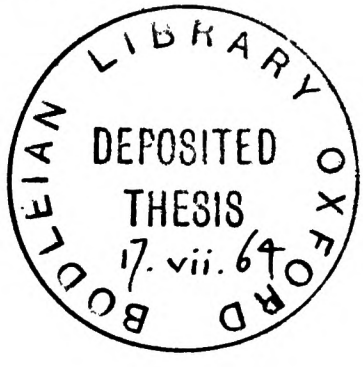
SOME PROBLEMS IN THE THEORY OF SOLIDS.

A Thesis Submitted for the Degree of Doctor of Philosophy

by

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This thesis is concerned with the application of lattice dynamical theories to problems of current physical interest. The first part is a calculation of the lattice dynamics of calcium fluoride, with a detailed discussion of the various types of model which may be used. On the basis of this discussion the Born model is used in the numerical calculation and the results are presented in the form of dispersion curves and density-of-states curves.

The second part of the thesis deals with the theory of the vibrations of crystal lattices perturbed by the introduction of defects. The object is to develop the theory into a form such that it becomes easy to perform numerical calculations, using existing lattice dynamical calculations, so that physical properties of defects which involve changes of force constants as well as mass changes may be computed.

The third part deals with such a defect which has received some experimental attention recently, namely, the hydrogen ion in calcium fluoride crystals. This is an interesting theoretical problem as not only is the theory of defects in crystal lattices concerned, but also that of anharmonicity. From the optical observations it is possible to calculate some of the anharmonic force constants involved.

CHAPTER I

Introduction

The theory of lattice dynamics has a long and interesting history extending over fifty years, dating from the basic papers of Debye (1912) and Born and Von Karman (1912). For most of these years, experimental techniques have been insufficiently refined to provide a detailed investigation of the motion of individual vibrating atoms, so the theories have been directed towards the understanding of the macroscopic behaviour of crystals. However, refinements in X-ray techniques and the introduction of slow neutron scattering facilities have proved very fruitful in the detailed investigation of the dispersion curves of the lattice vibrations, while the introduction of a defect to probe the crystal environment, as in the Mossbauer effect, fluorescence spectra, etc., seems likely to provide an important tool also. In addition, the advent of large and powerful computing machines has made it possible to perform calculations of the theories based on somewhat more realistic models than has hitherto been possible.

This thesis is concerned therefore, with the theory of lattice vibrations and the introduction of defects into

otherwise perfect crystals. On the basis of these theories, detailed calculations will be made for some physical models of current interest.

The equilibrium positions of the particles constituting a crystalline solid are arranged on a regular lattice, but as a result of zero-point motion and thermal fluctuations, the particles execute small oscillations about these lattice points. The potential energy of the crystal may be expanded in powers of these small displacements, and what is known as the harmonic approximation is obtained if all terms past the quadratic are neglected. The anharmonic terms, involving cubes, fourth powers, etc. of the displacements decrease quite rapidly with increasing order; the ratio of two successive terms is of order (mean particle displacement)÷(lattice spacing) $\sim \frac{1}{10}$ for reasonable temperatures.

In principle the displacements of both electrons and nuclei ought to be considered, but in the Born model of the crystal the electronic co-ordinates are neglected. The electrons do not stay fixed; on the contrary, they accommodate themselves so rapidly to the nuclear motion that the electronic state may be treated as if it were a unique function of the values of the nuclear co-ordinates at that moment. This adiabatic approximation was justified by Born and Oppenheimer (1927).

Within the harmonic approximation, the Hamiltonian of the crystal may be exactly diagonalised; for the unperturbed lattice, the resulting normal co-ordinates are waves, a consequence of the translational symmetry of the lattice. Each normal co-ordinate is a solution of the equations of motion in which all the particles vibrate with the same frequency, so the main object of a lattice dynamical calculation is to compute these frequencies as a function of the wave vector of the corresponding normal co-ordinate. Each of these corresponds to the wave-like propagation of one type of vibration executed by the particles of the unit cell; consequently there are three times as many branches to the $\omega(\underline{k})$ curves as there are particles in a unit cell.

The calculation of the crystal potential directly from quantum mechanical foundations is not possible within the present state of knowledge of the subject, so the constants describing the potential are treated as arbitrary parameters to be fixed by the experimental data. Clearly given a sufficient number of these parameters any dispersion curve may be fitted to the experimental results, and accordingly care must be taken to have a sufficiently physical model so that a reasonable meaning may be attached to each derived constant.

The object of the exercise is not to calculate an algebraic function which corresponds to the observed dispersion curves. For this reason it is felt that the smaller the number of parameters the better; accordingly they are only fixed from the initial values and slopes of the dispersion curves, that is, the infra-red absorption frequencies and the elastic and dielectric constants. Within this framework, the theory of lattice vibrations has been extensively worked out in the book by Born and Huang (1954) and the results summarised in review articles by de Launay (1956), Blackman (1955) and Leibfried (1955).

A somewhat better approximation to the actual crystal potential may be obtained by including the electronic co-ordinates up to terms involved in the dipole approximation. Thus the individual particles are allowed to become polarisable and their interaction is due both to short range terms and the long range Coulomb interaction. In order to retain the ideal of describing interactions with a minimum number of parameters, the short range forces are simplified to nearest neighbour forces only and the question of which model to use depends upon the relative importance of the short range and polarisation forces. The adiabatic approximation is still retained and this model results in similar although rather more complicated equations of motion.

The introduction of defects into these perfect lattices destroys the translational symmetry and consequently changes the form of the normal co-ordinates. However, within the harmonic approximation the normal co-ordinates are well defined and may be exactly calculated by the methods of Chapter III.

The frequency changes to be expected may be predicted from a theorem due to Lord Rayleigh (1877) which states that in a vibrating system a perturbation which has the form of mass increase in one of the particles or a force constant decrease, will cause all the eigenfrequencies to decrease in such a way that the levels always lie in the gap between an unperturbed level and its nearest neighbour levels. The converse effect is produced by decreasing one of the masses or increasing a force constant.

In this case there is a possibility of the highest eigenvalue lifting out of the band of unperturbed frequencies resulting in the formation of a localised mode of vibration; the amplitude of the normal co-ordinate decreases with increasing distance from the defect. As the frequency of a localised mode gets further from the edge of the band the

attenuation of the mode increases. However, as the modes are normalised so that the amplitude squared multiplied by the mass of the atom, summed over all atoms is a constant, a well localised mode has a large amplitude at the defect. In fact this sum rule shows that the amplitude of the localised mode at a defect is of order $\sqrt{N}$ times that of a band mode. Any physical property therefore, which depends upon the amplitude squared, will be made up of 2 parts; a contribution of order $\frac{1}{N}$ from N band modes and a contribution of order 1 from the localised mode, both of the same order of magnitude.

The modes may be classified according to their symmetry about the defect. It may happen that for some mass and force constant changes some of the symmetry types are not perturbed. This classification by symmetry is of interest for a further reason: physical properties in the vicinity of the defect are governed not so much by the vibrations of the individual atoms as by the symmetric combinations. Thus the width of the F-centre absorption line is a function of the amplitude of the dilation mode about the defect. Previous calculations of this width have assumed that this dilation mode vibrates at a few frequencies only (see for example Aberenkovetal 1960, 1961) but in reality it responds at every frequency of the lattice with an amplitude determined by the change in force

constants at the F-centre itself.

