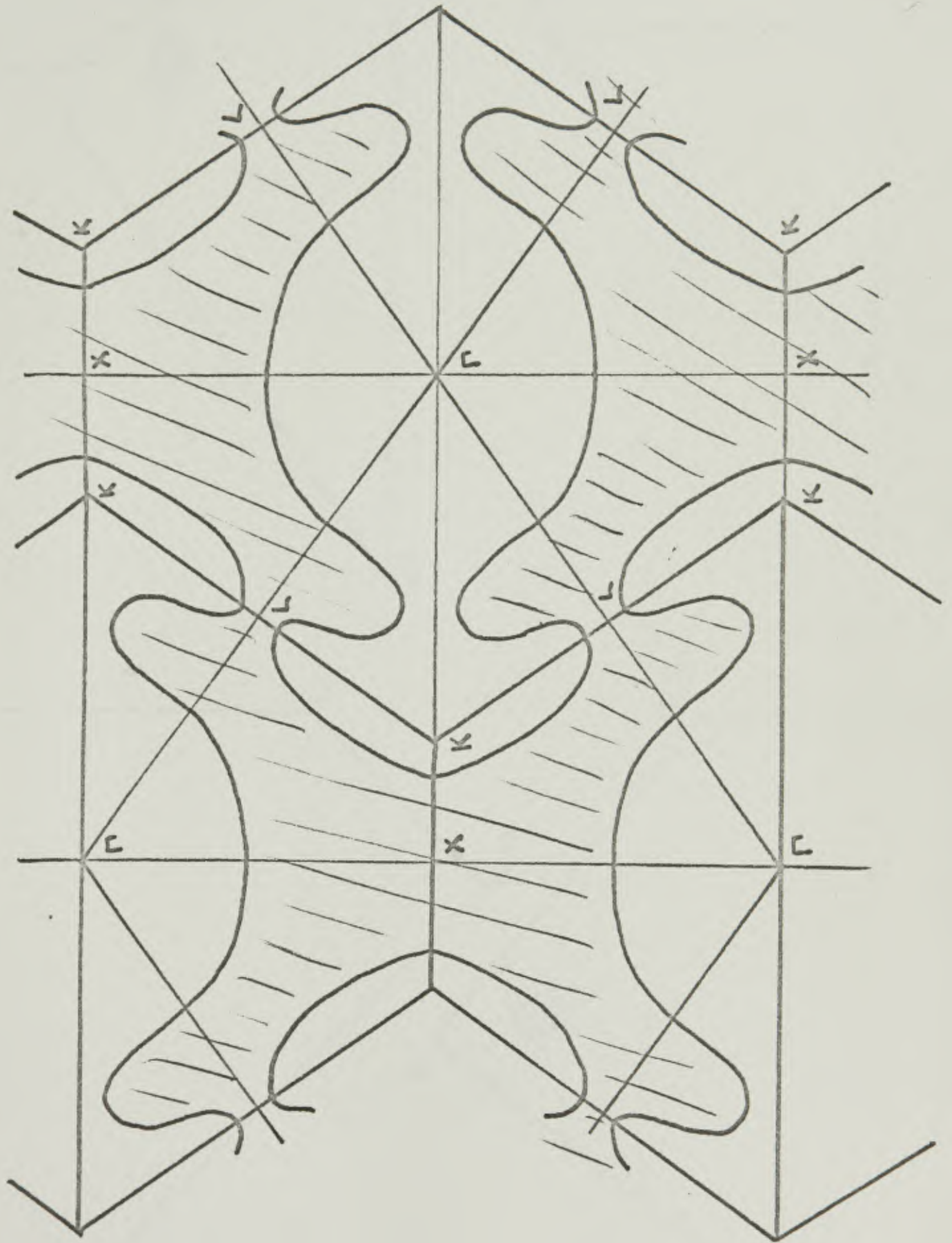
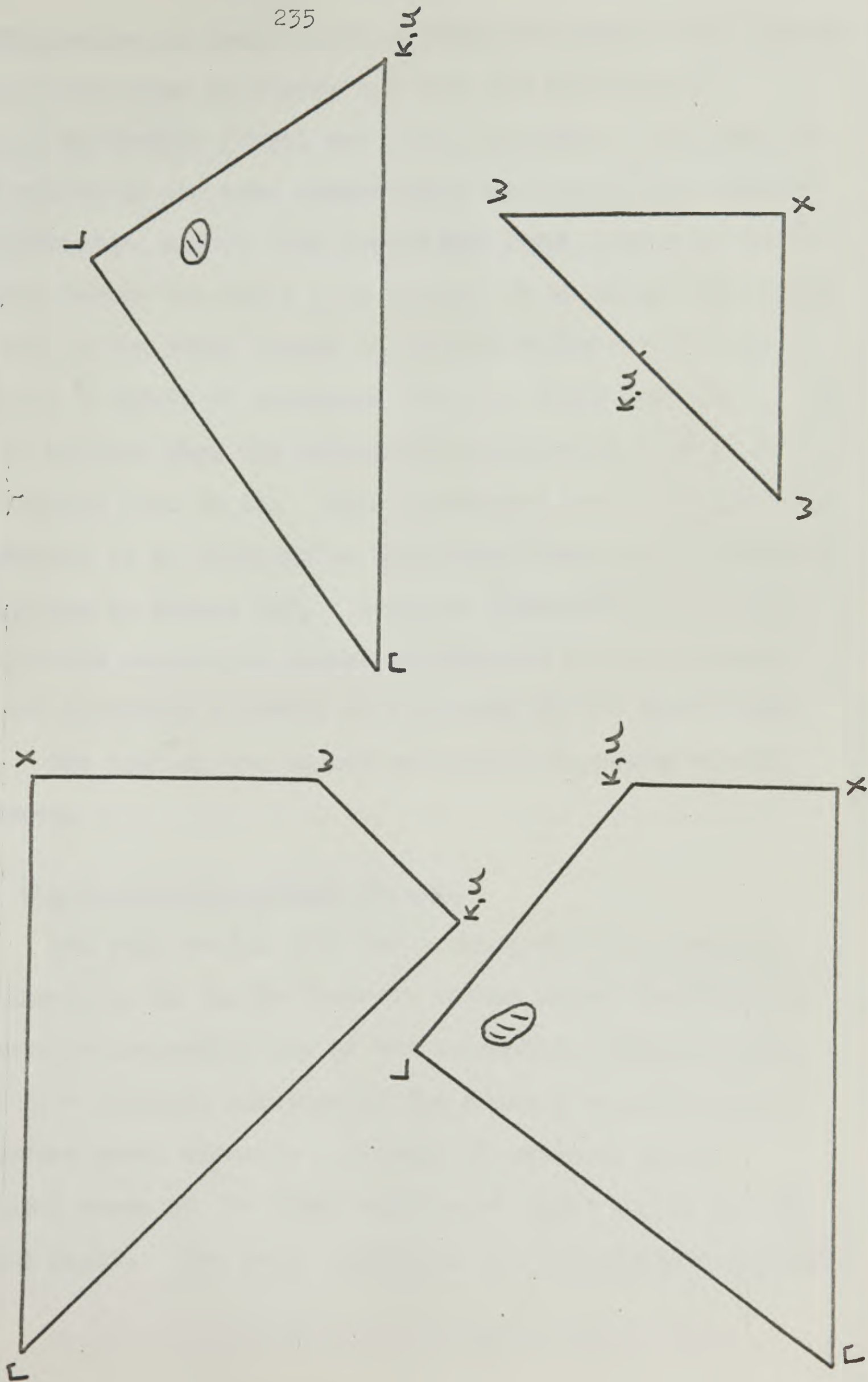


FIGURE 6.7 (contd.)

Band 3, sections, with electrons shaded.



It is therefore of interest to compare the Fermi surface whose sections are given in Figure 6.7 with the Fermi surface obtained by Bradley (1964) for h.c.p. scandium. We seem in Sc to encounter the same trouble with the point W as occurred with aluminium, namely that though the Fermi energy we have computed leaves the level E at W empty it is within the range of error of the Fermi energy to make it occupied and thus introduce a pocket of electrons into the third band at W. It will be noticed that the ordering of the levels at W in Sc is different from in Al. Thus, accepting the Fermi surface as computed it is entirely in the second band and it is shown in sections in Figure 6.7. A slight increase in the Fermi energy would remove the pocket of holes at W in the second band and introduce a pocket of electrons in the third band at W. The rest of the second band would be substantially unaltered.

6.7 The de Haas-van Alphen Effect.

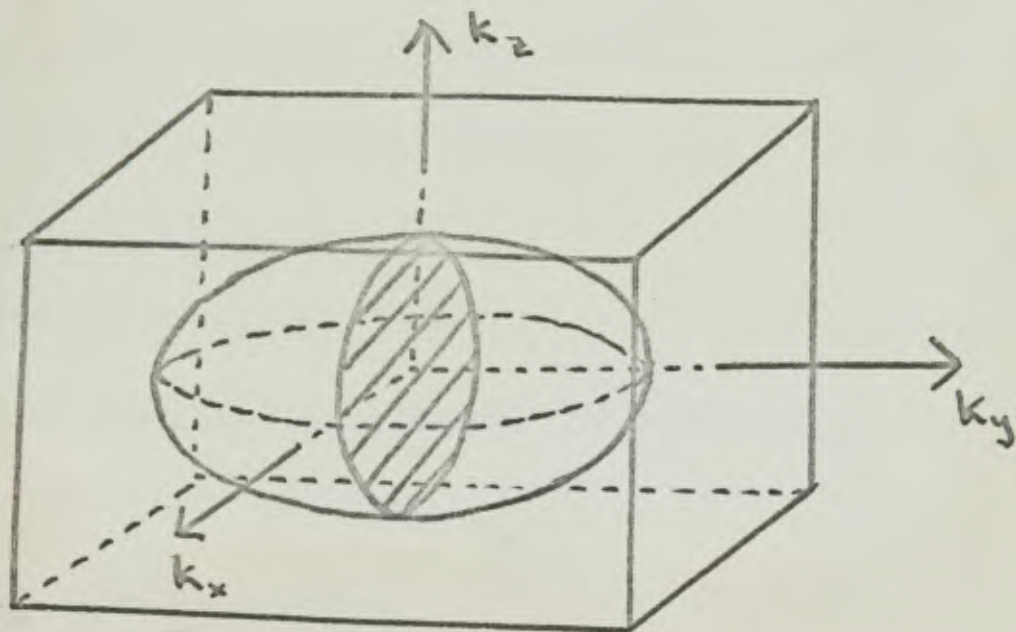
One very useful tool for probing the Fermi surface experimentally is the de Haas-van Alphen effect in which the diamagnetic susceptibility of the conduction electrons in a metal is a periodic function of the applied magnetic field. The effect gives directly a measure of extremal cross sectional areas of the Fermi surface at right angles to the applied field. The basic equation, see e.g. Shoenberg (1957)

or Pippard (1960), is

$$\Delta\left(\frac{1}{H}\right) = \frac{2\pi e}{\hbar c \mathcal{A}_0} = 2.67 \times 10^{-9} / \text{O} \quad (6.7.1)$$

where $\mathcal{A}_0$ is an extremal area of cross section of the Fermi surface in atomic units and H is in gauss; examples of extremal cross sectional areas are shown in Figure 6.8.

FIGURE 6.8 EXAMPLES OF EXTREMAL AREAS OF CROSS SECTION OF THE FERMI SURFACE.



In the example of Figure 6.8 the Fermi surface is assumed to be a tri-axial ellipsoid (i.e. an orthorhombic metal) with semi-axes (in $\underline{k}$ space) of lengths a , b , and c . Thus the shaded area is $\mathcal{A}_0$ for the case of the magnetic field applied along the k_y axis, and its area is πac . For the case of the field along the k_x axis $\mathcal{A}_0$ is πbc , so that these two de Haas-van Alphen periods would determine ac and bc ; a third period using the axis of suspension of the crystal along k_y and the field along k_z would determine the product ab . Thus from these three products a , b , and c could be found.

In a real metal the Fermi surface is much more

complicated but by measuring the de Haas-van Alphen periods for all directions of the field any proposed Fermi surface model can be accurately probed.

For two of the metals considered here, Al and Ca, there are good sets of experimental de Haas-van Alphen data available, and comparisons of them with our models will be made. It is dubious whether any useful de Haas-van Alphen results can be expected for Sc and Co because Sc is h.c.p. rather than f.c.c. at low temperatures and Co is ferromagnetic.

(1) Aluminium.

Ashcroft (1963) has given a "frankly phenomenological" treatment of the Fermi surface of aluminium based largely on the interpretation of the de Haas-van Alphen measurements on Al. As mentioned already the general outlines of the Fermi surface of Al appear to be well determined by a mixture of theory and experiment. The point to which most doubt attaches is W, and as already mentioned also, there would seem to be a small pocket of electrons at W in the third band, and thus the first and second bands, which are degenerate at W, are also occupied. Ashcroft (1963) lists three groups of de Haas-van Alphen frequencies,

Group I: oscillations corresponding to extremal areas of $4/3$ of the area of the hexagonal face of the zone, and $3/4$ of the area of the square face; the field directions being $[110]$ and $[111]$ for the first and $[100]$ for the second.

Group II; oscillations corresponding to extremal areas

about 1/100th of the area of the hexagonal face, present for most directions of the field.

Group III: oscillations corresponding to an extremal area 10 times smaller than those of group II.