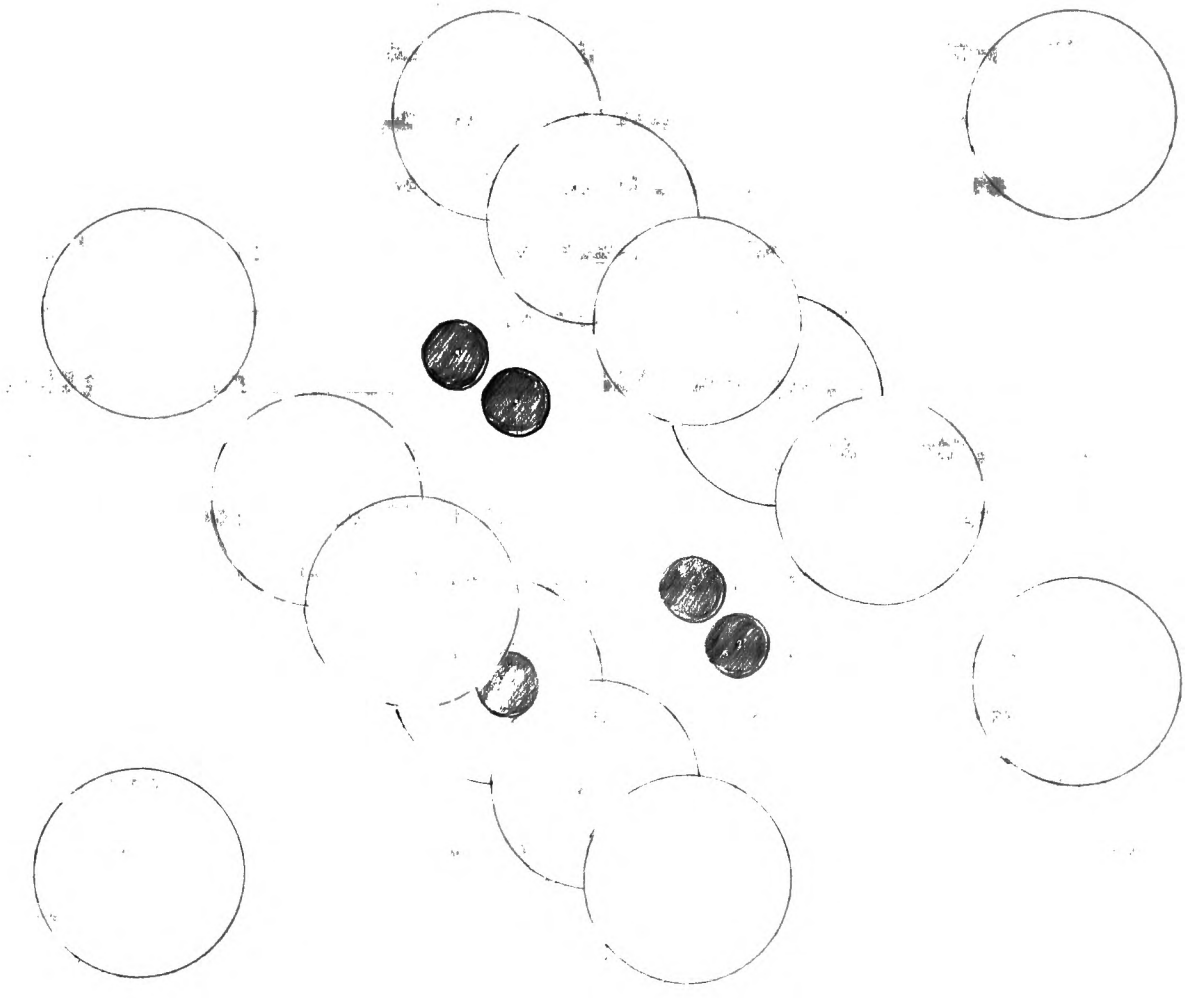
Another example of the use of these methods is in the calculation of fluorescence spectra, due for example to rare earth ions in crystal lattices. Here an optical transition which is forbidden in the free ion becomes allowed in the environment of the crystal, due to the influence of lattice vibrations. The interaction operator here is usually interpreted as the crystal field potential expanded in terms of the displacements of the rare earth ion and its nearest neighbours. If the environment is symmetrical enough only the dilation mode contributes, giving an absorption spectrum proportional to the density of states multiplied by the amplitude of the dilation mode around the defects.

The large amplitude of vibration of a very light impurity atom makes it important to consider anharmonic effects. The addition of the anharmonic terms to the harmonic potential results in the normal modes no longer being so well defined; the localised modes are mixed into the band modes and vice versa. There are a great many possible processes which these anharmonic terms can bring about, introducing quite strong temperature dependences in the case of the admixture of band modes

and lighting up harmonics in the case of the admixture of local modes.

This is the case in the infra-red absorption due to hydrogen and deuterium impurities in the alkaline earth fluorides, which have been the subject of recent experimental studies. This gives rise to fundamental absorption lines and harmonics whose position and width are temperature dependent. The interest in this case attaches to the fact that it is possible to measure the anharmonic force constants directly rather than infer them from the thermodynamic data.

This thesis therefore, is concerned with successive approximations to the dynamical behaviour of crystal lattices, in particular calcium fluoride. In the second chapter the lattice dynamics of the pure crystal will be considered, using both the rigid ion and the polarisable ion approximations. The effects of the introduction of defects are next considered in Chapter III, followed in Chapter IV by considerations of better approximations to the crystal potential, including the effects of anharmonicity.



The calcium fluoride structure: the larger circles represent calcium ions.

CHAPTER II.

The Lattice Dynamics of Calcium Fluoride.

The calculation of the lattice vibration frequencies alcium fluoride is an interesting problem for a number easons. The calculation itself is rather more plicated than that for previous crystals which have been empted in any detail, and also other authors (Grabier 63; Ganesan and Srinivasan 1962) have been at some agreement as to some aspects of the calculations. The lcium fluoride lattice is also of considerable physical erest as it is used as a host lattice for a variety of fects, particularly the rare earth ions. In this spect it is helpful to know the way in which the crystal vironment affects the defect, which in principle it is ssible to calculate once the lattice vibration spectrum is own.

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The theoretical background will be briefly sketched, principally to establish the notation; a complete list of symbols and their meanings may be found in Appendix 1. The theory of the Born model will be presented first of all, followed by a treatment with polarisable ions due to Cochran (1959) following the model proposed by Dick and Overhauser (1958).

In the Born model therefore, the potential is written as a function of the ionic displacements, and this potential expanded to include terms up to second order in the displacements:-

$$V - V_0 + \sum_{\alpha\beta ll'} \underline{u}_\alpha(l) \underline{K}_{\alpha\beta}(ll') \underline{u}_\beta(l') \qquad \ldots(2.1)$$

$\underline{u}_\alpha(l)$ is the displacement of the αth ion in the lth cell and the force constant matrix $K_{\alpha\beta}(ll')$ has components equal to the second derivatives of the interatomic potential with respect to the displacements in the cells l and l'.

The coefficients $K_{\alpha\beta}(ll')$ are invariant under lattice translations and can only be a function of the relative cell index

$$\underline{K}_{\alpha\beta}(ll') = \underline{K}_{\alpha\beta}(l-l')$$

and consequently the normal co-ordinates are waves

$$\underline{u}_\alpha(l) = \frac{1}{\sqrt{N}} \sum \alpha_\alpha^j(k) e^{2\pi i \underline{k}.\underline{r}_\alpha(l)} q_j(k) \qquad \ldots(2.2)$$

The lattice has N unit cells and the N quasi-continuous values of $\underline{k}$ fill the first Brillouin zone. If there are s particles in a unit cell, $\alpha = 1 \ldots s$, there are 3s branches specified by j.

On substituting the transformation into the equations

of motion

$$M_\alpha \ddot{u}_\alpha(\ell) + \sum \underline{\underline{K}}_{\alpha\beta}(\ell\ell') \underline{u}_\beta(\ell') = 0 \qquad \ldots(2.3)$$

one obtains, for each normal mode,

$$\frac{M_\alpha}{\sqrt{N}} \underline{\sigma}_\alpha^j(\underline{k}) e^{2\pi i \underline{k}.\underline{r}_\alpha(\ell)} \ddot{q}_j(k) + \frac{1}{\sqrt{N}} \sum \underline{\underline{K}}_{\alpha\beta}(\ell\ell') \underline{\sigma}_\beta^j(k) e^{2\pi i \underline{k}.\underline{r}_\beta(\ell')} q_j(k) = 0 \qquad \ldots(2.4)$$

Each normal co-ordinate has an exponential time dependence

$$\ddot{q}_j(\underline{k}) = -\omega_j^2(\underline{k}) q_j(\underline{k}) \qquad \ldots(2.5)$$

so that

$$M_\alpha \underline{\sigma}_\alpha^j(\underline{k}) \omega_j^2(\underline{k}) - \sum \underline{\underline{A}}_{\alpha\beta}(\underline{k}) \underline{\sigma}_\beta^j(\underline{k}) = 0 \qquad \ldots(2.6)$$

where the dynamical matrix $A_{\alpha\beta}(\underline{k})$ is the Fourier transform of the force constant matrices

$$A_{\alpha\beta}(\underline{k}) = \sum K_{\alpha\beta}(\ell\ell') e^{-2\pi i \underline{k}.\underline{r}_{\alpha\beta}\ell-\ell'}$$

The eigenvectors are orthogonal and normalised so that

$$\sum_\alpha M_\alpha \sigma_\alpha^{j\dagger}(\underline{k}) \sigma_\alpha^{j'}(\underline{k}) = \delta_{jj'} \qquad \ldots(2.7)$$

and satisfy the closure property

$$\sum_j \underline{\sigma}_\alpha^j(\underline{k}) \underline{\sigma}_\beta^{j\dagger}(\underline{k}) = \frac{1}{M_\alpha} \delta_{\alpha\beta} \qquad \ldots(2.8)$$

In second quantisation, the normal co-ordinates are

$$q_j(\underline{k}) = \sqrt{\frac{\hbar}{2\omega_j(\underline{k})}}\left(a_j(\underline{k}) + a_j^+(\underline{k})\right) \quad \ldots(2.8)$$

where $a_j(\underline{k})$ and $a_j^+(\underline{k})$ are annihilation and creation operators for phonons of type j and wave vector $\underline{k}$.

The plan of the calculation is therefore as follows:- given the form of the force constant matrices $\underline{K}_{\alpha\beta}(ll')$ based on some simple model, the dynamical matrix $\underline{A}_{\alpha\beta}(\underline{k})$ is calculated for a sample of $\underline{k}$ points within the first Brillouin zone. Each of these matrices is diagonalised in turn and the appropriate $\underline{k}$ value, eigenvectors $\underline{\varepsilon}^j(\underline{k})$ and eigenvalues $\omega_j^2(\underline{k})$ are calculated and tabulated, using equation (2.6). The force constant matrices are treated as arbitrary parameters, the values of these parameters being fixed by calculating the elastic constants and the infra-red and Raman active frequencies.

Before commencing this calculation the problem will be reduced to its simplest possible form by the application of the symmetry properties of the lattice.

1. The effect of Crystal Symmetry.

Any symmetry operation of the lattice can be divided

into rotational and translational parts, so that the symmetry operations are written $(S|\tau)$ representing a rotation S followed by a translation through a displacement τ. All of the symmetry information contained in the sub-group of lattice translations has been used in reducing the normal co-ordinates to waves, and consequently only the factor group of rotations and associated non-primitive translations will be considered. An operation of the form $(S|V(S))$ places a displacement $u_\alpha(l)$ at the lattice point $(\alpha' l')$ where $(S|V(S))^{-1}(\alpha' l') = (\alpha l)$. The potential in the two cases is the same so

$$\sum \underline{u}_\alpha(l_1)\, \underline{\underline{K}}_{\alpha\beta}(l_1 l_2)\, \underline{u}_\beta(l_2) = \sum \underline{u}_{\alpha'}(l_1')\, \underline{\underline{\tilde{S}}}\, \underline{\underline{K}}_{\alpha'\beta'}(l_1' l_2')\, \underline{\underline{S}}\, \underline{u}_{\beta'}(l_2') \qquad \ldots(2.10)$$

and evidently

$$K_{\alpha\beta}(l_1' l_2') = S K_{\alpha\beta}(l_1 l_2) \tilde{S} \qquad \ldots(2.11)$$

By considering only operations which leave the bond $(\alpha l_1) - (\beta l_2)$ invariant, the number of independent constants in any particular force constant matrix may be calculated. There is a further symmetry which these matrices possess, namely,

$$\underline{\underline{K}}_{\alpha\beta}(l_1 l_2) = \underline{\underline{\tilde{K}}}_{\beta\alpha}(l_2 l_1) \qquad \ldots(2.12)$$

which follows from the form (2.1) for the potential energy: any anti-symmetric part of the K's will not contribute to the potential energy, as this involves a sum over all the lattice points. The group of the bond therefore contains those operations leaving it invariant, together with the combination of the reversal operations and the transpose operator. The number of independent constants in the matrix is the number of times the identity representation is contained in the space spanned by a star of bonds, which by the character or the normality theorem is

$$n = \frac{1}{g}\sum \chi(S) \qquad \ldots(2.13)$$

where g is the number of operations in the group and $\chi(S)$ is the character of the operation S in the representation of S formed by the bonds. For an operation leaving $N(S)$ bonds invariant out of the star of bonds -

$$\chi(S) = N(S)\chi'(S) \qquad \ldots(2.14)$$

where $\chi(S)$ is the character of S in the polar vector representation: the force constant matrices transform like the direct product of 2 polar vectors. For operations which reverse $\tilde{N}(S)$ bonds

$$\chi(S) = \tilde{N}(S)\chi(S^2) \qquad \ldots(2.14a)$$

which arises because of the transpose operation. Accordingly

$$n = \frac{1}{g}\sum_S \left\{ N(S)\chi'(S) + \tilde{N}(S)\chi(S^{-1}) \right\} \qquad \ldots(2.15)$$

Using the relation (2.11) it is possible to derive the transformation properties of the dynamical matrix:

$$A_{\alpha\beta}(\underline{k}) = \sum K_{\alpha\beta}(l_1 l_2)\, e^{-2\pi i \underline{k}.\underline{r}_{\alpha\beta}(l_1 - l_2)}$$

$$= \sum \tilde{S} K_{\alpha'\beta'}(l_1' l_2')\, S\, e^{-2\pi i \underline{k}.\underline{r}_{\alpha\beta}(l_1 - l_2)}$$

$$= \tilde{S} A_{\alpha'\beta'}(S\underline{k})\, S \qquad \ldots(2.16)$$

where the S $\underline{k}$ comes from writing

$$\underline{k}.\underline{r}_{\alpha\beta}(l_1 - l_2) = S\underline{k}.S\underline{r}_{\alpha\beta}(l_1 - l_2)$$

$$= S\underline{k}.\underline{r}_{\alpha'\beta'}(l_1' - l_2') \qquad \ldots(2.17)$$

in the exponential.

The equation (2.6) implies

$$S\sigma_\alpha^j(k) = \sigma_{\alpha'}^j(Sk)$$

apart from a constant phase factor; equation (2.c) shows this to be $e^{2\pi i S\underline{k}.\underline{v}(S)} = e^{2\pi i \underline{k}.\underline{v}(S)}$

so that $$S\sigma_\alpha^j(\underline{k}) = e^{2\pi i \underline{k}.\underline{v}(S)}\, \sigma_{\alpha'}^j(Sk) \qquad \ldots(2.18)$$

Having derived the basic equations the actual CaF_2

2. The Born Model of CaF_2.

The calcium fluoride structure is face-centred cubic, with one calcium and two fluorine ions to a unit cell. These are labelled 1, 2 and 3 respectively corresponding to positions as follows:-

Ion	1 (Ca)	2 (F)	3 (F)
Position	(000)	$\frac{1}{2}r_0(111)$	$\frac{1}{2}r_0(\bar{1}\bar{1}\bar{1})$

Here $2r_0$ is the lattice constant; so that the primitive translation vectors are

$$a_1 = r_0(011) \qquad a_2 = r_0(101) \qquad a_3 = r_0(110)$$

Because the crystal is ionic the interionic forces may be roughly divided into two sets; a long range Coulomb interaction

$$C K^{ij}_{\alpha\beta}(l_1 l_2) = Z_\alpha Z_\beta \left[\frac{\partial^2}{\partial u^i_\alpha(l_1)\partial u^j_\beta(l_2)} \left\{ \frac{1}{|r_\alpha(l_1-l_2)+x|} \right\}_{x=0} \right] \quad \ldots(2.19)$$

where $\underline{x} = \underline{u}_\alpha(l_1) - \underline{u}_\beta(l_2)$ and where Z_α and Z_β are effective charges, and a repulsive short range interaction. Each of these contributions will be considered in turn.

The Ewaldsum Interaction.

The evaluation of (I.19) and its corresponding contribution to the dynamical matrix

$$C A^{ij}_{\alpha\beta}(k) = \sum_{\ell} \frac{\partial^2}{\partial x^i \partial x^j} \frac{e^{-2\pi i \underline{k}\cdot \underline{r}_{\alpha\beta}(\ell)}}{|r_{\alpha\beta}(\ell) + x|} Z_\alpha Z_\beta \qquad \ldots(I.20)$$

is beset with three difficulties. First of all, the forces are long range and the sum (I.20) does not converge rapidly, secondly there is not a well defined limit as $k \to 0$; thirdly, it is not apparent to what extent the reformulation may be neglected. Ewald attacked the first problem (Ewald 1917) using the identity

$$\frac{2}{\sqrt{\pi}} \int_0^\infty e^{-|r(\ell)+x|^2 \rho^2} \, d\rho = \frac{1}{|r(\ell)+x|} \qquad \ldots(I.21)$$

followed by the theta function transformation

$$\frac{2}{\sqrt{\pi}} \sum_{\ell} e^{-|r(\ell)+x|^2\rho^2 + 2\pi i \underline{k}\cdot r(\ell) + x} = \frac{2\pi}{V} \sum_{\underline{h}} \frac{1}{\rho^3} e^{-\frac{\pi^2}{\rho^2}|h+y|^2 - 2\pi i k\cdot x} \qquad \ldots(I.22)$$

to divide the sum (I.20) into two parts; a sum in real space ($\sum_\ell$) and a sum in reciprocal space ($\sum_{\underline{h}}$) both of which could be made rapidly convergent. This method was used

by Kellerman (1940) who also resolved the retardation difficulty, showing that this could be neglected except in the limit $k=0$ when the crystal may absorb or emit infrared radiation. Finally, it was shown by Huang (Huang 1949) that the Ewald transformation allowed the separation of that part of the Coulomb sum which did not have a well defined limit as $k \to 0$. It was shown that this contribution could be thought of as a macroscopic electric field, depending on the shape of the specimen and hence having an ill defined limit.