Ashcroft attributes the Group I oscillations to the Fermi surface in the second band, in the model here suggested we too attribute these to the second band Fermi surface; one oscillation to the maximal cross-sectional area of the hole surface centred on Γ and which is very roughly spherical (see Figure 6.5, 100 and 110 sections unshaded object) and the other oscillation to the minimal cross-sectional area centred on X of the arms of the electron Fermi surface in the second band.

The difference between our model and that of Ashcroft is that in our band structure the third level at W is below the third level at U. Consequently if there is only a small spill over of electrons into the third band a pocket of electrons in the third band will be formed at W, whereas Ashcroft's band structure (1963, Fig 17) leads to a pocket of electrons at U rather than W, since the third level at U, with his bands, is lower than the third level at W. Thus the only difference between the two models is in whether the third band Fermi surface consists of a pocket of electrons at U or a pocket of electrons at W. In either case it is quite possible to attribute the group II and group III oscillations to this pocket of electrons. Since there are

many of these pockets in different orientations it is difficult from experiments alone to fix the shapes of these pockets uniquely and one really requires better band calculations to determine their shape completely.

(11) Calcium.

Good measurements of the de Haas-van Alphen effect in calcium by Condon and Marcus (1964) have recently become available. They find three periods which are shown in the first column of Table 6.5; they tried to explain their results in terms of the model of the Fermi surface for calcium proposed by Harrison (1963) but with only limited success. The Harrison model predicts more orbits than were found by experiment, in particular his model has a "monster" of holes in the first band with a large orbit (not found experimentally) round the waist of the monster, with a period of $0.085 \times 10^{-7} \text{ gauss}^{-1}$. Pictures of the monster are given by both Harrison (1963) and Condon and Marcus (1964). On the other hand the Fermi surface proposed in Figure 6.6 for Ca leads only to three de Haas-van Alphen periods which are shown in the second column of Table 6.5. These can be seen to agree qualitatively well enough with the results of Condon and Marcus. For comparison, in Table 6.6 are shown all the orbits predicted by Harrison (1963).

TABLE 6.5 DE HAAS-VAN ALPHEN PERIODS FOR CALCIUM.

Exptl values.	Calc values.	Orbit label
0.77	3.8	α
0.57	1.2	β (δ)
3.0	8.3	γ

Note: the units are 10^{-7} gauss $^{-1}$.

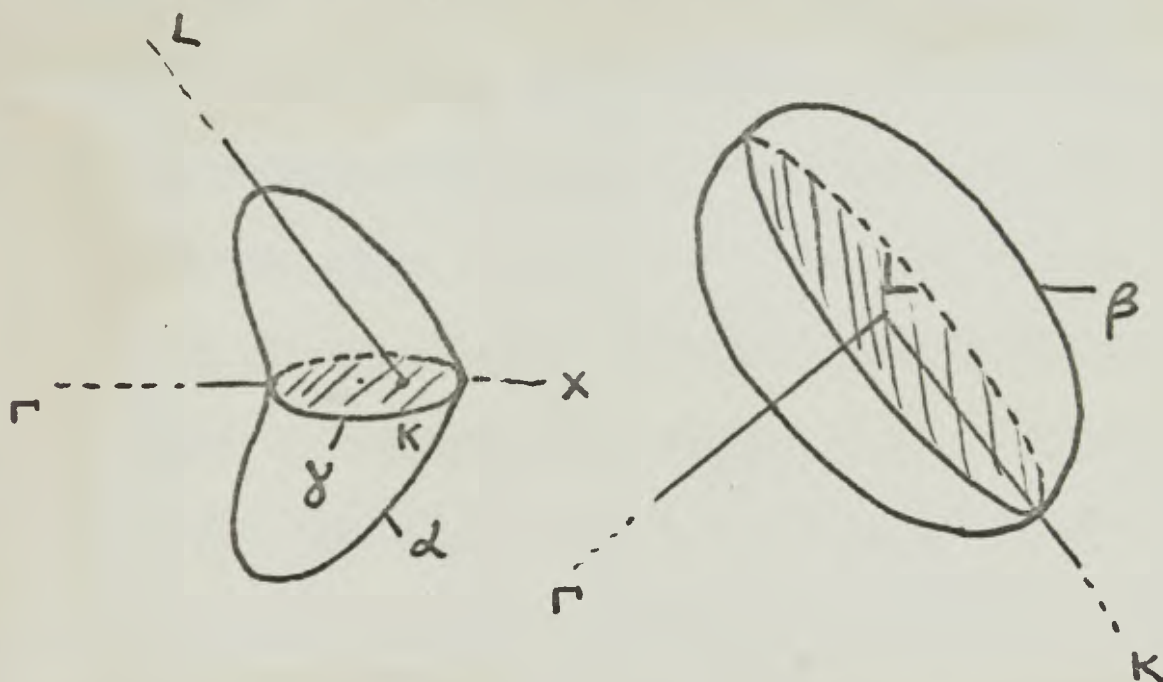
TABLE 6.5 DE HAAS-VAN ALPHEN PREDICTIONS OF HARRISON (1963).

Field axis	Area (a.u.)	Period (10^{-7} G $^{-1}$)
[110]	0.0062	4.3
[100]	0.035	0.76
[110]	0.038	0.71
[110]	0.054	0.50
[100]	0.064	0.42
[100]	0.09	0.30
[100]	0.31	0.085

The orbits are illustrated in Figure 6.9; the labels of the last column of Table 6.5 are in the Figure. If the magnetic field is applied along one of the crystal axes then orbit γ is seen, this agrees with the direction in which Condon and Marcus found orbit γ . Orbit α was also found by them in the direction which agrees with our model, namely the magnetic field being in the 110 direction. According to our model the orbit β should appear with the field in the same

direction as for orbit γ - it appears however in fact with the magnetic field along one of the crystal axes. As the field direction is changed so the various extremal areas change slowly and in ways which generally are not inconsistent with the results of Condon and Marcus since their work on the angular dependence of the periods is hampered by the fact that their specimens were seldom perfect single crystals though by no means polycrystalline.

FIGURE 6.9 THE FERMI SURFACE FOR CALCIUM.



(a) holes,
1st band.

(b) electrons,
2nd band.

Thus the Fermi surface model proposed here does not predict any orbits which are not found experimentally as Harrison's model does, and it gets the angular dependence of the orbits roughly correct. For example Harrison's model, see Table 6.6, predicts for the $[100]$ direction of the magnetic field alone the four periods 0.76, 0.42, 0.30 and

$0.085 \times 10^{-7} \text{ gauss}^{-1}$, only two periods being observed experimentally at the most in this direction, the biggest failure being the non-appearance of the very short period corresponding to a very large orbit. The areas of the orbits are, from Table 6.5, for our model too small by a factor varying between 2 and 4, so that the linear dimensions of our Fermi surface are too small by a factor varying between 1.5 and 2.

(iii) Scandium and Cobalt.

Scandium as computed here is not the stable form so that without knowing how the Fermi surface is affected by a change in the structure of the metal it is not possible to connect the predictions made on our Fermi surface model with any experiments even if they had been performed. In Table 6.7 are the de Haas-van Alphen periods predicted from the Fermi surface shown in sections in Figure 6.7. Orbits (a) and (b) arise from the two cross sectional areas shown in the (100) section in Figure 6.7 of the Fermi surface of electrons in the second band in Sc. Orbit (c) is the extended orbit in the (110) section of the same Fermi surface; orbits (d) and (e) are orbits in planes normal to the (110) section and round the arms near the point L and correspond to field directions along ΓL and LK which are roughly $[111]$ directions. Orbit (f) is approximately independent of direction and is due to the very small pocket of electrons in the third band in Sc.

Co is ferromagnetic so that there is little chance of any de Haas-van Alphen experiments being done as above the

Curie point the temperature would be much too high for any de Haas-van Alphen effects to be observable.

TABLE 6.7 PREDICTED DE HAAS-VAN ALPHEN PERIODS FOR Sc.

Orbit	Field axis	Area (a.u.)	Period $10^{-7} \text{ gauss}^{-1}$
a	[100]	0.095	0.28
b	[100]	0.032	0.84
c	[110]	0.158	0.17
d	[111]	0.004	6.7
e	[111]	0.008	3.3
f	any direction	0.004	6.7

6.8 The Behaviour of Calcium at Very High Pressure.

Stager and Drickamer (1964) have found that unlike magnesium, for which the nearly free electron picture is so successful, calcium and strontium at high pressures become semiconducting. Using the ordinary values for the compressibility of calcium and its dependence on pressure it is easy to deduce the % changes in lattice constant which occur at various pressures and these are shown in Table 6.8

(P.T.O.)

TABLE 6.8 THE VARIATION OF THE LATTICE CONSTANT OF CALCIUM
WITH PRESSURE.

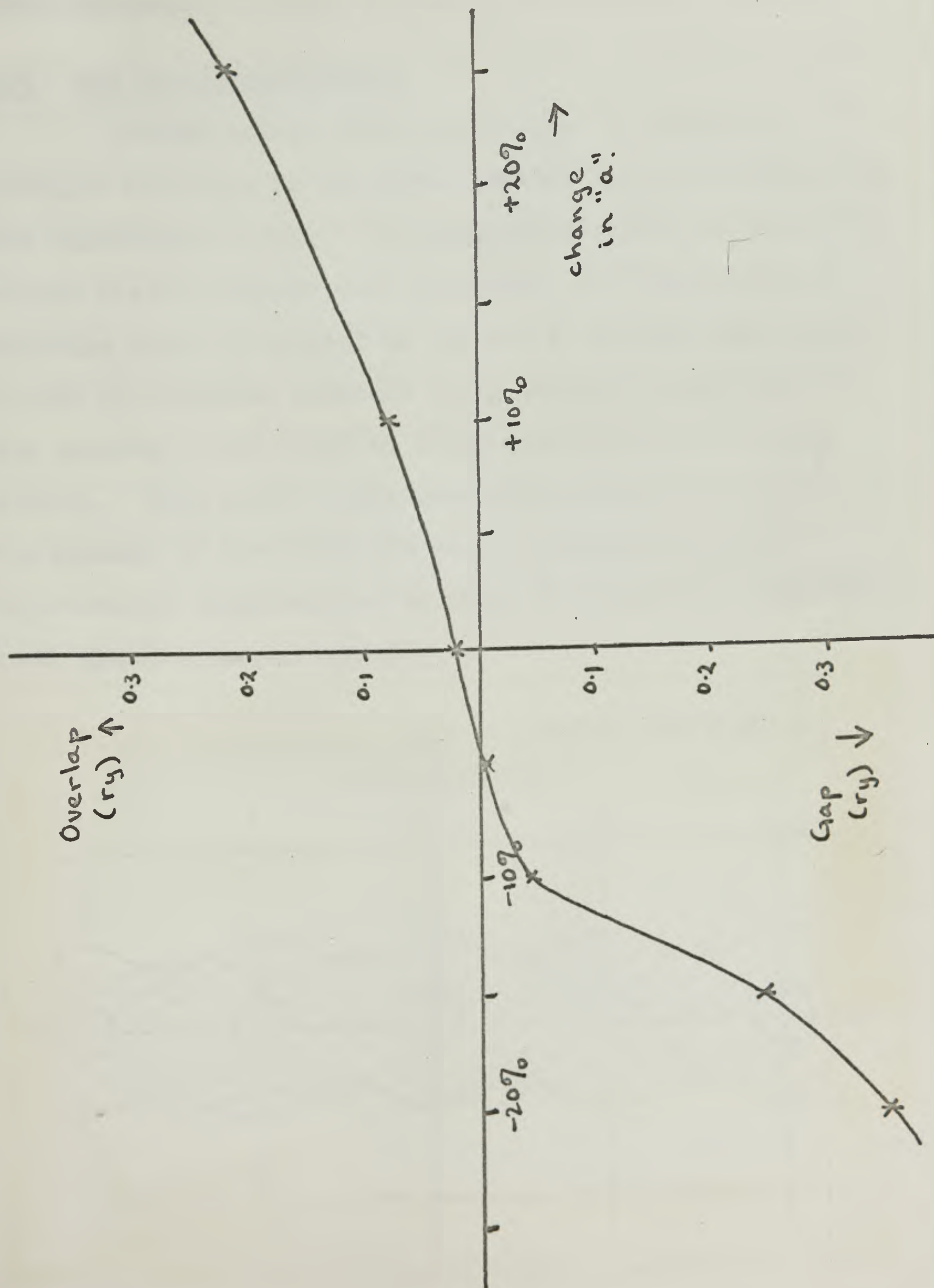
% decrease in a	pressure (Kbars.)
1	5.3
2	11.1
3	17.5
4	24.8
5	33.0
6	42.7
7	54.2
8	68.5
9	87.6
10	115.9
11	171.8
12	∞

Note: the compressibility is assumed to be $5.9 \times 10^{-6} \text{ bar}^{-1}$ and its coefficient of variation with pressure $(= \frac{1}{\beta} \left(\frac{\partial \beta}{\partial P} \right))$ is assumed to be $-1.7 \times 10^{-5} \text{ bar}^{-1}$.

If calcium were a nearly free electron metal it would seem reasonable that a change of 10% in lattice constant which occurs at the pressure at which it becomes a semiconductor will still leave it an approximately free electron like metal in its band structure so that the only appreciable effect on the band structure on changing the lattice constant would be to alter the scale of the bands by a factor proportional to a^2 .