The actual form of the Kellerman coefficients (2.20) for the calcium fluoride lattice has already been derived by Srinivasan (1959) who has also calculated the Coulomb contribution to the elastic constants. The only difference from his working is that here the charge on the ions will be left as a parameter to be determined, rather than the electron charge.

The Short Range Interaction.

The experimental facts which serve to fix the force constant are the 3 elastic constants, the reststrahl absorption frequency , the Raman frequency and the frequency

of the l.o. mode at $k=0$ obtained from the Lyddane-Sachs Teller relationship. This leaves five constants available to describe the short range interaction. Force constants out to third neighbours will be considered, and one must choose which are the five most important.

(1) The nearest neighbours of the calcium ion are eight fluorine ions; the second neighbours of the fluorine ions are fluorines on a non-equivalent site, while the second neighbours of the calcium ions are those calcium ions in the neighbouring unit cells, thus being the same distance apart as the third neighbours of the fluorine ions. We now apply symmetry arguments to each of these types in turn.

(i) K_{11} (000;000); K_{22} (000,000); K_{33} (000,000).

K_{11} is invariant under the symmetry group and can only be of the form

$$K_{11} = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{pmatrix} \qquad \ldots(2.23)$$

K_{22} and K_{33} are interchanged by the inversion (which leaves the force constant matrices invariant) and the rest of the group ensures that they are proportional to the unit matrix.

$$K_{22}(000\ 000) = K_{33}(000\ 000) = \beta 1 \qquad \ldots(2.24)$$

(ii) $K_{12}(0,0)$, $K_{13}(0,0)$, etc.

The number of independent constants in these matrices may be found using equation (2.15):

$$n_{12} = \frac{1}{48} \sum_S \left(N(S)\chi^2(S) + \tilde{N}(S)\chi(S^2) \right)$$

where S is an operation of the group, which in this case is the group O_h. $\chi(S)$ is the polar vector representation of this group, in this case the Γ_{15}^- representation, N(S) is the number of bonds left invariant by S and $\tilde{N}(S)$ is the number reversed. Thus one arrives at

$$n_{12} = \frac{1}{48} \{ 8 \times 9 + 4 \times 6 \times 1 \} = 2.$$

and it is easily seen that

$$K_{12}(000;000) = \begin{pmatrix} \gamma & \delta & \delta \\ \delta & \gamma & \delta \\ \delta & \delta & \gamma \end{pmatrix} = K_{13}(000;000) \qquad \ldots(2.25)$$

(iii) $K_{23}(000;100)$, etc.

There has been some controversy over the nature of this force constant matrix, and this may be resolved as follows. The bonds form a cube centred about the Ca ion; opposite edges of this cube are separated by a lattice translation, so an invariant subset of 6 of the edges may be taken. A two-fold x-rotation and a diagonal mirror plane leave two out of these six bonds invariant; the inversion reverses all of

them, and the product of this operation with the previous two will also reverse two of the bonds. Consequently,

$$N_{23} = \frac{1}{48}\{6 \times 9 + 3 \times 2 \times 1 + 6 \times 2 \times 1 + 6 \times 3 + 3 \times 2 \times 3 + 6 \times 2 \times 3)$$

$$= 3$$

Inversion renders the matrix symmetric; δ_{2x} kills off the xy and xz terms, while σ_{yz} makes the y and z terms equivalent. Thus the matrix is of the form

$$K_{23} = \begin{pmatrix} C & 0 & 0 \\ 0 & A & B \\ 0 & B & A \end{pmatrix} \qquad \ldots(2.26)$$

in agreement with Cribier (1953)

(iv) K_{11}, K_{22}, etc.

In a similar way it may be shown that

$$K_{11}(000;100) = \begin{pmatrix} a & o & o \\ o & b & c \\ o & c & b \end{pmatrix} \qquad \ldots(2.27)$$

$$K_{22}(000;100) = K_{33}(000;100) = \begin{pmatrix} d & o & o \\ o & e & f \\ o & f & e \end{pmatrix}$$

$$\ldots(2.28)$$

The wave vector $\underline{k}$ is measured in units of $\frac{1}{2r_0}$ so that

$$\underline{k} = \frac{1}{2r_0}(q_x + q_y + q_z)$$

where $-1 \leq q_x, q_y, q_z \leq 1$ and the L point, for example, is given by

$$q_x = q_y = q_z = \tfrac{1}{2}.$$

In this form the components of the dynamical matrix are as follows:-

$$A_{11}^{xx} = \tfrac{1}{2}\alpha + a\left(e^{\pi i(q_y+q_z)} + e^{\pi i(q_y-q_z)}\right) + b\left(e^{\pi i(q_x+q_z)} + e^{\pi i(q_x+q_y)} + e^{\pi i(q_x-q_z)} + e^{\pi i(q_x-q_y)}\right) + c.c.$$

$$A_{11}^{yz} = c\left(e^{\pi i(q_y+q_z)} - e^{\pi i(q_y-q_z)}\right) + c.c.$$

$$A_{12}^{xy} = \gamma\left(e^{-\frac{\pi i}{2}(q_x+q_y+q_z)} + e^{\frac{\pi i}{2}(-q_x+q_y+q_z)} + e^{\frac{\pi i}{2}(q_x-q_y+q_z)} + e^{\frac{\pi i}{2}(q_x+q_y-q_z)}\right)$$

$$A_{12}^{yz} = \delta\left(e^{-\frac{\pi i}{2}(q_x+q_y+q_z)} + e^{\frac{\pi i}{2}(-q_x+q_y+q_z)} - e^{\frac{\pi i}{2}(q_x-q_y+q_z)} - e^{\frac{\pi i}{2}(q_x+q_y-q_z)}\right)$$

$$A_{22}^{xx} = \tfrac{1}{2}\beta + d\left(e^{\pi i(q_y+q_z)} + e^{\pi i(q_y-q_z)}\right) + e\left(e^{\pi i(q_x+q_z)} + e^{\pi i(q_x+q_y)} + e^{\pi i(q_x-q_z)} + e^{\pi i(q_x-q_y)}\right) + c.c.$$

$$A_{22}^{yz} = f\left(e^{\pi i(q_y+q_z)} - e^{\pi i(q_y-q_z)} + c.c.\right)$$

$$A_{23}^{xx} = A\left(e^{\pi i q_y} + e^{\pi i q_z}\right) + C e^{\pi i q_x} + c.c.$$

$$A_{23}^{yz} = B e^{-\pi i q_x} - B e^{\pi i q_x}$$

To this has to be added the contribution to the dynamical matrix from the long range Coulomb part of the interaction. The form of this matrix may be found in the paper by Srinivasan.

One is thus left with 14 constants:

$$\alpha\ \beta\ \gamma\ \delta;\ A\ B\ C;\ a\ b\ c;\ d\ e\ f;\ \text{and}\ Z$$

The last of these measures the effective charge on the ions. The first two α and β are determined by the translational invariance condition

$$\sum_{\rho l'} K_{\alpha\rho}(l l') = 0.$$

which requires

$$\left.\begin{aligned} \alpha + 4(a+2b) + 8\gamma &= 0 \\ \beta + 2(C+2A) + 4(e+2d) + 4\gamma &= 0 \end{aligned}\right\} \qquad \ldots(2.30)$$

and ensures that the equations

$$\sum A_{\alpha\rho}(k)\,\sigma_\rho^j(k) = M_\alpha \omega_j^2(k)\,\sigma_\alpha^j(k) \qquad \ldots(2.31)$$

have three solutions $\omega = 0$ at $k \to 0$. The meaning of the rest of these constants is as follows:

γ = Ca-F central force constant

$\delta - \gamma$ = Ca-F non-central force constant

C = F-F central force

$A \pm B$ = F-F non-central force

α = Ca-Ca central force

$b \pm c$ = Ca-Ca non-central force

d = F-F central force

$e \pm f$ = F-F non-central force

One can fix three of these constants from the frequencies of vibration at Γ, the zone centre, which may be measured and also the three elastic constants may be used to fix three more.

3. Calculation of the Elastic Constants and Infra-red Absorption Frequencies.

The dynamical matrix at Γ is written as the sum of short range and Coulomb parts as follows:

Short Range
$$\begin{pmatrix} -8\gamma & 4\gamma & 4\gamma \\ 4\gamma & -(4\gamma+2(C+2A)) & 2(C+2A) \\ 4\gamma & 2(C+2A) & -(4\gamma+2(C+2A)) \end{pmatrix}$$

Coulomb
$$\frac{4\pi Z^2}{3V}\begin{pmatrix} 4 & -2 & -2 \\ -2 & 1 & 1 \\ -2 & 1 & 1 \end{pmatrix}$$

The matrices have been written in terms of 3x3 unit matrices so that both of these in fact represent 9x9 matrices. The macroscopic field contribution has the effect of increasing the frequency of the longitudinal optical mode. This effect may be represented by adding a contribution

$$-\frac{4\pi Z^2}{v}\begin{bmatrix} 4 & -2 & -2 \\ -2 & 1 & 1 \\ -2 & 1 & 1 \end{bmatrix}$$

to the dynamical matrix, where now each of the numbers multiplies the three by three matrix

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

and it has been assumed that the propagation is along the x-direction. Adding these three contributions, one then has to solve the equations (2.31)

This is easily done to give

$$\omega_R^2 = -\frac{4}{m_2}(\gamma + C + 2A)$$

$$\omega_{T_0}^2 = -4\left(\frac{2}{m_1}+\frac{1}{m_2}\right)\left(\gamma + \frac{2\pi}{3}\frac{Z^2}{v}\right)$$

$$\omega_{L_0}^2 = -4\left(\frac{2}{m_1}+\frac{1}{m_2}\right)\left(\gamma - \frac{2\pi}{3}\frac{Z^2}{v}\right)$$

γ is of course, an essentially negative quantity.

We turn now to the evaluation of the elastic constants. This is done by expanding the dynamical matrix in powers of the wave vector:

$$A_{\alpha\beta}(q) = A_{\alpha\beta}^{(0)} + i A_{\alpha\beta}^{(1)}(q) + A_{\alpha\beta}^{(2)}(q) \ldots \qquad \ldots(2.32)$$

and solving the successive approximations to (2.6)

The full analysis will not be given here as the method is well known, and also as we are not interested in the piezo-electric constants, the macroscopic field contribution will also be dropped. The essential point in the calculation is that the long wave acoustic modes, which correspond to the elastic waves in the limit $q \to 0$ have a frequency which tends linearly to zero for small values of q; and consequently the $\omega^2 q$ term only contributes to the second order equation.

The zeroth order equation

$$\sum A^{(0)}_{\alpha\beta}\, \sigma^{(0)}_{\beta} = 0 \qquad \ldots(2.33)$$

is of course, satisfied identically by the acoustic mode solutions

$$\sigma^{(0)}_{\alpha} = \sigma \qquad \ldots(2.34)$$

The first order equation is:

$$\sum A^{(1)}_{\alpha\beta}(q)\, \sigma^{(0)}_{\beta} + \sum A^{(0)}_{\alpha\beta}\, \sigma^{(1)}_{\beta} = 0 \qquad \ldots(2.35)$$

$$\nu - \pi \begin{bmatrix} 0 & 2\delta T & -2\delta T \\ -2\delta J & 0 & 2BJ \\ 2\delta J & -2BJ & 0 \end{bmatrix} \begin{bmatrix} \sigma \\ \sigma \\ \sigma \end{bmatrix} - 5\cdot 02^{2}\, \frac{\pi Z^{2}}{U} \begin{bmatrix} 0 & 2J & -2J \\ -2J & 0 & 0 \\ 2J & 0 & 0 \end{bmatrix} \begin{bmatrix} \sigma \\ \sigma \\ \sigma \end{bmatrix}$$

$$= \frac{4\pi}{3} \frac{Z^{2}}{U} \begin{bmatrix} 4 & -2 & -2 \\ -2 & 1 & 1 \\ -2 & 1 & 1 \end{bmatrix} \begin{bmatrix} \sigma^{(1)}_{1} \\ \sigma^{(1)}_{2} \\ \sigma^{(1)}_{3} \end{bmatrix} + \begin{bmatrix} -4\gamma & 4\gamma & 4\gamma \\ 4\gamma & -(4\gamma + 2(C+2A)) & 2(C+2A) \\ 4\gamma & 2(C+2A) & -(4\gamma + 2(C+2A)) \end{bmatrix} \begin{bmatrix} \sigma^{(1)}_{1} \\ \sigma^{(1)}_{2} \\ \sigma^{(1)}_{3} \end{bmatrix}$$

$$\ldots(2.36)$$

where $J = \begin{pmatrix} 0 & q_z & q_y \\ q_z & 0 & q_x \\ q_y & q_x & 0 \end{pmatrix}$ and

where the numerical values for the Coulomb calculation have been taken from the paper by Srinivasan. Evidently

$$2\sigma_1^{(1)} = \sigma_2^{(1)} + \sigma_3^{(1)}$$

so choosing

$$\sigma_1^{(1)} = 0$$

then

$$2\pi\left(-B + 8.028\frac{Z^2}{v} + \delta\right)J\sigma = -4(\gamma + C + 2A)\sigma_2^{(1)} \qquad \ldots(2.37)$$

The second order equation is as follows:

$$M_\alpha \omega^2 \sigma_\alpha^{(0)} = \sum A_{\alpha\rho}^{(0)} \sigma_\rho^{(0)} - \sum A_{\alpha\rho}^{(1)} \sigma_\rho^{(1)} + \sum A_{\alpha\rho}^{(2)} \sigma_\rho^{(0)} \qquad \ldots(2.38)$$

or

$$\sum A_{\alpha\rho}^{(0)} \sigma_\rho^{(2)} = M_\alpha \omega^2 \sigma_\alpha^{(0)} + \sum A_{\alpha\rho}^{(1)} \sigma_\rho^{(1)} - \sum A_{\alpha\rho}^{(2)} \sigma_\rho^{(0)} \qquad \ldots(2.38a)$$

This is a set of inhomogeneous equations in $\sigma_\beta^{(2)}$ and the condition for a solution to exist is that the inhomogeneous part, the R.H.S., must be orthogonal to any solution of the homogeneous part, the L.H.S. But the homogeneous solutions are just the acoustic modes (2.34) and so the solubility condition is

$$\sum_\alpha \left\{ M_\alpha \omega^2 \sigma_\alpha^{(0)} + \sum A_{\alpha\rho}^{(1)} \sigma_\rho^{(1)} - \sum A_{\alpha\rho}^{(2)} \sigma_\rho^{(0)} \right\} \sigma_\alpha^{(0)} = 0 \qquad \ldots(2.39)$$

or using (2.34)

$$\left(\sum M_\alpha\right)\omega^2 \sigma = \sum_{\alpha\beta} \left(A_{\alpha\beta}^{(0)} \sigma_\beta^{(0)} - A_{\alpha\beta}^{(1)} \sigma_\beta^{(0)} \right) \qquad \ldots(2.40)$$

Equation (2.40) may be written

$$\frac{(\sum M_k)}{N}\omega^2\sigma_i = \frac{\pi^2}{r_0^2}\sum_j\left\{\sum_{kl}\left([ij,kl]+(ik,jl)\right)q_k q_l\right\}\sigma_j \qquad (2.41)$$

where

$$\sum_{kl}[ij,kl]\,q_k q_l = \frac{r_0^2}{\pi^2 N}\sum_{\alpha\beta}A^{(2)}_{\alpha\beta}(q) \qquad (2.42)$$

and

$$\sum_{kl}(ik,jl)\,q_k q_l = -\frac{r_0^2}{\pi^2 N}\sum_{\alpha\beta}A^{(1)}_{\alpha\beta}\sigma^{(1)}_\beta \qquad (2.43)$$

However, the Green-Christoffel equations of motion for an elastic solid are

$$\rho\omega^2\sigma_i = \frac{\pi^2}{r_0^2}\sum_j\left\{\sum_{kl}C_{ikjl}\,q_k q_l\right\}\sigma_j \qquad (2.44)$$

Comparison of equations (2.44) and (2.41) leads to equations relating the elastic constants to the bracket symbols (2.42), (2.43). As pointed out by Huang (1950) there is a unique solution satisfying all the symmetry requirements, which is

$$C_{ikjl} = [ij,kl] + [jk,il] - [jl,ik] + (ik,jl) \qquad (2.45)$$

The elastic constants are therefore derived from the relations

$$[xx, xx] = -\frac{1}{r_0}(\gamma + 2\beta + 4\varepsilon + C) + \frac{3.276}{r_0}\frac{Z^2}{v}$$

$$[xx, yy] = -\frac{1}{r_0}(\alpha + \beta + \gamma + 2(\delta+\varepsilon) + A) - \frac{1.527}{r_0}\frac{Z^2}{v}$$

$$[xy, xy] = -\frac{1}{r_0}(2\varepsilon + 4\phi + 2\delta) - \frac{3.461}{r_0}\frac{Z^2}{v}.$$

$$(xx, xx) = 0$$

$$(xx, yy) = (xy, xy) = -\frac{(B - \delta - 5.028\frac{Z^2}{v})^2}{r_0(\gamma + C + 2A)} \qquad \ldots (2.46)$$

Using (2.46) and Voigts notation for the elastic constants

$$C_{11} = [xx, xx] = -\frac{1}{r_0}[\gamma + 2\beta + 4\varepsilon + C] + \frac{3.276}{r_0}\frac{Z^2}{v}$$

$$C_{12} = [xy, xy] + [yx, xy] - [yy, xx] + (xx, yy)$$

$$= 2[xy, xy] - [xx, yy] + (xx, yy)$$

$$= -\frac{1}{r_0}[4\delta + 4\varepsilon + 8\phi - (\alpha + \beta + \gamma + 2(\delta+\varepsilon) + A)] - \frac{5.395}{r_0}\frac{Z^2}{v}$$

$$C_{44} = [yy, zz] + [zy, yz] - [yz, yz] + (yz, yz)$$

$$= [xx, yy] + (xy, xy)$$

$$= -\frac{1}{r_0}(\alpha + \beta + \gamma + 2(\delta+\varepsilon) + A) - \frac{1.527}{r_0}\frac{Z^2}{v}$$

$$- \frac{(B - \delta - 5.028\frac{Z^2}{v})^2}{r_0(\gamma + C + 2A)} \qquad \ldots (2.47)$$

Finally, we apply a number of transformations, with the aim of simplifying the numerical calculations. These are firstly the elimination of the explicit appearance of the mass in the problem, and secondly the transformation to real variables.