No change in the overlap between the bands expressed as a fraction of the Fermi energy would be observed. But with our model which is far from free electron like, on reducing the lattice constant an electron at the edge of the Wigner-Seitz cell sees a less screened nucleus than before and the bands become less free electron like and the overlap between the first and second bands is reduced. This has been tested by re-computation of the important energy levels using the same potential field but different values of the lattice spacing. The overlap between the first and second bands, as shown by the separation of the levels KA_1 and LA_{2u} , for various values of the lattice constant is shown in Figure 6.10. It is clear that when the overlap ordinarily present in calcium vanishes and the gap becomes of the order of kT the metal becomes a semiconductor. This can be seen to occur at about a 4-5% contraction in the lattice constant, that is, from Table 6.8, at about 30-40 kbars. The experimental value appears to be between 150 kbars and 300 kbars from the work of Drickamer and Stager (1964). This therefore seems to suggest that, because it predicts this change to a semiconductor which the nearly free-electron model could never do, our Fermi surface is very nearly correct. It would seem both from this compressibility evidence and from the de Haas-van Alphen evidence just considered that the Fermi surface of calcium should be a very little more free-electron like than our model, which would increase both the actual over-

FIGURE 6.10. CALCIUM AS A SEMICONDUCTOR AT HIGH PRESSURE.

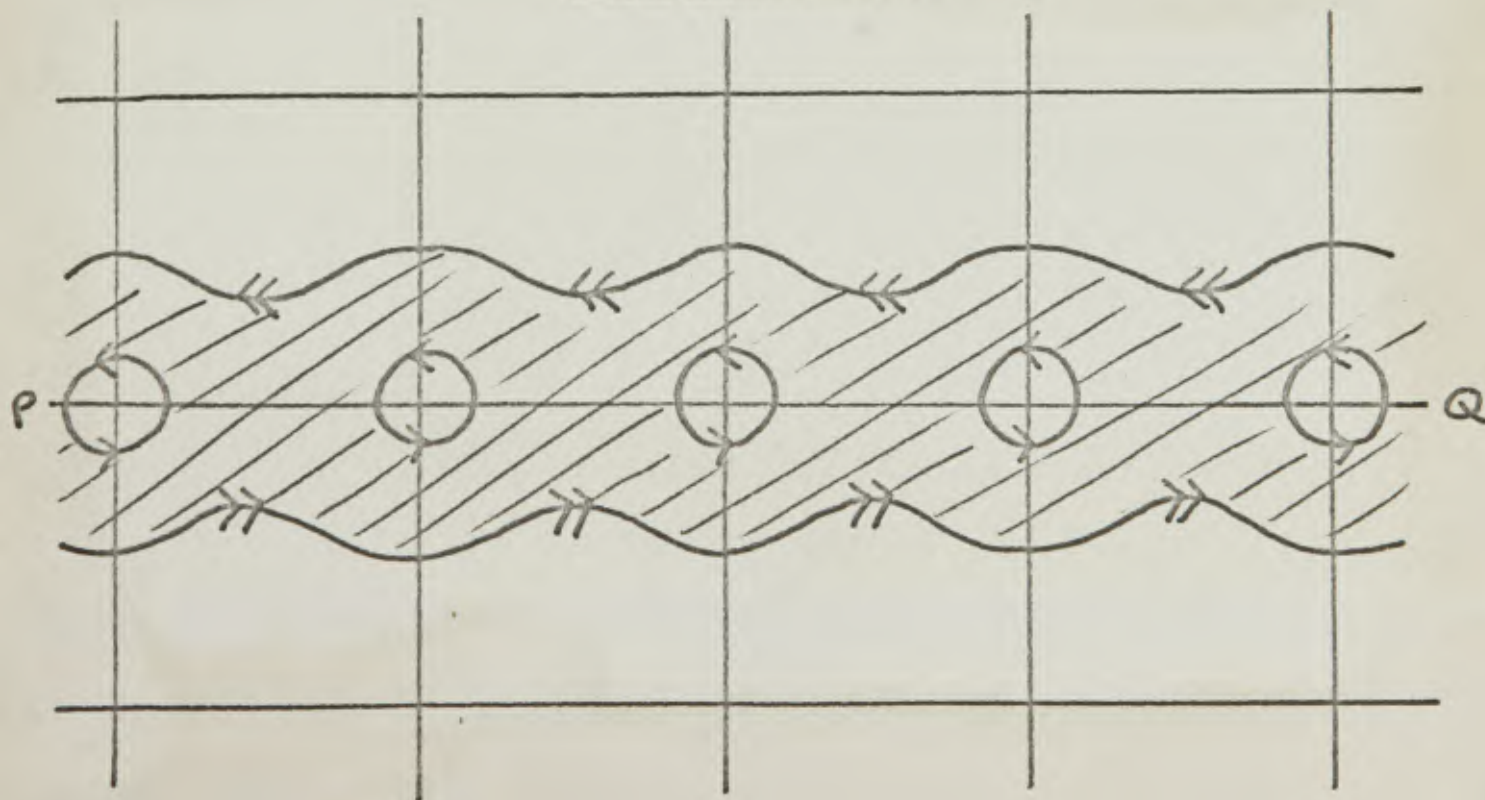


lap between the first and second bands and the size of the Fermi surface.

6.9 The Magnetoresistance.

Another effect which can be used to probe the detailed structure of the Fermi surface is the saturation of the magnetoresistance. The magnetoresistance is simply the change in the ordinary d.c. resistance of a metal when a magnetic field is applied to it, and in sufficiently large fields it saturates provided that, for the orientation of the magnetic field which is being used there are no open orbits. Open orbits occur when a Fermi surface touches the boundary of the Brillouin zone, a section through a hypothetical Fermi surface is shown in Figure 6.11 showing both closed and open orbits.

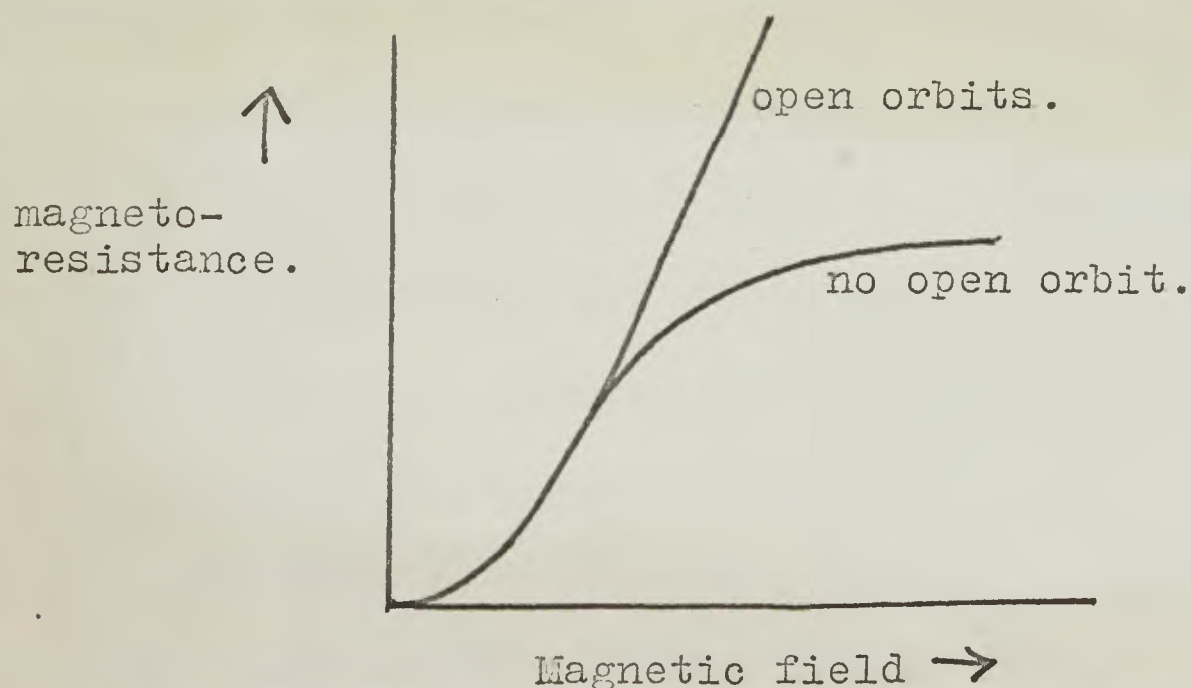
FIGURE 6.11 OPEN AND CLOSED ORBITS ON A FERM SURFACE.



In Figure 6.11 holes are shaded, and the closed orbits are marked with single arrows and the open orbits with double arrows. If the Fermi surface of Figure 6.11 is now assumed to be extended to three dimensions by rotating it about the line PQ to form a set of tubes and spheres, for the case of the magnetic field applied along the axis of the tubes there will be no open orbits but just closed orbits round the tubes and round the spheres; but if it is applied at right angles to the axis of the tubes there will still be open orbits.

If there are no open orbits possible then the magnetoresistance saturates as we have already mentioned; but if there are open orbits possible then the magnetoresistance does not saturate but varies as H^2 . This is shown roughly in Figure 6.12.

FIGURE 6.12 THE SATURATION OF THE MAGNETORESISTANCE.



Thus it is possible to determine experimentally whether or not a given metal has any open orbits and if so to test whether their appearance and disappearance as the orientation of the

field is changed is consistent with a particular model of the Fermi surface.

We now consider each of the Fermi surface models described before to see which, if any, should lead to open orbits and how their appearance and disappearance will depend on the orientation of the field.

In the Fermi surface proposed for aluminium the second band Fermi surface of holes is a set of distorted spheres which do not touch and the third band pockets of electrons at W are isolated from one another so that in no orientation of the magnetic field in aluminium is it possible to get open orbits. Therefore in aluminium our model is committed to having the magnetoresistance always saturated at large fields; though if the third band pockets of electrons were extended to embrace U and K as well open orbits would be possible.

The Fermi surface in calcium consists of small pockets of holes in the first band at K and small isolated pockets of electrons in the second band at L. No open orbits are possible and the magnetoresistance does not saturate for any direction of the magnetic field.

In scandium extended orbits appear if the field is in the $[110]$ direction which means that a higher magnetic field is needed before the magnetoresistance saturates; but since there are no proper open orbits it does eventually saturate.

6.10 The Knight Shift.

The theory of the Knight Shift, the difference between the nuclear paramagnetic resonance frequency in a single atom of a metal and in a large sample of the metal, is given, for example, by Townes, Herring and Knight (1950). And semi-empirical calculations of the Knight shift were made by Knight (1956).

The resonance frequency is shifted because the magnetic field at the nucleus is altered by a contribution due to the alignment of the spins of some of the electrons when the external field is applied. In the paper of Townes et al., (1950) it is shown that for metals possessing cubic symmetry the shift is dependent only on the s-contribution (i.e. $l = 0$) to the wave function. The case of non-cubic symmetry in metals need not detain us here; it is considered adequately by Bloembergen and Rowland (1953). The difference between the applied field and the actual field at the nucleus is the contribution due to these electrons which is:

$$\Delta H = 8\pi/3 \times$$

(mean density of spin moment at the nucleus).

$$\text{i.e. } \Delta H = 8\pi/3 \times (\chi_p M) H \langle |\psi_F(0)|^2 \rangle_{av},$$

where $\chi_p M$ is the susceptibility per atom, and $\langle |\psi_F(0)|^2 \rangle_{av}$ is the probability density of electrons on the Fermi surface,

1.e. in a suitable state to contribute to the magnetic moment at the nucleus, averaged over the Fermi surface. And only s type wave functions contribute non-zero components to $\Psi_F(0)$. Thus

$$\frac{\Delta H}{H} = \frac{8\pi}{3} \chi_p \langle |\Psi_F(0)|^2 \rangle_{av} \quad (1)$$

χ_p can readily be put in terms of the density of states at the Fermi surface and has already been calculated, or alternatively experimental values of χ_p can be used; since there are considerable discrepancies between these two sets of values of χ_p both will be used and the two results compared with the experimental Knight shift.

Apart from numerical factors the only thing remaining to be found in order to calculate the Knight shift is the average value of the proportion of the s-type contribution to the wave function on the Fermi surface at the nucleus. For $\langle |\Psi_F(0)|^2 \rangle$ an interpolation routine, very similar to that used for interpolating the energies $E(\underline{k})$ and described in section 5.2 was used.

$$|\Psi_F(0)|^2 = \frac{\int \Psi^* \Psi d\tau}{\int d\tau}$$

the volume of integration being some small volume near the nucleus. Using the expansion for $\Psi = \sum_{l\nu} B_{l\nu} X_{l\nu}(\theta, \phi) R_l(r)$

$$\text{then } |\Psi_F(0)|^2 = \lim_{r \rightarrow 0} \left[\int_{\theta, \phi} \left\{ \sum_{l\nu} B_{l\nu}^* X_{l\nu}^*(\theta, \phi) R_l(r) \right\} \times \left\{ \sum_{l\nu} B_{l\nu} X_{l\nu}(\theta, \phi) R_l(r) \right\} r^2 \sin \theta dr d\theta d\phi / 4\pi r^2 dr \right]$$

$$= \lim_{r \rightarrow 0} \left[\sum |b_l|^2 R_l^2(r)/4\pi \right] \text{ (since the } X_{lv}(\theta, \phi) \text{ are orthonormalised).}$$

Now
$$\lim_{r \rightarrow 0} [R_l(r)]^2 = \begin{cases} 0 & l \neq 0 \\ \text{constant} & l = 0 \end{cases}$$
 and since ψ as determined

is in atomic units then in c.g.s. units

$|\psi_F(0)|^2 = |b_0|^2 R_0(0)^2 / 4\pi a_0^3$, where a_0 is the Bohr radius.