One has the equation

$$\sum A_{\alpha\beta}(q)\,\sigma_\beta^j(q) = M_\alpha\,\omega_j^2(q)\,\sigma_\alpha^j(q)$$

By redefining

$$A'_{\alpha\beta}(q) = A_{\alpha\beta}/\sqrt{M_\alpha M_\beta}\;;\quad \sigma_\alpha^{j\prime}(q) = \sqrt{M_\alpha}\,\sigma_\alpha^j(q)$$

this is transformed to

$$\sum A'_{\alpha\beta}(q)\,\sigma_\beta^{j\prime}(q) = \omega_j^2(q)\,\sigma_\alpha^{j\prime}(q) \qquad \ldots(2.48)$$

The general dynamical matrix is of the form

$$\begin{pmatrix} A & B & B^* \\ B^* & C & D^* \\ B & D & C \end{pmatrix} = R \qquad \ldots(2.49)$$

where A and C are real matrices and every matrix is symmetric. The similarity transformation $R' = SRS^{-1}$ where

$$S = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{i}{\sqrt{2}} & -\frac{i}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{pmatrix} \qquad \ldots(2.50)$$

reduces R to the form

$$R' = \begin{pmatrix} A & \sqrt{2}\,B_2 & \sqrt{2}\,B_1 \\ \sqrt{2}\,B_2 & C-D & D_2 \\ \sqrt{2}\,B_1 & D_2 & C+D_1 \end{pmatrix} \qquad \ldots(2.51)$$

where

$$B = B_1 + iB_2 \; ; \quad \delta = D_1 + iD_2$$

In effect one is using σ_1 and the real and imaginary parts of σ_3 as eigenvectors.

4. Selection of the Force Constants.

The first five constants on Page II.14 include the first neighbours and the second neighbour fluorine - fluorine interaction. However, the constant B representing the arrisotropy in the non-central force about the bond is likely to be small, and less than the calcium - calcium central force constant, a. But if this latter constant is included and B put equal to zero, to be consistent the fluorine - fluorine interaction ought also to be considered as this 3rd neighbour interaction is as far apart as the second neighbour calcium interaction. There appear to be two possibilities therefore; either the non-central force constants are retained only in the nearest neighbours resulting in the selection I

$$\delta \quad \gamma \quad C \quad b=c \quad e=f$$

or alternatively, the interaction is cut off after the fluorine second neighbour interaction giving selection II.

$$\delta \quad \gamma \quad A \quad B \quad C$$

4. The Shell Model.

This description of the crystal has quite a long ancestry; at the outset of Born's rigid ion description of the lattice, he also considered the possibilities of the ions becoming polarisable. Born and Huangs' book contains much of the fundamental calculations for this model, which has recently received a detailed exposition at the hands of Cowley (1963). The original impetus for this work came from the failure of the Born model to predict the phonon dispersion curves obtained by inelastic neutron scattering data. It became apparent that many neighbour forces would be necessary to obtain a fit to the data, leading Dick and Overhauser to suggest that long range forces, of the type which would be introduced by polarisable ions, were the cause of the disagreement. Cochrane actually performed the calculation, introducing the very easily visualised idea that the polarisation on the ions was due to the displacement of a shell of electrons from its parent core, thus describing the polarisability by 2 parameters a shell charge and a core-shell force constant, one of which is redundant. Following Cochrane's success with the application of this model to Ge there has been considerable interest in applying the model to other crystals. Again, the theory will be sketched first of all, followed by the detailed application to calcium fluoride.

The notation of Cowley will be followed as closely as possible; a list of the meanings of the symbols is contained in Appendix I.

The potential energy, to second order in the displacements and the dipole moments is now written:

$$V = \sum u_\alpha(l)\, K^{(1)}_{\alpha\beta}(ll')\, u_\beta(l') + \sum u_\alpha(l)\, K^{(2)}_{\alpha\beta}(ll')\, q_\beta(l') + \sum q_\alpha(l)\, K^{(3)}_{\alpha\beta}(ll')\, u_\beta(l') + \sum q_\alpha(l)\, K^{(4)}_{\alpha\beta}(ll')\, q_\beta(l') \qquad \ldots(2.52)$$

Clearly, one has

$$K^{(4)}_{\alpha\beta}(ll') = K^{(3)}_{\beta\alpha}(l'l) \qquad \ldots(2.53)$$

as any antisymmetric part will drop out of the summation. The matrices $K^{(1)}_{\alpha\beta}(ll')$ are just the force constant matrices previously used in the Born model. The other matrices

$$K^{(2)}_{\alpha\beta}(ll'),\quad K^{(3)}_{\alpha\beta}(ll'),\quad K^{(4)}_{\alpha\beta}(ll')$$

have a similar form as they too reflect the symmetry of the lattice, the only difference being that $K^{(2)}$ and $K^{(3)}$ obey the symmetry property implied by equation (2.53) rather than the simpler

$$K^{(4)}_{\alpha\beta}(ll') = K_{\beta\alpha}(l'l) \qquad \ldots(2.54)$$

In point of fact, if one restricts the interaction to nearest neighbour forces only, all four matrices have precisely the same form, as no symmetry operation can reverse a l-k bond, which would be necessary in order to reduce the number of constants. In order to aid the visualisation of this model, the polarisation is conceived of as arising from the rigid displacement of the electronic shells surrounding the ions, which are attached to the ion cores by means of an isotropic force constant. The dipole moment of the ion is then given by the charge on the shell, Y_α, multiplied by its displacement from the core $w_\alpha(l)$:

$$q_\alpha(l) = Y_\alpha w_\alpha(l)$$

In this form the equations of motion become

$$-M_\alpha \omega^2 u_\alpha(l) = \sum K^{(1)}_{\alpha\beta}(ll')\, u_\beta(l') + \sum K^{(2)}_{\alpha\beta}(ll')\, w_\beta(l')$$

$$0 = \sum K^{(3)}_{\alpha\beta}(ll')\, u_\beta(l') + \sum K^{(4)}_{\alpha\beta}(ll')\, w_\beta(l')$$

...(2.55)

where now of course, the force constants have a slightly different meaning. Putting the L.H.S. of the last equation equal to zero is equivalent to the Born-Oppenheimer approximation, that in effect the shells move sufficiently rapidly to be always in equilibrium with the nuclei. These equations may then be solved using translational invariance in the usual way, so that the normal co-ordinates are waves

$$U_\alpha(k) = \frac{1}{\sqrt{N}} \sum_l e^{-2\pi i k \cdot r_\alpha(l)} u_\alpha(l)$$

$$W_\alpha(k) = \frac{1}{\sqrt{N}} \sum_l e^{-2\pi i k \cdot r_\alpha(l)} w_\alpha(l) \qquad \ldots(2.56)$$

and in vector notation

$$M\omega^2(k)\, U(k) = A(k)U(k) + B(k)W(k)$$
$$0 = C(k)U(k) + D(k)W(k) \qquad \ldots(2.57)$$

The variable W is eliminated from these equations and the resulting equation solved for U. Here

$$A_{\alpha\beta}(k) = \sum K^{(1)}_{\alpha\beta}(ll')\, e^{2\pi i k \cdot r_\beta(l-l')}$$
$$= R + Z\, b\, Z \qquad \ldots(2.58)$$

is the Fourier transform of the force constant matrices, which as usual is divided into short and long range parts. In a similar way

$$B = C^+ = S + Z\, b\, Y$$
$$D = T + Y\, b\, Y \qquad \ldots(2.59)$$

The matrix C is the matrix of Kellerman co-efficients appropriate to the lattice under consideration, while Z and Y are effective charge matrices. The form of Z is determined by the requirement that the unit cell should be neutral so

$$\underline{Z} = \begin{pmatrix} Z & & \\ -1 & & \\ & -1 & \end{pmatrix} Z \qquad \ldots(2.60)$$

whereas symmetry makes Y of the form

$$\underline{Y} = \begin{pmatrix} Y_1 & & \\ & Y_2 & \\ & & Y_3 \end{pmatrix} \qquad \ldots(2.61)$$