$R_0(0)$ is a function only of the energy of the electrons and not of k so that for electrons at the Fermi surface $R_0(0)$ is some constant for each of the metals which are considered here. Therefore

$$\langle |\psi_F(0)|^2 \rangle_{av} = R_0^2 |b_0|^2_{av} / 4\pi a_0^3 \quad (11).$$

Thus it is necessary to find R_0 , which is found using the Fermi energy from the outwards integration routine of the cellular calculation; and for $|b_0|^2_{av}$ the interpolation routine used to obtain $E(k)$ earlier, in section 6.2 was used in exactly the same way as described there using $|b_0|^2$ at the special points of symmetry and along the special lines of symmetry, instead of $E(k)$.

Equation (1) can now be put into the following form:-

$$\frac{\Delta H}{H} = \frac{8\pi}{3} (\chi_p M) \frac{1}{4\pi a_0^3} R_0^2 |b_0|^2,$$

where χ_p is the molar susceptibility and M is the mass of 1 atom, thus

$$\Delta H/H = 746 \chi_p R_0^2 |b_0|^2_{av} \% \quad (111)$$

In Table 6.9 the interpolated values of $|b_0|^2$ for the

lowest bands of Al, Ca and Sc are given. This is done so that the results may be used, with other Fermi surface models to predict values of the Knight shift.

TABLE 6.9 $|b_0|^2$ FOR Al, Ca and Sc.

Note:

The coefficients are listed only for the representative portion of the Brillouin zone with all the components of $\underline{k}$ positive, and with $k_y > k_x > k_z$.

The coefficients are listed as percentages; before insertion into equation (iii) they should be divided by 100.

$k_z \backslash k_y$	0.1	0.2	0.3	(P.T.O.)
0.1	25.4			
0.2	70.0	70.0		
0.3	82.4	82.4	82.4	
0.4	24.4	43.7	43.7	70.7
0.5	27.2	66.5	66.5	82.5
0.6	11.4	18.8	18.8	31.2
0.7	2.8	8.0	8.0	
0.8	0.3	0.7		

$k_z \backslash k_y$	0.1	0.2	0.3	$k_z \backslash k_y$	0.4	0.5
0.1	77.8			0.1	18.4	
0.2	25.7	25.7		0.2	66.5	66.5
0.3	29.1	29.1	29.1	0.3	14.7	14.7
0.4	82.0	82.0	82.0	0.4	2.8	2.8
0.5	25.4	25.4		0.5		
0.6	0.3					

(1) Aluminium.Band 1.

		<u>$k_z = 0.$</u>					
$k_y \backslash k_x$		0.1	0.2	0.3	0.4	0.5	0.6
0.2		94.1					
0.3		87.7	86.7				
0.4		80.2	80.8	76.1			
0.5		71.6	72.8	69.3	62.6		
0.6		61.2	61.5	59.0	51.4	48.5	
0.7		48.0	45.9	35.3	36.8	37.4	33.9
0.8		30.4	15.2	17.5	20.1	22.0	18.8
0.9		3.0	4.0	4.0	5.9	6.1	
1.0		0.0	0.0	0.0	0.0		

		<u>$k_z = 0.1.$</u>				
$k_y \backslash k_x$		0.2	0.3	0.4	0.5	0.6
0.3		85.4				
0.4		79.0	72.9			
0.5		69.6	63.8	54.2		
0.6		56.4	45.7	43.1	39.7	
0.7		27.9	28.5	29.3	28.5	21.8
0.8		11.4	12.9	14.7	14.4	
0.9		2.9	4.0	4.7		
1.0		0.9	2.2			

		<u>$k_z = 0.2.$</u>		
$k_y \backslash k_x$		0.3	0.4	0.5
0.4		72.8		
0.5		55.3	48.6	
0.6		39.6	37.2	34.7
0.7		24.5	25.3	24.2
0.8		12.2	13.7	
0.9		4.4		

		<u>$k_z = 0.3.$</u>	
$k_y \backslash k_x$		0.4	0.5
0.5		49.0	
0.6		40.7	43.6
0.7		29.6	
0.8		15.8	

Band 2.

		<u>$k_z = 0.$</u>					
$k_y \backslash k_x$		0.1	0.2	0.3	0.4	0.5	0.6
0.2		2.0					
0.3		2.1	0.5				
0.4		0.9	1.2	0.5			
0.5		1.5	3.6	3.2	1.5		
0.6		6.2	9.7	8.6	7.3	0.8	
0.7		16.2	20.4	25.3	16.2	7.2	5.4
0.8		31.6	43.8	35.9	26.4	18.5	23.2
0.9		54.1	47.1	37.3	26.9	19.2	
1.0		45.2	33.9	22.6	11.3		

		<u>$k_z = 0.1.$</u>				
$k_y \backslash k_x$		0.2	0.3	0.4	0.5	0.6
0.3		3.3				
0.4		4.2	4.4			
0.5		7.6	7.3	7.2		
0.6		14.4	17.9	12.0	6.9	
0.7		34.0	27.6	20.3	15.6	24.0
0.8		44.1	35.7	28.1	25.5	
0.9		45.7	35.6	25.0		
1.0		55.5	38.5			

		<u>$k_z = 0.2.$</u>		
$k_y \backslash k_x$		0.3	0.4	0.5
0.4		12.0		
0.5		17.4	17.4	
0.6		23.1	21.0	20.2
0.7		30.2	26.9	27.5
0.8		37.6	33.7	
0.9		50.3		

		<u>$k_z = 0.3.$</u>	
$k_y \backslash k_x$		0.4	0.5
0.5		25.1	
0.6		27.2	25.7
0.7		31.0	
0.8		41.1	

Band 3.

		<u>$k_z = 0.$</u>					
$k_y \backslash k_x$		0.1	0.2	0.3	0.4	0.5	0.6
0.2		1.0					
0.3		0.8	0.1				
0.4		0.0	0.7	0.8			
0.5		0.2	0.5	5.8	16.7		
0.6		0.1	3.1	11.7	23.4	36.1	
0.7		0.7	5.8	13.0	24.4	34.2	38.2
0.8		1.3	4.8	12.1	19.0	24.5	30.1
0.9		0.8	5.3	7.7	9.1	10.8	

		<u>$k_z = 0.1.$</u>				
$k_y \backslash k_x$		0.2	0.3	0.4	0.5	0.6
0.3		0.5				
0.4		0.5	4.9			
0.5		3.5	11.2	21.8		
0.6		7.4	14.9	25.5	33.5	
0.7		7.9	15.8	23.2	28.2	31.6
0.8		8.7	13.8	17.6	21.0	
0.9		11.2	12.6	12.5		
1.0		24.8	20.9			

		<u>$k_z = 0.2.$</u>						
$k_y \backslash k_x$		0.3	0.4	0.5	$k_y \backslash k_x$		0.4	0.5
0.4		4.0			0.5		5.6	
0.5		9.2	14.5		0.6		10.7	12.1
0.6		13.7	18.2	21.0	0.7		17.1	
0.7		15.6	18.7	21.5	0.8		30.1	
0.8		18.2	21.1					
0.9		29.9						

(11) Calcium.

Band 1.

		<u>$k_z = 0.$</u>					
$k_y \backslash k_x$		0.1	0.2	0.3	0.4	0.5	0.6
0.2		92.7					
0.3		85.0	82.0				
0.4		74.1	73.5	69.4			
0.5		62.2	63.6	62.0	56.1		
0.6		50.4	53.3	53.6	46.6	38.2	
0.7		39.6	43.2	39.7	34.3	25.9	16.6
0.8		30.7	29.8	27.4	22.0	14.6	8.8
0.9		23.5	22.3	19.1	13.9	8.4	
1.0		20.1	17.0	12.6	7.0		

		<u>$k_z = 0.1.$</u>				
$k_y \backslash k_x$		0.2	0.3	0.4	0.5	0.6
0.3		77.1				
0.4		69.1	64.8			
0.5		61.0	57.7	48.7		
0.6		51.9	45.4	36.7	25.7	
0.7		36.5	31.6	23.0	13.7	8.1
0.8		25.2	20.6	14.0	8.7	
0.9		20.0	15.7	10.2		
1.0		21.1	15.1			

		<u>$k_z = 0.2.$</u>		
$k_y \backslash k_x$		0.3	0.4	0.5
0.4		66.1		
0.5		52.5	39.4	
0.6		36.0	21.7	7.7
0.7		21.0	10.2	5.6
0.8		14.6	10.3	
0.9		18.3		

		<u>$k_z = 0.3.$</u>	
$k_y \backslash k_x$		0.4	0.5
0.5		18.3	
0.6		0.3	3.8
0.7		3.1	
0.8		0.5	

		$k_z = 0.$					
$k_y \backslash k_x$		0.1	0.2	0.3	0.4	0.5	0.6
0.2		0.2					
0.3		0.2	0.0				
0.4		0.0	0.4	0.2			
0.5		0.2	0.7	0.5	0.1		
0.6		0.3	0.7	0.4	0.0	0.1	
0.7		0.2	0.4	0.1	1.3	1.6	0.8
0.8		0.1	0.0	3.4	6.7	8.5	7.2
0.9		0.0	5.5	12.8	20.5	27.4	
1.0		9.4	19.1	29.0	39.3		

		$k_z = 0.1.$				
$k_y \backslash k_x$		0.2	0.3	0.4	0.5	0.6
0.3		1.1				
0.4		1.4	1.1			
0.5		1.3	0.7	0.1		
0.6		7.0	0.1	0.6	1.1	
0.7		0.1	2.1	3.8	4.8	4.6
0.8		3.8	7.9	12.0	15.1	
0.9		8.9	16.8	25.7		
1.0		5.7	18.6			

		$k_z = 0.2.$		
$k_y \backslash k_x$		0.3	0.4	0.5
0.4		1.8		
0.5		1.0	0.1	
0.6		0.9	2.2	4.1
0.7		4.6	7.2	9.4
0.8		9.7	13.7	
0.9		9.0		

		$k_z = 0.3.$	
$k_y \backslash k_x$		0.4	0.5
0.5		0.3	
0.6		4.2	6.5
0.7		8.9	
0.8		7.4	

(111) Scandium.Band 1.

		<u>$k_z = 0.$</u>					
$k_y \backslash k_x$		0.1	0.2	0.3	0.4	0.5	0.6
0.2		92.0					
0.3		83.7	81.2				
0.4		72.1	72.4	67.9			
0.5		58.3	60.9	59.3	52.7		
0.6		44.2	48.3	49.0	42.0	32.5	
0.7		31.2	36.7	34.7	29.5	20.6	9.3
0.8		22.0	24.1	21.4	17.2	10.3	3.2
0.9		17.3	14.7	11.7	8.2	4.3	
1.0		12.6	9.4	6.4	3.1		

		<u>$k_z = 0.1.$</u>				
$k_y \backslash k_x$		0.2	0.3	0.4	0.5	0.6
0.3		77.0				
0.4		68.0	62.3			
0.5		57.4	53.5	44.3		
0.6		46.5	40.9	33.1	22.5	
0.7		31.5	27.5	21.3	13.6	4.4
0.8		18.8	15.5	11.1	6.1	
0.9		11.1	8.2	4.9		
1.0		7.6	4.7			

		<u>$k_z = 0.2.$</u>		
$k_y \backslash k_x$		0.3	0.4	0.5
0.4		61.6		
0.5		49.1	41.6	
0.6		35.6	28.9	20.7
0.7		22.5	11.2	12.0
0.8		12.1	9.0	12.0
0.9		6.0		

		<u>$k_z = 0.3.$</u>	
$k_y \backslash k_x$		0.4	0.5
0.5		43.1	
0.6		30.4	26.3
0.7		18.5	
0.8		10.2	

Band 2.

		<u>$k_z = 0.$</u>					
$k_y \backslash k_x$		0.1	0.2	0.3	0.4	0.5	0.6
0.2		0.0					
0.3		0.0	0.0				
0.4		0.0	0.0	0.0			
0.5		0.0	0.0	0.0	0.0		
0.6		0.0	0.0	0.0	0.0	0.0	
0.7		0.0	0.0	0.0	0.0	0.0	0.0
0.8		0.0	0.0	0.0	0.0	0.0	
0.9		0.0	0.0	0.0	0.0		
1.0		0.0	0.0	0.0			

		<u>$k_z = 0.1.$</u>				
$k_y \backslash k_x$		0.2	0.3	0.4	0.5	0.6
0.3		0.0				
0.4		0.0	0.0			
0.5		0.0	0.0	0.0		
0.6		0.0	0.0	0.0	0.0	
0.7		0.0	0.0	0.0	0.0	0.0
0.8		0.0	0.0	0.0	0.0	
0.9		0.0	0.0	0.0		
1.0		0.0	0.0			

		<u>$k_z = 0.2.$</u>		
$k_y \backslash k_x$		0.3	0.4	0.5
0.4		0.1		
0.5		0.1	0.1	
0.6		0.1	0.1	0.2
0.7		0.1	0.1	0.1
0.8		0.1	0.1	
0.9		0.0		

		<u>$k_z = 0.3.$</u>	
$k_y \backslash k_x$		0.4	0.5
0.5		0.4	
0.6		0.3	0.2
0.7		0.2	
0.8		0.0	

Computed values of R_0 are entered in column two of Table 6.10. Values of $|b_0|^2_{av}$ have been calculated very roughly for each metal using Table 6.9 and the Fermi surface models of section 6.6, and they are entered in column three of Table 6.10. In the fourth and fifth columns of the same Table are entered the values of $\Delta H/H$ calculated using the calculated and experimental values respectively of χ_p taken from Table 6.4. The experimental values of the Knight shift shown in the last column of Table 6.10 are taken from Knight (1956) for Al and Ca, and from Blumberg et al (1960) for Sc.