Each of the matrices R, S and T, representing the short range forces are of the same form, which is

$$R = \begin{pmatrix} A & C & C \\ C & B & C \\ C & C & B \end{pmatrix} \qquad A = \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_1 & 0 \\ 0 & 0 & \alpha_1 \end{pmatrix} \qquad B = \begin{pmatrix} \beta_1 & 0 & 0 \\ 0 & \beta_1 & 0 \\ 0 & 0 & \beta_1 \end{pmatrix}$$

$$C = \begin{pmatrix} \gamma_1 f_1(q_x q_y q_z) & \delta_1 f_2(q_x q_y q_z) & \delta_1 f_2(q_y q_z q_x) \\ \delta_1 f_2(q_x q_y q_z) & \gamma_1 f_1(q_x q_y q_z) & \delta_1 f_2(q_x q_y q_z) \\ \delta_1 f_2(q_y q_z q_x) & \delta_1 f_2(q_x q_y q_z) & \gamma_1 f_1(q_x q_y q_z) \end{pmatrix} \qquad \ldots(2.62)$$

where $f_1 = e^{-\frac{2\pi i}{3}(q_x+q_y+q_z)} + e^{\frac{2\pi i}{3}(-q_x+q_y+q_z)} + e^{\frac{2\pi i}{3}(q_x-q_y+q_z)} + e^{\frac{2\pi i}{3}(q_x+q_y-q_z)}$

and f_2 is the function

$$f_2 = e^{-\frac{2\pi i}{3}(q_x+q_y+q_z)} + e^{\frac{2\pi i}{3}(-q_x+q_y+q_z)} - e^{\frac{2\pi i}{3}(q_x-q_y+q_z)} - e^{\frac{2\pi i}{3}(q_x+q_y-q_z)}$$

The matrix R contains the constants $\alpha_1, \beta_1, \gamma_1, \delta_1$ as indicated; S and T contain the constants $\alpha_2, \beta_2, \gamma_2, \delta_2$; $\alpha_3, \beta_3, \gamma_3, \delta_3$. Four of these constants are determined from the condition that the acoustic modes at $\underline{k} = 0$ have zero eigenfrequencies. These

acoustic modes are of the form

$$U = \text{a constant vector}$$
$$W = 0$$

and this condition leads to the four equations

$$\begin{aligned} \alpha_1 + \delta\gamma_1 &= 0 \\ \beta_1 + \epsilon\gamma_1 &= 0 \\ \alpha_3 + \delta\gamma_2 &= 0 \\ \beta_3 + \epsilon\gamma_3 &= 0 \end{aligned} \qquad \ldots(2.63)$$

Thus $\alpha_1, \beta_1, \alpha_3, \gamma_2$ are determined. Of the other constants α_2 and β_2 are the force constants connecting shells to nuclei and so are related to the crystal polarisabilities of the appropriate ion, while the other force constants represent central and non-central interactions between shells and cores of nearest neighbouring ions. The other constants involved in Z and Y are the effective charges on the shells and the ions.

5. Determination of the Elastic and Dielectric Constants for the Polarisable Case

These constants are determined from the elastic and dielectric constants and the infra-red absorption frequencies, which we shall now derive. This is done as before, using the method of long waves and making an expansion out to second order in the wave vector:-

$$A(q) = A^{(0)} + i A^{(1)}(q) + A^{(2)}(q) + \ldots \qquad \ldots(2.64)$$

with similar expressions for B_x, C_x, D_x. However, in order to obtain the dielectric constant we now include the macroscopic field contribution explicitly, separating this part from the rest of the Coulomb matrix as was previously discussed. This contribution is written as a vector having components equal to the field at the lattice points

$$E = -\frac{4\pi}{v}\hat{k}\hat{k}.P \qquad \ldots(2.65)$$

where $\hat{k}$ is a unit vector in the direction of propagation and P the polarisation is given by

$$P = YW + ZU \qquad \ldots(2.66)$$

The expansion of the first dynamical matrix is written out in full as follows:

$$A^{(0)} = \begin{pmatrix} 2 & -1 & -1 \\ -1 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix} \beta_1 + \frac{4\pi}{3}\frac{Z^2}{v}\begin{pmatrix} 4 & -2 & -2 \\ -2 & 1 & 1 \\ -2 & 1 & 1 \end{pmatrix}$$

$$A^{(1)} = -2\begin{pmatrix} 0 & \delta_1 J & -\delta_1 J \\ -\delta_1 J & 0 & 0 \\ \delta_1 J & 0 & 0 \end{pmatrix} - 5.03\frac{Z^2}{v}\begin{pmatrix} 0 & 2J & -2J \\ -2J & 0 & 0 \\ 2J & 0 & 0 \end{pmatrix}$$

$$\sum_{q^2} \frac{A^{(1)}}{\pi^2} = -\begin{bmatrix} +\gamma_1 q^2 & 2\delta_1 q_x q_y & 2\delta_1 q_x q_z \\ 2\delta_1 q_y q_x & \gamma_1 q^2 & 2\delta_1 q_y q_z \\ 2\delta_1 q_z q_x & 2\delta_1 q_z q_y & \gamma_1 q^2 \end{bmatrix}$$

$$+\frac{Z^2}{V}\begin{bmatrix} 3.276 q_x^2 - 1.527(q_y^2+q_z^2) & -3.461 q_x q_y & -3.461 q_x q_z \\ -3.461 q_y q_x & 3.276 q_y^2 - 1.527(q_x^2+q_z^2) & -3.461 q_y q_z \\ -3.461 q_z q_x & -3.461 q_z q_y & 3.276 q_z^2 - 1.527(q_x^2+q_y^2) \end{bmatrix} \quad \ldots(2.67)$$

One then obtains the following zero order equations

$$0 = A^{(0)} U^{(0)} + B^{(0)} W^{(0)} - Z E^{(0)}$$
$$0 = C^{(0)} U^{(0)} + D^{(0)} W^{(0)} - Y E^{(0)} \quad \ldots(2.68)$$

with the acoustic mode solutions, $U^{(0)}$=a constant vector, U $W^{(0)} = 0$, $E^{(0)} = 0$.

The first order equations are:

$$0 = A^{(1)} U^{(0)} + A^{(0)} U^{(1)} + B^{(0)} W^{(1)} + B^{(1)} W^{(0)} - Z E^{(1)}$$
$$0 = C^{(1)} U^{(0)} + C^{(0)} U^{(1)} + D^{(0)} W^{(1)} + D^{(1)} W^{(0)} - Y E^{(0)} \quad \ldots(2.69)$$

These have a solution

$$U_1^{(1)} = 0 \quad , \quad U_2^{(1)} - U_1^{(1)} = -\frac{4\pi(\delta_1'\beta_2 + \delta_2'\beta_1)JU}{\beta_1\beta_2 - \beta_3^2} \quad \ldots(2.70)$$

and

$$W_2^{(1)} - W_1^{(1)} = -\frac{4\pi(\delta_1'\beta_3 + \delta_3'\beta_1)JU}{\beta_1\beta_2 - \beta_3^2} \quad \ldots(2.71)$$

with similar equations for the other components. Here, J is the matrix previously defined

$$J = \begin{bmatrix} 0 & q_z & q_y \\ q_z & 0 & q_x \\ q_y & q_x & 0 \end{bmatrix}$$

and to simplify the appearance, the quantities δ_3' and δ_1' have been introduced:

$$\delta_1' = \delta_1 + 5.03\delta \frac{Z^2}{U} \quad ; \quad \delta_3' = \delta_3 + 5.02 \frac{ZX_2}{U} .$$

The second order equations are

$$M\omega^2 U^{(0)} = A^{(1)} U^{(0)} - A^{(1)}U^{(1)} + A^{(0)}U^{(2)} - B^{(1)}W^{(1)} + B^{(1)}W^{(0)} - ZE^{(}$$
$$0 = C^{(2)} U^{(0)} - C^{(1)}U^{(1)} + C^{(0)}U^{(2)} - D^{(1)}W^{(1)} + D^{(0)}W^{(2)} - YE^{(}$$

...(2.72)

or

$$A^{(0)}U^{(2)} + B^{(0)}W^{(2)} = M\omega^2 U^{(0)} - A^{(2)}U^{(0)} + A^{(1)}U^{(1)} + B^{(1)}J^{(1)} + ZE^{(2}$$
$$C^{(0)}U^{(2)} + D^{(0)}W^{(2)} = -C^{(2)}U^{(0)} + C^{(1)}U^{(1)} + D^{(1)}W^{(1)} + YE^{(2}$$

...(2.72a)