TABLE 6.10. VALUES OF THE KNIGHT SHIFT FOR Al, Ca, and Sc,
CALCULATED AND EXPERIMENTAL.

Metal	R_0	$ b_0 ^2_{av}$	$\Delta H/H$ (%) calc.	$\Delta H/H$ (%) calc.	$\Delta H/H$ (%) expt.
Al	6.38	0.24	3.1	2.2	0.16
Ca	8.18	0.11	1.1	2.4	0.31
Sc	10.05	0.04	0.10	0.95	0.28

In view of the fact that the procedure for evaluating $|b_0|^2_{av}$ from the data of Table 6.9 and the Fermi surface could be very much improved and in view of the discrepancies between the calculated and experimental values of χ_p the agreement between the calculated and experimental values of the Knight shift, which is usually within an order of magnitude is not

absolutely disastrous. And for Sc the experimental value, 0.28, even lies between the two calculated values, 0.1 and 0.95.

6.11 The Effective Mass, m^* , and Cyclotron Resonance.

If one accepts the nearly-free-electron approximation of the behaviour of the electrons in the metal it is possible to find an effective mass for the electrons from the modified free-electron equation $E = \hbar^2 k^2 / 2m^*$, which will of course only lead to an unique value of m^* if the bands in the metal are both isotropic and parabolic. The formula is thus of little use except near Γ in the first band, where it is possible to use it to gain some idea of the anisotropy of the effective mass. The values of m^* for k along the $[100]$, $[110]$, and $[111]$, directions near Γ were computed for calcium and the values are given in Table 6.11.

TABLE 6.11. m^* FOR CALCIUM NEAR Γ .

dirn.	k units of $2/a$.	$E(\text{ry})$ rel to A_{1g}	m^*
100	/3/12,0,0	0.0254	0.148
110	(/1.5,/1.5,0)/12	0.0252	0.149
111	(1,1,1)/12	0.0240	0.157

Whereas in semiconductor s , because there is an unique effective mass and because an external magnetic field can penetrate the specimen easily it is possible to find effective masses relatively easily by cyclotron resonance, this is by

no means the case in metals. The analysis of cyclotron resonance in metals is very complicated for a real metal, and is given by e.g. Pippard (1960) for ellipsoidal Fermi surfaces, the expressions used involve the effective mass at points on the Fermi surface, the effective mass then being defined properly as $m^* = \hbar^2 \frac{d^2 \epsilon / dk^2}{2\pi}$, instead of by the free-electron-approximation equation given before. Here $\frac{d^2 \epsilon}{dk^2}$ is the rate of change of the area of the orbit of the electron in k -space with energy. It is quite clear that since our Fermi surfaces are complicated and since any effective masses would be only very approximate there is little that we can usefully do with regard to cyclotron resonance in the metals we have considered.

6.12 The Electrical Conductivity and the Electronic Mean Free Path.

The knowledge of the conductivity of a specimen of a metal at ordinary temperatures is related to the mean free path, and time between collisions with either phonons, electrons, or imperfections in the lattice structure. The electronic velocity is $v_0 = 1/\hbar \cdot \text{grad}_{\underline{k}} E(\underline{k})$ and in an electric field this electron would, neglecting collisions simply go on accelerating indefinitely. As it is it suffers collisions and so a merely finite conduction current is set up, and, as shown by Pippard (1960) p 190, the conductivity is given by

$$\sigma = \frac{e^2 S \bar{l}}{12 \pi^3 \hbar}$$

for a cubic metal, S being the area of the Fermi surface and $\bar{l}$ the average over the Fermi surface of the electrons' mean free paths. Thus given the conductivity σ , and the Fermi surface which we have calculated the average mean free path may readily be computed: it is

$$\bar{l} = \frac{12 \pi^3 \hbar}{e^2} \left(\frac{\sigma}{S} \right)$$

and using $e = 4.803 \times 10^{-10}$ e.s.u.

and $1 \text{ ohm} = 10^9 / e^2$ e.s.u. of resistance

we have $\bar{l} = 4.83 \times 10^{-5} (\sigma / S) \text{ cm}$, if σ is in $(\text{microhm cm})^{-1}$

and S is in atomic units, thus:

$$\bar{l} = 4.83 \times 10^3 (\sigma / S) \text{ \AA}$$

Estimated values of S , the area of the Fermi surface produced in Section 6.6, the experimental values of σ at various temperatures (from Kaye and Laby (1956)), and the final values for $\bar{l}$, the mean free path are given in Table 6.12.

Cusack (1958) calculates mean free paths of between $100 \text{ \AA}$ and $600 \text{ \AA}$ at 0°C for various elements but not for any of those we have considered.

(P.T.O.)

TABLE 6.12. THE FERMI SURFACE AREA AND ELECTRONIC MEANFREE PATH FOR Al, Ca, and Sc.

	S (a.u.)	Temp ($^{\circ}\text{C}$)	σ (microhm cm) $^{-1}$	I ($\text{\AA}^{\circ}$)
Al	5.1	-195	3.33	3,100
		0	0.41	390
		100	0.28	260
		300	0.17	160
		700	0.04	38
Ca	1.48	0	0.29	950
		100	0.20	650
Sc	6.35	-	-	-

6.13 Conclusions; and the Rigid Band Model.

The temperature coefficient of the electronic specific heat, the Pauli spin paramagnetic susceptibility and various effects which probe the geometry of the Fermi surface (e.g. the de Haas-van Alphen effect and the magnetoacoustic effect) all give detailed means of testing the accuracy of our results; the agreement between our calculations and experiment was found to be not at all unsatisfactory, and where disagreement occurs some satisfactory explanation usually exists.

The saturation of the magnetoresistance if there are no open orbits present, together with the high pressure behaviour of the ordinary electrical resistance of calcium,

the Knight shift, and the effective mass for cyclotron resonance, while lacking in quantitative accuracy or possibility are still useful tests of the calculations.

With regards to the various metals which we have considered; for aluminium, while our calculations are as good as those of Heine (1956) it is doubtful whether they are much better, their general outline is satisfactory, and, indeed a recent set of magnetoacoustic measurements on aluminium by Kamm and Bohm (1963) seem to agree with the accepted model of the Fermi surface -certainly at least as far as the second band is concerned. For calcium our Fermi surface model differs substantially from that of Harrison (1963) but the experiments seem to be in favour of our model. For scandium the f.c.c. form is not the stable form and there is only scanty experimental evidence available. For cobalt, nothing further than a rough density of states curve has been produced for the reason given in the note on Figure 5.6.

Before concluding this chapter a few comments should perhaps be made about the rigid band model. The rigid band model is in the unfortunate position of being worshipped in some quarters and of being heresy in others; the truth appears to be somewhere between these two extremes. While a slavish adherence to the rigid band model would be foolish it is not unreasonable that from one element to the next, either across or ~~along~~ ^{down} the periodic table, the band structures will be very

little different, provided the crystal structures of the two elements being compared are the same. This is illustrated in Figures 7.2 and 7.3 where the band structures of solid argon and metallic calcium are shown.

The next chapter will be devoted to one aspect of the problem of improving the calculations.

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CHAPTER VII. A SELF-CONSISTENT FIELD FOR CALCIUM.

7.1 The Problem of the Field.

Of the total effort expended in the whole field of band calculations, both in relatively simple metals and in the transition and rare earth metals, the vast majority has gone into the detailed solution of Schrödinger's equation assuming the potential field $V(r)$ to be given. Relatively small consideration has been given to attempting to construct a realistic potential $V(r)$ within the metal, most workers being satisfied to assume the potential field of a "suitable" ion of the metallic element, though there have been one or two notable exceptions, e.g. Heine (1957), Falicov (1962), Harrison (1963) and Heine and Abarenkov (1964), though even these considerations were confined to relatively simple metals. For the transition metals little more than guesswork is involved in choosing the ion core to provide the potential field.

It is fairly obvious that merely to take a "suitable" free ion with the appropriate number of free electrons and assume this potential to exist in the metal is not very satisfactory because as illustrated in Chapter IV, Figure 4.3, it is possible to get very different sets of bands if different ions such as Co^+ , Co^{2+} , or Co^{6+} are used. The treatments given to aluminium by Heine (1957) and to magnesium by Falicov (1962) mentioned above would be quite difficult to

adapt for complicated metals like the transition metals so that the alternative approach to be described here was developed for a simple metal, calcium, where the relative perturbations of core and conduction electrons on the free ion levels can be studied more easily than in a transition metal like cobalt.

In this chapter we describe a self-consistent field calculation in the sense of Hartree (1957) which has been applied to the electrons in the conduction band in calcium, and indicate how this could easily be extended to cover the electrons in the ion core too. A very crude model which has been used to estimate the magnitude of the improvement which would be effected by considering a full S.C.F. on all the core electrons as well is then separately described.

We assumed in the calculations of Chapter V that the potential seen by a conduction electron in a metal to be that due to a free ion of the metal of valency n together with the potential due to $(n-1)$ other conduction electrons, assumed to be perfectly free. The ion core potential is obtained from an independent Hartree-Fock calculation on a free ion of that atomic number and valency. For calcium the potential is thus:

$$1s^2 2s^2 2p^6 3s^2 3p^6 + 1 \text{ free electron,}$$

the free electron being contained in a sphere of volume equal to the volume of the Wigner-Seitz cell. The two sources of

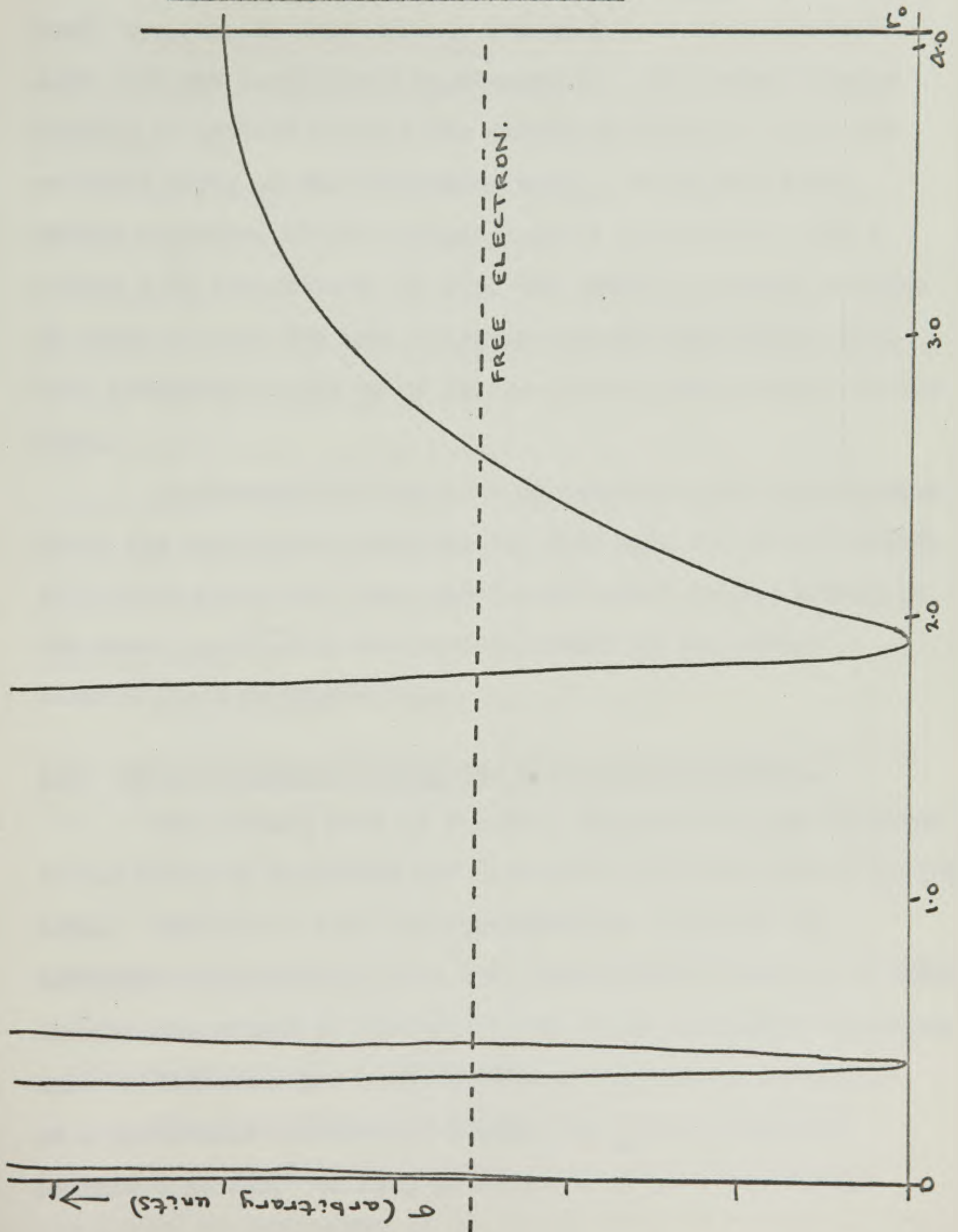
substantial errors in this potential are (i) the effect of the other components of the metal, i.e. all the other ions and all the conduction electrons, on the ion core electrons, and (ii) the fact that the other conduction electrons are not free and their contribution to the potential will thus be different from that which was assumed above. The effects which we shall consider will be solely due to the conduction electrons. We neglect the effect of the other ion-cores since the treatment of them by Heine (1957) showed that this is a small effect in aluminium and it is not likely to be very much bigger in the case of the transition metals. We also neglect the exchange effects among the conduction electrons, these being treated by Pines (1955).

Essentially therefore we are attempting a Hartree type self-consistent-field calculation for the electrons in the metal, considering in detail the conduction electrons and outlining the scheme for the consideration of the core electrons too.

7.2 The Charge Distribution of the Conduction Electrons.

The assumption of an uniform charge distribution for the conduction electrons, i.e. that the conduction electrons are contained in an infinite potential well of radius equal to the radius of the Wigner-Seitz equivalent sphere, is in fact not quite true. There is in the metal a build up of electronic charge in the outer regions of the cell, which causes a

FIGURE 7.1 CHARGE DENSITY FOR ELECTRONS IN
THE CONDUCTION BAND OF CALCIUM.



reduction in the screening of the nucleus at most radii less than the radius of the equivalent sphere so that the actual bands are, due to this effect, slightly less free-electron-like than the bands shown in Chapter V. The actual charge density is plotted against the radius in Figure 7.1 for the occupied parts of the conduction band. Since the total charge contained in the spherical shell of thickness dr at radius r is proportional to $r^2 \sigma$, the excess of charge density at large r , over the free electron density corresponds to a very substantial pile up of charge in the outer regions of the cell.

An attempt has been made to achieve a self consistency among the conduction electrons and this will now be described. It's first stage will show exactly how great is the change in the bands produced by the non-uniformity of the charge density shown in Figure 7.1.

7.3 Self Consistency among the Conduction Electrons.

The spatial part of the wave function for any electron in the metal is different for different points in the Brillouin Zone. This means that the contributions to $Z(r)$, the effective nuclear charge for the electric field seen by a given electron at radius r , due to all the other conduction electrons must be different for each electron. If the wave function of a particular electron is denoted by $\psi_i(k, r)$ then its contribution $Z(r)^i$ to $Z(r)$ at radius r is just the charge

contained in a sphere of radius r , i.e. is just $\int_0^r \psi_i^* \psi_i d\tau$, if $r \leq r_0$, the radius of the equivalent sphere, and is 1 if $r > r_0$. Therefore the total field inside the cell is that due to the ion core plus an average contribution from the conduction electrons, i.e.

$$Z(r) = Z(r)^{\text{Ca}^{2+}} + 2/N \sum_i^r \psi_i^* \psi_i d\tau \quad (i)$$

$$\text{or} \quad Z(r) = Z(r)^{\text{Ca}^{2+}} + 2/N \sum_i Z(r)^i.$$

The summation over i ranges only over occupied states in the Brillouin Zone, that is over states beneath the Fermi surface. To find the field acting on a given conduction electron, with label j , which may be in an unexcited state or in an excited state, the contribution $Z(r)^j$ due to this electron is removed from the total potential of equation (i) which would be seen by a test charge. Thus the field in which this electron moves is

$$Z(r)_j = Z(r)^{\text{Ca}^{2+}} + 2/N \sum_i Z(r)^i - Z(r)^j \quad (ii).$$

Thus each electron moves in a potential field different from that seen by any of the other electrons. Ideally then one needs to find the contributions to $Z(r)$ from all the approximately 10^{24} electrons in one mole of the metal. In practice one obviously has to restrict the number of different fields used and therefore also to restrict the number of different values of i to some finite number.

For the practical evaluation of the expression for $Z(r)_j$, the representative portion of the Brillouin Zone, which has 1/48th of the volume of the whole Zone, is assumed to be

divided into 19 pieces of equal volume, which are centred on the 6 points of symmetry, and the points of intersections of the lines Σ , Δ , and Λ with the planes $k_x + k_y + k_z = n\pi/2a$, where $1 \leq n \leq 5$. The actual shapes of these pieces are assumed not to affect the answer appreciably. This means that we are considering separate fields for each band and for 912 $\underline{k}$ -vectors in the Brillouin Zone. All the electrons in a given piece (1/912th) of the Zone are assumed to have approximately the same wave function so that as the volumes of all these pieces are all taken to be the same we can re-write equation (ii) as

$$Z(r)_j = Z(r)^{\text{Ca}^{2+}} + 2/N \sum_{i=1}^{i=n} Z(r)^i - Z(r)^j \quad (\text{iii})$$

where i now ranges over the occupied pieces of the Brillouin Zone, and $n = 19$ therefore here. We have restricted ourselves to having each 1/912th piece of the Brillouin Zone either full or empty but this is not a serious drawback.

A programme has been written which uses the values of E_i and ψ_i computed by the cellular programme to construct a set of fields, one for each band and each of the 19 pieces of the representative portion of the Brillouin Zone.

7.4 The SCF Programme.

A brief description of the programme used to evaluate the $\underline{k}$ -dependent fields $Z(r)_j$ will now be given. The programme is a two-chapter routine with a master and one subchapter. The subchapter was the routine described in

Chapter II, section 2.9 as "subroutine J" of the cellular programme. Given a set of 40_8 r values and an energy E_i it forms the functions $G_1(\rho)$ and $G_1'(\rho)$ which are simply related to the radial part of the wave function. The master routine supplies the data to this subchapter and in addition computes the $Z(r)_j$ as given by equation (iii), where i ranges over occupied states but j ranges over all states in the bands which are to be computed. The chief duty of the routine is to evaluate $\int_0^r |\psi_j|^2 dr$.

$$\psi_j(r, \theta, \phi) = \sum_{\nu} B_{1\nu}^j x_{1\nu}^j(\theta, \phi) R_1(z, r)$$

where B and $B_{1\nu}$, a complex number, are determined by the cellular computations. Thus:

$$\begin{aligned} \int_0^r |\psi_j|^2 d\tau &= \int_0^r \int_0^\pi \int_0^{2\pi} \left\{ \sum_{\nu} B_{1\nu}^{j*} x_{1\nu}^{j*}(\theta, \phi) R_e(E, r) \right\} \times \\ &\quad \left\{ \sum_{\nu} B_{1\nu}^j x_{1\nu}^j(\theta, \phi) R_e(E, r) \right\} r^2 \sin \theta dr d\theta d\phi \\ &= \sum_{\nu} \int_0^r |B_{1\nu}^j|^2 R_e^2(E, r) r^2 dr \times \\ &\quad \int_0^\pi \int_0^{2\pi} |x_{1\nu}^j(\theta, \phi)|^2 \sin \theta d\theta d\phi \\ &= \sum_{\nu} \int_0^r |B_{1\nu}^j|^2 R_e^2(E, r) r^2 dr \\ &= \sum_{\nu} \int_0^r |b_e|^2 R_e^2(E, r) r^2 dr \\ &\quad \text{where } |b_e|^2 = \sum_{\nu} |B_{1\nu}^j|^2 \end{aligned}$$

This defines the contribution to $Z(r)$ due to the j th conduction electron inside the equivalent sphere so that the complete contribution to $Z(r)$ due to it is :

$$\left\{ \begin{array}{ll} \sum_i |b_i|^2 R_i^2(E, r) r^2 dr & r \leq r_0 \\ 1 & r > r_0. \end{array} \right.$$

Thus the data supplied to the programme must include, for each 1/912thth piece of the Brillouin Zone and for each band, the $|b_i|^2$, E , and a coding of whether that portion of the Zone is occupied or not, i.e. whether or not its contribution is to be included in the summation over "i" in the formula used for $Z(r)_j$.

For the first iteration the data E and $|b_i|^2$ are supplied from the initial cellular calculation and for successive iterations from the previous iteration.

There is one drawback which would seem to prevent the programme with the radial integration routine as it stands from being applied to the electrons in the ion core as well as to the conduction electrons and it is that the last maximum of the wave function of a core electron, 3p, 3s etc., occurs at well below r_0 so that the computed wave functions for the core electrons may well have spurious "tails" to them. To eliminate these it would be necessary to perform an inwards integration and match it with the outwards integration as is done in atomic calculations. The difficulty does not arise for the conduction electrons because, for instance in calcium they are of 4s-3d type and have their last radial maxima

nearer to the equivalent radius.

7.5 Results of SCF Programme.

This programme thus can be taken together with the cellular programme described earlier and the interpolation programme to form a large self-consistent programme which operates as follows. Starting with a field $Z(r)$ due to a free metal ion and the appropriate number of conduction electrons a cellular calculation was done giving a set of bands for the metal; using this band structure the interpolation routine determined the Fermi energy and hence the Fermi surface thus enabling one to know which $\underline{k}$ -vectors in each band are to be included in the summation over i in the equation for $Z(r)_j$. Perhaps it should have been made clear that subscripts refer to the fields acting on electrons while superscripts refer to the field contributions due to electrons. With all these results a set of $\underline{k}$ -dependent fields were then calculated using the programme of section 7.4. The iterative process then consists in using these new fields to perform the entire cellular calculation again to give a new band structure from which another set of $\underline{k}$ -dependent fields can be obtained. Each cycle, even for a simple metal like calcium, thus takes of the order of 10 hours of computing time per band for the cellular calculation together with about 5 hours for the other programmes; this makes a total of about 25 hours for calcium. In addition to this the three separate programmes are not connected automatically, the

results of each one needing to be prepared, away from the computer, as data for the next one. Thus each iteration is a fairly lengthy process, which could of course in the future be automated completely. In fact only two iterations were performed, but the convergence seemed to be so good, (to 3 figures at least in the energy), that there seemed to be little need to go farther at present.

Some samples of k -dependent fields and their deviations from the initial "free conduction electron" potential are given in Table 7.1. To the number of figures quoted in this Table the fields were exactly the same in the first and second iterations, the differences being in fact never more than 10^{-5} in $Z_p(r)$. These fields were then used to repeat the cellular calculations for calcium, and the results, together with the original results are shown in Table 7.2. The bands are not redrawn since 5% changes in them are so small as to make the two sets of bands appear almost identical. The fourth column shows the difference between the first SCF iteration results and the initial cellular calculation, the effects noticed are that the metal becomes less "free-electron-like" when the correct charge distribution of the conduction electrons is considered. This is shown by (i) the fact that the band structure is narrower and therefore the Fermi energy is lower, and (ii) the overlap between the first and second bands, i.e. the separation of the levels KA_1 and LA_{2u} is diminished. Having done one complete re-

calculation of the cellular energy values and wave functions using the corrected fields a second iteration was tried to see how nearly convergent the process is.

The results of the second iteration are also shown in Table 7.2. And the differences between the results of the first and second iterations are very small indeed as is shown by the last column of this Table, and what is more important they are random in sign. In nearly all cases the agreement is to three figures in the energy, and in many cases to four figures or more; also as already mentioned the fields $Z_p(r)$ obtained for any $\underline{k}$ -vector in the first and second iterations differ by only about 10^{-5} . The coefficients in the wave function, B_{1j} , however have not converged as is illustrated in Table 7.3 for the case of LA_{1g} where the coefficients in the initial cellular calculation, and in the first and second iterations are given. But in spite of this the values of $|b_1|^2 (= \sum_j |B_{1j}|^2)$ have converged in a fashion very similar to that of the energy, as is shown by Table 7.4, again, for example, for the case of LA_{1g} . It is well known to be a general feature of SCF calculations that the wave function always takes more iterations before it converges than does the energy so that the non-convergence of B_{1j} need not cause us too much distress.

TABLE 7.1 SAMPLES OF k -DEPENDENT FIELDS, $z_p(r)$. r values as Table 5.2.

Original field	1st band		2nd band	
	A_{1g}	WB_2	T_{2g}	LA_{2u}
19.789	19.789	19.789	19.789	19.789
19.730	19.729	19.730	19.729	19.730
19.653	19.652	19.653	19.653	19.653
19.555	19.554	19.556	19.555	19.556
19.431	19.429	19.431	19.429	19.431
19.272	19.270	19.272	19.270	19.272
19.070	19.068	19.071	19.068	19.070
18.816	18.814	18.817	18.814	18.817
18.499	18.496	18.500	18.497	18.500
18.109	18.106	18.110	18.106	18.110
17.635	17.631	17.637	17.631	17.636
17.071	17.066	17.074	17.066	17.073
16.412	16.405	16.415	16.405	16.414
15.652	15.643	15.657	15.645	15.655
14.784	14.773	14.791	14.775	14.789
13.791	13.777	13.799	13.780	13.797
12.655	12.638	12.665	12.641	12.663
11.381	11.358	11.393	11.363	11.389
10.022	9.995	10.037	10.001	10.032
8.683	8.650	8.701	8.659	8.695
7.453	7.412	7.475	7.426	7.467
6.324	6.275	6.352	6.295	6.343
5.207	5.147	5.242	5.173	5.229
4.029	3.958	4.072	3.995	4.057
2.904	2.827	2.955	2.880	2.936
2.079	2.001	2.130	2.076	2.107
1.573	1.493	1.601	1.585	1.574
1.295	1.201	1.273	1.286	1.242
1.122	1.016	1.059	1.062	1.025
1.014	0.995	1.000	0.998	0.996
1.000	1.000	1.000	1.000	1.000
1.000	1.000	1.000	1.000	1.000

TABLE 7.2 RESULTS OF THE FIRST TWO ITERATIONS OF THE CONDUCTION ELECTRONS SCF COMPARED WITH THE INITIAL RESULTS.

Band 1.

Point	Initial calcn.E	1st shot SCF E'	2nd shot SCF E''	E'-E	E''-E	E''-E'
ΓA_{1g}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Σ_1	0.0220	0.0097	0.0099	-0.0123	-0.0121	0.0002
Σ_2	0.0767	0.0653	0.0653	-0.0114	-0.0114	0.0000
Σ_3	0.1496	0.1377	0.1376	-0.0119	-0.0120	0.0001
Σ_4	0.2345	0.2198	0.2199	-0.0147	-0.0146	0.0001
Σ_5	0.3223	0.3046	0.3051	-0.0177	-0.0172	0.0005
$K A_1$	0.3749	0.3066	0.2843	-0.0683	-0.0906	0.0223
ΓA_{1g}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Λ_1	0.0154	0.0031	0.0031	-0.0123	-0.0123	0.0000
Λ_2	0.0532	0.0418	0.0419	-0.0114	-0.0113	0.0001
Λ_3	0.1211	0.0940	0.0940	-0.0271	-0.0271	0.0000
Λ_4	0.1791	0.1484	0.1485	-0.0307	-0.0306	0.0001
Λ_5	0.2177	0.1912	0.1913	-0.0265	-0.0264	0.0001
$L A_{1g}$	0.2348	0.2283	0.2283	-0.0065	-0.0065	0.0000
ΓA_{1g}	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Δ_1	0.0403	0.0284	0.0285	-0.0119	-0.0118	0.0001
Δ_2	0.1356	0.1235	0.1236	-0.0121	-0.0120	0.0001
Δ_3	0.2233	0.2055	0.2056	-0.0178	-0.0177	0.0001
$X A_{1g}$	0.2577	0.2432	0.2432	-0.0145	-0.0145	0.0000
$W B_2$	0.3360	0.2989	0.2989	-0.0471	-0.0471	0.0000

Energies are referred to ΓA_{1g} as zero in each case.

TABLE 7.2 (contd.)

Band 2.

Point	Initial calen.E	1st shot SCF E'	2nd shot SCF E''	E'-E	E''-E	E''-E'
Γ T_{2g}	0.6329	0.6107	0.6108	-0.0222	-0.0221	0.0001
ϵ_1	0.6349	0.5396	0.5398	-0.0953	-0.0951	0.0002
ϵ_2	0.5348	0.7107	0.7108	0.1759	0.1760	0.0001
ϵ_3	0.4691	0.4362	0.4362	-0.0329	-0.0329	0.0000
ϵ_4	0.4356	0.4022	0.4023	-0.0334	-0.0333	0.0001
ϵ_5	0.4303	0.3940	0.3940	-0.0363	-0.0363	0.0000
K B_2	0.4432	0.4044	0.4044	-0.0388	-0.0388	0.0000
Γ T_{2g}	0.6329	0.6107	0.6108	-0.0222	-0.0221	0.0001
Λ_1	0.6314	0.5908	0.5909	-0.0406	-0.0405	0.0001
Λ_2	0.5520	0.5230	0.5233	-0.0290	-0.0287	0.0003
Λ_3	0.4708	0.4530	0.4530	-0.0178	-0.0178	0.0000
Λ_4	0.4336	0.3970	0.3970	-0.0366	-0.0366	0.0000
Λ_5	0.3781	0.3606	0.3606	-0.0175	-0.0175	0.0000
L A_{2u}	0.3673	0.3298	0.3298	-0.0375	-0.0375	0.0000
Γ T_{2g}	0.6329	0.6107	0.6108	-0.0222	-0.0221	0.0001
Δ_1	0.5735	0.6024	0.6023	0.0289	0.0288	0.0001
Δ_2	0.4797	0.4614	0.4614	-0.0183	-0.0183	0.0000
Δ_3	0.4180	0.5102	0.5102	0.0922	0.0922	0.0000
X B_{2g}	0.3964	0.3926	0.3926	-0.0038	-0.0038	0.0000
W A_1	0.5566	0.5336	0.5336	-0.0230	-0.0230	0.0000

Energies are referred to ΓA_{1g} as zero in each case.

TABLE 7.3 THE WAVE FUNCTION COEFFICIENTS B_1 FOR LA_{18} .

l	ν	Initial calculation.	First iteration.	Second iteration.
0	1	0.1264	0.1469	0.6901
		(0.7129	(0.7063	(0.2101
2	3	0.1201	0.1408	0.6512
		(0.6779	(0.6766	(0.2013
4	1	0.0066	0.0078	0.0366
		(0.0369	(0.0375	(0.0112
4	4	0.0023	0.0030	0.0141
		(0.0129	(0.0144	(0.0043
6	1	0.0013	0.0013	0.0059
		(0.0073	(0.0060	(0.0018
6	5	0.0016	0.0020	0.0094
		(0.0039	(0.0097	(0.0029
6	13	0.0014	0.0019	0.0089
		(0.0077	(0.0091	(0.0027

Note: the real and imaginary parts of $a + ib$ are written as $\begin{pmatrix} a \\ b \end{pmatrix}$ in the Table.

TABLE 7.4 THE CONVERGENCE OF $|b_1|^2$ ILLUSTRATED FOR LA_{18} .

l	Initial calculation.	First iteration.	Second iteration.
0	0.5241	0.5205	0.5203
2	0.4740	0.4777	0.4777
4	0.0015	0.0016	0.0017
6	0.0004	0.0002	0.0003

7.6 Conduction Electrons SCF: Conclusions.

In this section we attempt to draw some useful conclusions from the results which we have just presented.

(i) The charge distribution of the conduction electrons in a metal is not that of a free electron but there is a substantial build up of charge in the outer regions of the cell as shown in Figure 4.1; this reduces the screening of the nucleus.

(ii) On using the more realistic average charge distribution of the conduction electrons the band structure becomes less "free-electron-like" and the Fermi energy is reduced by about 5%. The change in the relative positions of the levels, and therefore in the Fermi surface is very slight.

(iii) In view of the very good convergence of E , $|b_1|^2$, and the fields $\chi(r)_j$ even after only two iterations we can claim that we have a Hartree self consistent field for metallic calcium. A few more iterations would be necessary before the wave function could be said to have converged.

7.7 The Effect of the Conduction Electrons on the Ion Core.

Now we turn our attention to the core electrons. The field used initially for the cellular calculation on the conduction electrons in calcium is

$$\chi(r)^{\text{Ca}^{2+}} + \chi(r)^{\text{one free electron}}$$

$$= 1s^2 2s^2 2p^6 3s^2 3p^6 + 1 \text{ free electron.}$$

It is also possible to compute the new levels for the electrons in the ion core when the calcium ion is moved into a metal and Wigner-Seitz type boundary conditions are applied.

The fields would be:

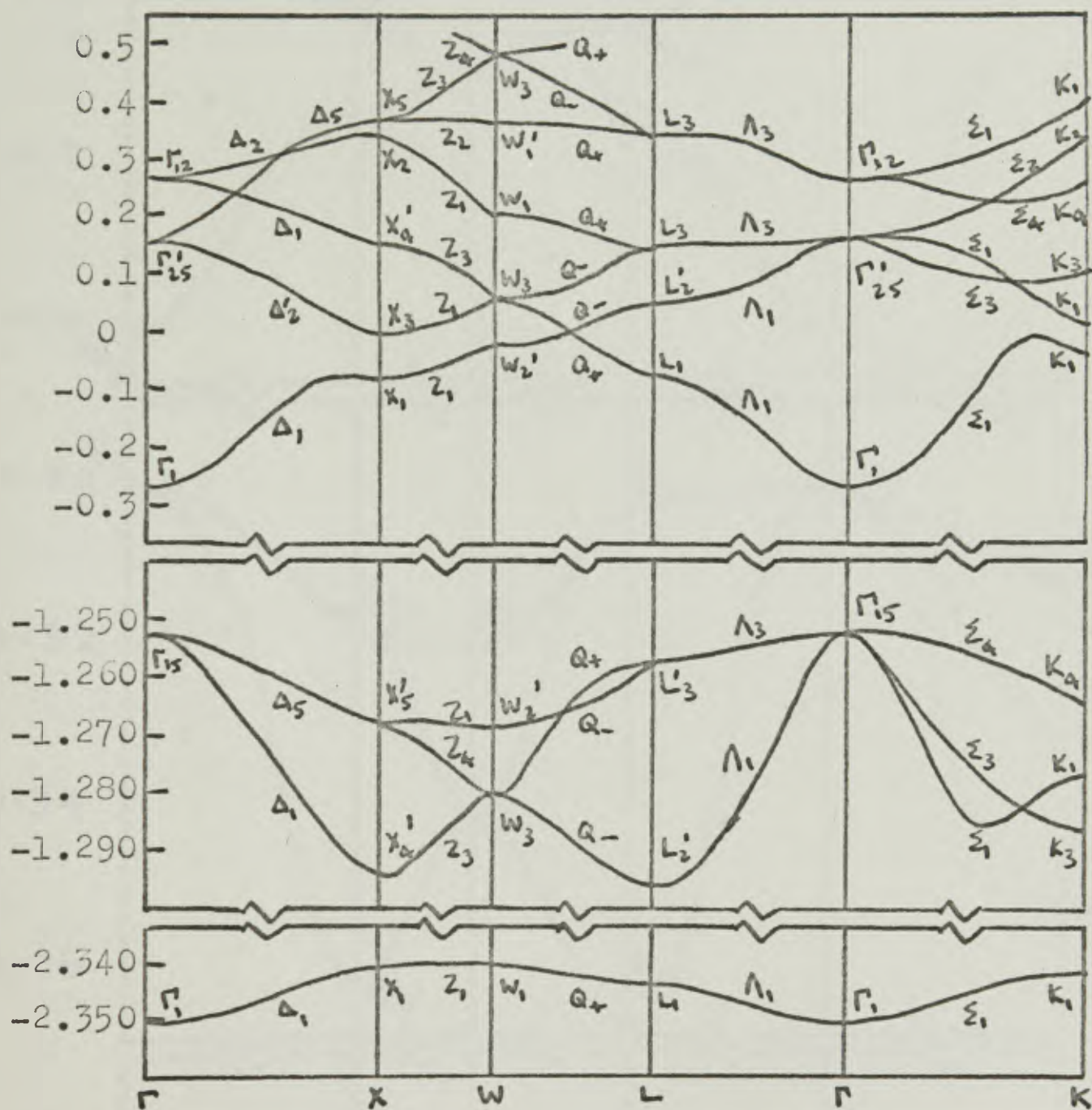
$$1s^2 2s^2 2p^6 3s^2 3p^5 + 2 \text{ free electrons}$$

and $1s^2 2s^2 2p^6 3s 3p^6 + 2 \text{ free electrons}$

for 3p and 3s electrons respectively.

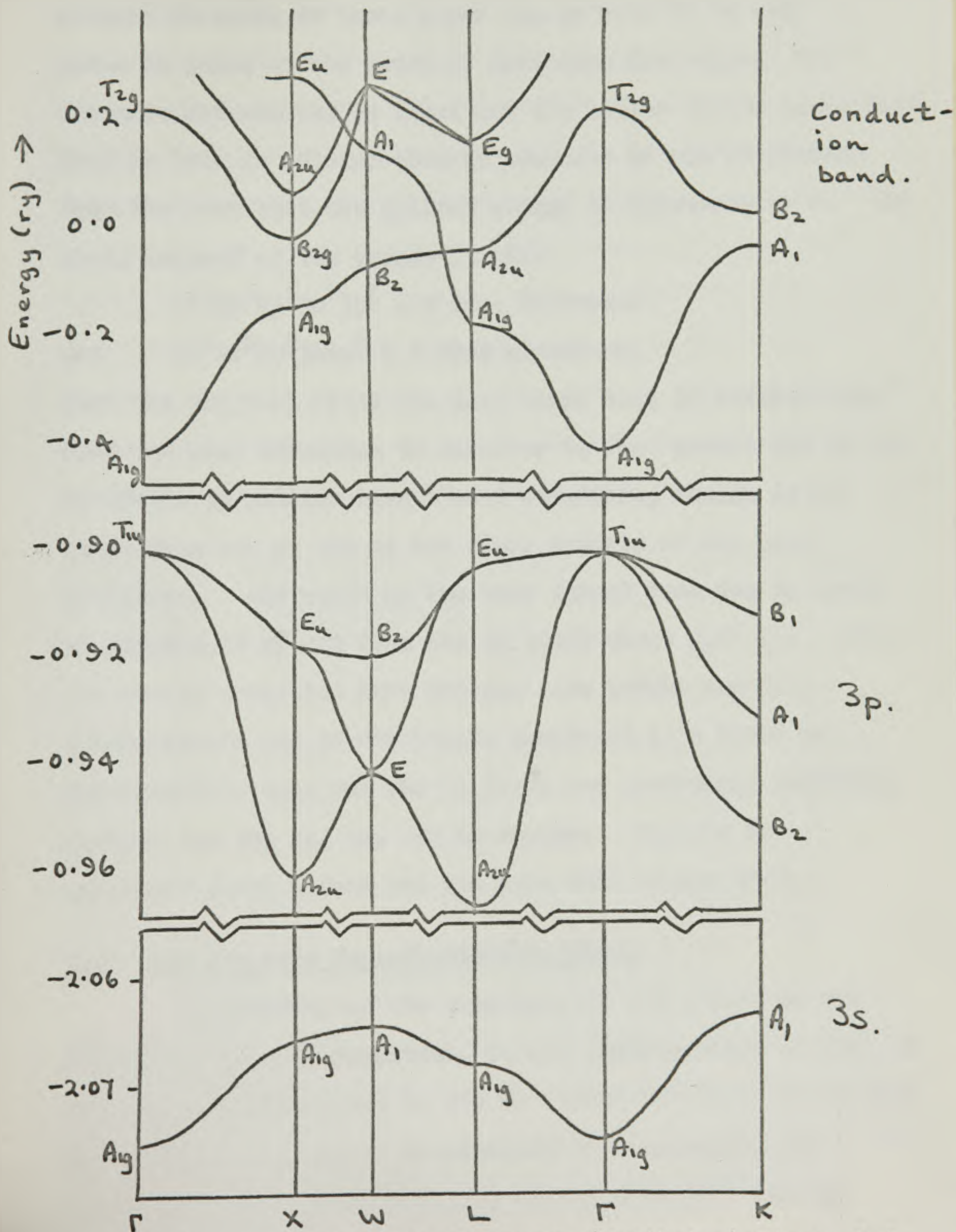
It is sometimes claimed that since these levels are in the ion core they will still, in the metal be very similar to atomic levels and to a very good approximation independent of k . Though this is doubtless true for electrons deep within the ion core it would not seem to be true for the outer electrons within the core. For instance Mattheiss (1963) in his calculation of the band structure of solid argon found that the 3s level was nearly independent of k , it varied by only about 0.01 ry but the 3p levels were strongly dependent on k , being in fact broadened into bands of width about 0.04 ry. Since Fermi energies are only of the order of 0.5 ry then it is clear that in argon the 3p levels are significantly broadened. The band structure of argon obtained by Mattheiss is shown in Figure 7.2, the change of scale on the energy scale should be noticed. The band structure of calcium is not very significantly different from that of argon, as is shown by a re-drawing in Figure 7.3 of the bands we gave in Chapter V for calcium. The 3s and 3p levels have also been

FIGURE 7.2 ENERGY BANDS OF SOLID ARGON.



After Mattheiss (1963).

FIGURE 7.3 ENERGY BANDS OF CALCIUM.



Compare with bands for argon (Mattheiss) Figure 7.2.

computed and they are included in Figure 7.3 also. The general features of these bands can be seen to be very close to those of the bands of Mattheiss for argon; the distance between the 3p level and the bottom of the conduction band is less in calcium than in argon as is not surprising from the fact that the nuclear charge is increased by 2. In fact, instead of the proper fields:

$$1s^2 2s^2 2p^6 3s^2 3p^5 + 2 \text{ free electrons}$$

and $1s^2 2s^2 2p^6 3s 3p^6 + 2 \text{ free electrons},$

just the original field was used since this is sufficiently near the real situation to discover to what extent the 3p and 3s levels in calcium have a band structure, though it may invalidate one or two of the finer details of the band structure. The width of the band formed from the 3p level is about 0.06 ry and from the 3s level about 0.01 ry. Thus the common assertion that the ion core levels are like atomic levels and do not become broadened into bands is approximately true for the 3s level and presumably perfectly alright for the 2p, 2s, and 1s levels. But for the outermost shell within the ion core this is not true.

7.8 The Ion Core Contributions to $Z(r)$.

An estimate of the magnitude of the effect on the energies and, more important, on the contributions to $Z(r)$ of the inner electrons due to the 4s atomic electrons going into the conduction band may be obtained from comparing the energies of the inner electrons in the free Ca^{2+} ion and

in the Ca atom. These are shown in the second and fourth columns of Table 7.5. It is clear from the Table that the energies are very little different, of the order of 0.03 ry which agrees quite well with the order of magnitude of the values found above. If it were not for the difference between the boundary conditions in the cases of a free atom and an atom in a metal the real metal would have ion core energy levels somewhere between those of the case where the conduction electrons are perfectly free, and the case of the Ca atom where the 4s electrons are completely bound to the atom. The former case with Ca^{2+} ion and two perfectly free conduction electrons is shown in the third column of Table 7.5.

TABLE 7.5 ENERGY LEVELS IN THE ION CORE OF CALCIUM FOR
VARIOUS FIELDS.

	Ca^{2+} .	CaFAP.	Ca atom.
1s	0	0	0
2s	265.092	265.104	265.084
2p	271.473	271.483	271.471
3s	294.274	294.288	294.239
3p	296.077	296.084	296.049

after Mayers (1964)

The CaFAP field is a self consistent field between a Ca^{2+} ion core and two free electrons contained in a sphere of volume equal to the volume of the Wigner-Seitz cell. In this way, since it is still an essentially atomic calculation it is possible to perform an accurate and relatively quick

calculation and study approximately the effect of the conduction electrons on the core electrons, and to include exchange interactions between the core electrons and the conduction electrons. This computation has been programmed and performed for us by Dr D.F. Mayers of the Oxford University Computing Laboratory as an adaptation of his atomic scf programme, and his results for the field are shown in Table 7.6. The second column is the field due to a free calcium ion plus one free electron, in the third column a self consistent field calculation between the ion and the free electrons has been performed, and the fourth column shows the field due to a free calcium atom with one free electron removed from it. The field in the second column of Table 7.6 is the field which was used in the calculations of chapter V.

It will be seen from Table 7.6 that the CaFAP values of $Z(r)$ differ only slightly from those of the second column and that where they do differ they are, for most r values, smaller, though at large r values they become larger than the original values. That means that in the metal the nucleus is, at most r values more screened by the core electrons than in the free ion, though at large r values it is less screened. In both these fields the other conduction electrons in the cell have been treated in the same way so that all the differences between the two fields are due to differences in the $1s^2 2s^2 2p^6 3s^2 3p^6$ core in the two cases. It seems

likely therefore that the CaFAP field will on balance, have the effect of making the computed band structure a little more free-electron-like than that computed in Chapter V. In the last column of Table 7.6 is listed for comparison the field of the Ca neutral atom with one free electron removed, since this means that the other conduction electron is being treated as a 4s electron it is not easy to make good comparisons between the behaviour of the cores in this and the other two fields as there are differences between the treatment of the outer (4s) electrons in the two cases. But the combined effect of the core and outer electrons is to make this field less compressed than either of the other two and therefore it will give a band structure which will be less "free-electron-like" than either of the ones produced by the other two fields. It is hardly necessary to repeat the cellular calculations on calcium with these two fields since we have just noted that the differences from the original field are so small and have predictable effects.

A comparison with the case of cobalt, where the bands for $\Gamma - \Delta - X$ were given in Figure 4.3 is instructive; the differences between the various cobalt fields are an order of magnitude larger than between the calcium fields, and this can be seen from Table 7.7. The bands obtained using these new calcium fields will be very similar to those of Chapter V, though the Fermi energy may be increased by a few percent. The reason for the large differences between the cobalt fields is

TABLE 7.6 THREE CALCIUM FIELDS, $Z_p(r)$.

r	$\text{Ca}^{2+} + f.e.$	$\text{CaFAP} + f.e.$	$\text{Ca atom} - f.e.$
0.00264	19.789	19.789	19.790
0.00339	19.730	19.730	19.730
0.00435	19.653	19.653	19.654
0.00559	19.555	19.555	19.556
0.00717	19.431	19.431	19.429
0.00920	19.272	19.271	19.273
0.01183	19.070	19.068	19.071
0.01518	18.816	18.816	18.818
0.01950	18.499	18.499	18.510
0.02503	18.109	18.109	18.503
0.03214	17.635	17.635	17.639
0.04127	17.071	17.070	17.077
0.05300	16.412	16.411	16.417
0.06805	15.652	15.651	15.670
0.08738	14.784	14.782	14.794
0.1122	13.791	13.786	13.802
0.1441	12.655	12.650	12.669
0.1850	11.381	11.374	11.399
0.2375	10.022	10.014	10.047
0.3050	8.683	8.672	8.714
0.3916	7.453	7.436	7.522
0.5028	6.324	6.303	6.376
0.6456	5.207	5.175	5.269
0.8290	4.029	4.021	4.144
1.064	2.904	2.938	3.101
1.367	2.079	2.103	2.314
1.755	1.573	1.590	1.849
2.254	1.295	1.303	1.525
2.894	1.122	1.126	1.385
3.715	1.014	1.018	1.284
4.771	1.000	1.000	1.122
6.126	1.000	1.000	1.036

After Mayers (1964)

TABLE 7.7 THE FIELDS, $Z(r)$, FOR Co^{6+} , Co^{2+} and Co^{+} .

The bands along - - X are shown in Figure 4.3 for these three fields.
r values are as in Table 7.6.

Co^{6+}	Co^{2+}	Co^{+}
26.682	26.680	26.679
26.593	26.590	26.589
26.478	26.474	26.472
26.331	26.327	26.324
26.144	26.138	26.135
25.907	25.900	25.896
25.608	25.600	25.595
25.236	25.223	25.218
24.776	24.762	24.753
24.216	24.197	24.187
23.547	23.522	23.509
22.758	22.726	22.710
21.841	21.779	20.695
20.776	20.722	20.695
19.543	19.470	19.437
18.120	18.024	17.981
16.521	16.393	16.337
14.816	14.640	14.571
13.097	12.860	12.772
11.407	11.092	10.982
9.678	9.283	9.145
7.865	7.391	7.211
6.076	5.522	5.300
4.547	3.966	3.678
3.390	2.873	2.534
2.500	2.222	1.840
1.737	1.815	1.445
1.142	1.391	1.215
0.997	1.004	1.086
1.000	1.000	1.025
1.000	1.000	1.005
1.000	1.000	1.000

After Mayers (1964)

probably to be found in the fact that as the ionisation is increased so more of the conduction electrons are treated as free electrons rather than as 3d electrons of the cobalt atom with the result that exchange between the core and conduction electrons is being increasingly neglected and the nucleus is becoming less and less screened; the effect of this is to make the band structure more compressed and to lower the Fermi energy. This trend for cobalt which has also been observed in titanium, vanadium, molybdenum and chromium by Bradley, Jeacocke, and Rousseau (1964) is however in the opposite sense from the trend in calcium, where an increase in the ionisation of the core is accompanied by an expansion of the band structure.

Though it is not conclusive evidence the X-ray work available, e.g. Skinner et al (1954), seems to suggest that the transition metals do not have large Fermi energies, and this seems to be good evidence in favour of using the field due to an ion of high ionisation, in many cases higher than the ordinary chemical valency. Thus we can postulate that, where there is no obvious ion to take for the core one should choose that ion which leaves the atom with no incomplete shells of electrons. This however may not even really be sufficient because as we have seen with calcium the last complete shell which is the 3p shell has a significant band structure. These electrons should not be considered just as ionic levels therefore, although the effect on $Z(r)$ is small, and they form

an isolated band way below the conduction band. Possibly a more serious problem is that by taking an ion core and a certain number of free conduction electrons the effects of exchange interactions are neglected for more and more electrons as the ionisation of the core is increased.

7.9 The SCF and the Ion Core Electrons.

Since it has just been shown that the 3p levels in calcium, and to a lesser extent the 3s levels, have a band structure it would be desirable to include them in a self consistent field calculation of the sort which we described for the conduction electrons. In principle this is not difficult but there are one or two snags of a practical nature which would have to be sorted out before a really good self consistent field could be produced. These are (i) the fact that the wave functions for these inner electrons by the time they reach the outer regions of the cell where the boundary conditions are fitted have passed their last maximum and, as no inwards integration is used, they are beginning to diverge rapidly, thus ruining the accuracy of the calculation, and (ii) the fact that going from just the conduction electrons to, for example the 3s and 3p bands as well, one has gone from the consideration of two electrons to the consideration of ten electrons altogether. To do the scf calculations allowing for both these points would necessitate large changes in the programmes as we already have them. In view of this, and also of the fact that as

we should then be about to produce a very good field it would be necessary to include the effects due to the other ions and due to exchange interactions, it is left as a problem to be tackled in the future to extend the scf to as much of the ion core as it is necessary to consider. It will thus be necessary for each metal to have an initial rough band structure calculation to discover how many of the ion core levels it is necessary to include for that metal.

7.10 Ion Core Electrons: Conclusions.

From the last three sections we can draw the following conclusions:

(i) The outer shells of the assumed ion core (the 3p and 3s in calcium) do have a band structure and thus are substantially altered from the levels in the free ion.

(ii) The effect of this on the field $Z(r)$ and on the energies of the conduction electrons is small but would be to make the situation in the band structure more "free-electron-like."

7.11 Conclusions about Calcium.

These conclusions were really anticipated in the previous chapter and they are that the effects of the better treatment of the ion core and of the conduction electrons act on the band structure in the opposite sense; the core leading to a more "free-electron-like" conduction band and the conduction band's own effect being to make itself less

"free-electron-like". In view of Chapter VI it would appear that the core should be expected to win and so make the band structure and Fermi surface a little more like the free electron case.

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