This double set of inhomogeneous equations has a solution if the RHS is orthogonal to any solution of the homogeneous RHS set. Thus we have

$$\left(\sum M_\alpha\right)\omega^2 U = \sum_\varphi A^{(1)}_\varphi U - \sum_\varphi (A^{(1)}U^{(1)} + B^{(1)}W^{(1)})$$

...(2.73)

This is an exactly analogous equation to that derived for the rigid ion case: one can consequently define similar bracket symbols as were obtained beforehand.

$$[xxxx] = -\frac{1}{r_0}\gamma_1 + 3.276\frac{Z^2}{r_0 V}.$$

$$[xxyy] = -\frac{1}{r_0}\gamma_1 - 1.527\frac{Z^2}{r_0 V}$$

$$[xyxy] = -\frac{1}{r_0}2\delta_1 - 3.461\frac{Z^2}{r_0 V}$$

$$(xy,xy) = (xxyy) - \frac{4(\delta_1'^2\beta_2 - \delta_2''^2\beta_1)}{r_0(\beta_1\beta_2 - \beta_3^2)} \qquad \ldots(2.74)$$

It is easy to see that these bracket symbols obey the same symmetry relations as those derived for the rigid ion case, and accordingly the elastic constants are derived from them via the same equations:

$$C_{11} = C_{1111} = [xxxx] + (xxxx)$$
$$= -\frac{1}{r_0}\gamma_1 + 3.276\frac{Z^2}{r_0 V}$$

$$C_{12} = C_{1122} = [xy,xy] + [yxxy] - [yyxx] + (xxyy) \qquad \ldots(2.75)$$
$$= -\frac{1}{r_0}[4\delta_1 - \gamma_1] - 5.395\frac{Z^2}{r_0 V}$$

$$C_{44} = C_{2323} = [xxyy] + (xyxy)$$
$$= -\frac{1}{r_0}\gamma_1 - 1.527\frac{Z^2}{r_0 V} - \frac{4(\delta_1'^2\beta_2 - \delta_2''^2\beta_1)}{r_0(\beta_1\beta_2 - \beta_3^2)}$$

As the fluorine ion becomes unpolarisable, $\beta_2 \to \infty$ the results of the rigid ion calculation in the nearest neighbour approximation are recovered.

We turn now to the calculation of the dielectric constants and the infra-red absorption frequencies. This

calculation is very considerably simplified if it is assumed that the calcium ion is unpolarisable, which eliminates the three constants $\alpha_2, \gamma_2, \delta_2$. The expressions for the elastic constants are unchanged, as these depend only on the fluorine polarisability. The first order equations are again solved for the displacements and the dipole moments to give

$$U_2^{(1)} + U_3^{(1)} = -\frac{(2\beta_2 Z + 2\beta_3 Y)E}{\beta_1'\beta_2' - \beta_3'^2} \qquad \ldots(2.76)$$

$$W_2^{(1)} + W_3^{(1)} = \frac{(2\beta_3 Z + 2\beta_2 Y)E}{\beta_1'\beta_2' - \beta_3'^2} \qquad \ldots(2.77)$$

where the primed quantities include the electrostatic interaction

$$\begin{aligned} \beta_1' &= \beta_1 - \frac{8\pi}{3v} Z^2 \\ \beta_2' &= \beta_2 - \frac{8\pi}{3v} Y^2 \\ \beta_3' &= \beta_3 + \frac{8\pi}{3v} ZY \end{aligned} \qquad \ldots(2.78)$$

The total polarisation in the cell is thus

$$\begin{aligned} \sum P_\alpha &= \sum_\alpha (Y_\alpha W_\alpha + Z_\alpha U_\alpha) \\ &= Y(W_2^{(1)} + W_3^{(1)}) + Z(U_2^{(1)} + U_3^{(1)}) \\ &= \frac{2(Z^2\beta_2 + 2Z\beta_3 Y + \beta_1 Y^2)}{\beta_1'\beta_2' - \beta_3'^2} E \end{aligned} \qquad \ldots(2.79)$$

and accordingly the zero frequency dielectric constant is

$$\epsilon_0 = 1 + \frac{\rho\bar{n}}{\nu} \frac{(Z^2\beta_2 + 2Z\gamma\beta_3 + \beta_1\gamma^2)}{\beta_1'\beta_2' - \beta_3'^2} \qquad \ldots(2.80)$$

The eigenvalues at Γ are solutions of the equations

$$\begin{aligned} A(o)\,y(o) + B(o)\,w(o) - z\,E(o) &= m\omega^2\,y(o) \\ C(o)\,y(o) + D(o)\,w(o) - \gamma\,E(o) &= 0 \end{aligned} \qquad \ldots(2.81)$$

Except for the l.o. mode, $E \neq 0$ and we have the relations

$$\omega_R^2 = \frac{\beta_1\beta_2 - \beta_3^2}{m_2\beta_2}$$

$$\omega_{TO}^2 = \left(\frac{2}{m_1} + \frac{1}{m_2}\right) \frac{\beta_1'\beta_2' - \beta_3'^2}{\beta_2'} \qquad \ldots(2.82)$$

$$\omega_{LO}^2 = \left(\frac{2}{m_1} + \frac{1}{m_2}\right) \frac{\beta_1''\beta_2'' - \beta_3''^2}{\beta_2''}$$

where

$$\begin{aligned} \beta_1' &= \beta_1 + \frac{\rho\bar{n}}{\nu} Z^2 \\ \beta_2' &= \beta_2 + \frac{\rho\bar{n}}{\nu} \gamma^2 \\ \beta_3' &= \beta_3 - \frac{\rho\bar{n}}{\nu} \gamma Z \end{aligned} \qquad \ldots(2.83)$$

includes the macroscopic field contribution. It is interesting to note that the Lyddane-Sachs-Teller relation

$$\frac{\omega_{L^2_0}}{\omega_{T^2_0}} = \frac{\epsilon_0}{\epsilon_\infty} \qquad \ldots(2.84)$$

holds if we take

$$\epsilon_\infty = 1 + \frac{8\pi}{v} \frac{\gamma^2}{\beta'_2}$$

That is, only the shells contribute to the high frequency dielectric constant, a result which may also be proved by applying the method of long waves to an optic mode.

6. Numerical calculation.

The three frequencies and three elastic constants enable 6 of the parameters to be fitted. For the case of the Born model these 6 could describe either general nearest neighbour forces together with central forces only on 2nd and 3rd neighbours or alternatively general first and second neighbour forces only. These are represented by

Selection I $Z, f, \delta, C, b = c, e = f, a = d = A = B = 0$

Selection II $Z, f, \delta, A, B, C. \quad a = b = c = d = e = f = 0$

Unfortunately Selection II cannot be fitted to the available data without requiring the force constants to be complex. Equally unfortunately, Selection I is overdetermined, as all the derived expressions are functions of $b + 2e$ only: however a best fit may be made to all the constants to within 10%. Rather than do this however, the approximation $b = e$

is made and the new parameter A introduced to account for the difference. This is presumably the largest of the remaining constants and describes non central interactions between fluorine ions. The constant B on the other hand represents the degree of anisotropy of this non central interaction which is not expected to be large.

With this selection of force constants the following values are arrived at:

Y	δ	A	C	$b=c=e=f$	Z^2/v
-1.6841	-..3621	0.2114	-1.6443	-0.0467	0.3483

The units are in 10^4 gms sec $^{-2}$. The value of represents an effective charge Z/e of 0.7789.

Turning now to the shell model with unpolarisable calcium ions it is again found, somewhat surprisingly, that this model may not be fitted to the input data. The reason for this appears to be due not so much to the neglect of the cation polarisability as to the neglect of second neighbour forces. As can be seen from the calculated values of selection I the constant C is larger than expected, although the others diminish with distance.

As has been remarked the elastic constants depend on the fluorine polarisability only through the sub-lattice strain contribution. In order therefore to obtain the elastic constants correctly on a nearest neighbour shell model the core-core force constants have to be made

artificially large, which results in difficulties in fitting the frequencies. If the calcium ion is allowed to be polarisable at least three other parameters are involved and many more than that if second neighbour forces are introduced. Furthermore there are not many rare earth halides possessing fluorite structure, or at least not so many as to form a series of compounds enabling one to derive crystal polarisabilities on a consistent basis, as has been successfully done by Hardy for the alkali halides.

Bearing these considerations in mind therefore, it appears that the best description of the crystal potential which is possible using six constants only is based on the rigid ion Born model and it is this model using the force constants of selection I which were used in the calculation.

The actual numerical work was done by Dr. F.A. Johnson of the Royal Radar Establishment, to whom the author wishes to express his gratitude. The results in the form of dispersion curves for symmetry directions are shown in figure I with a density of states curve in figure II. Unfortunately there are no published experiments to enable a comparison to be made. However, from unpublished neutron scattering data of Dribier it is possible to compare the dispersion curves along the Δ and Λ symmetry lines; these results

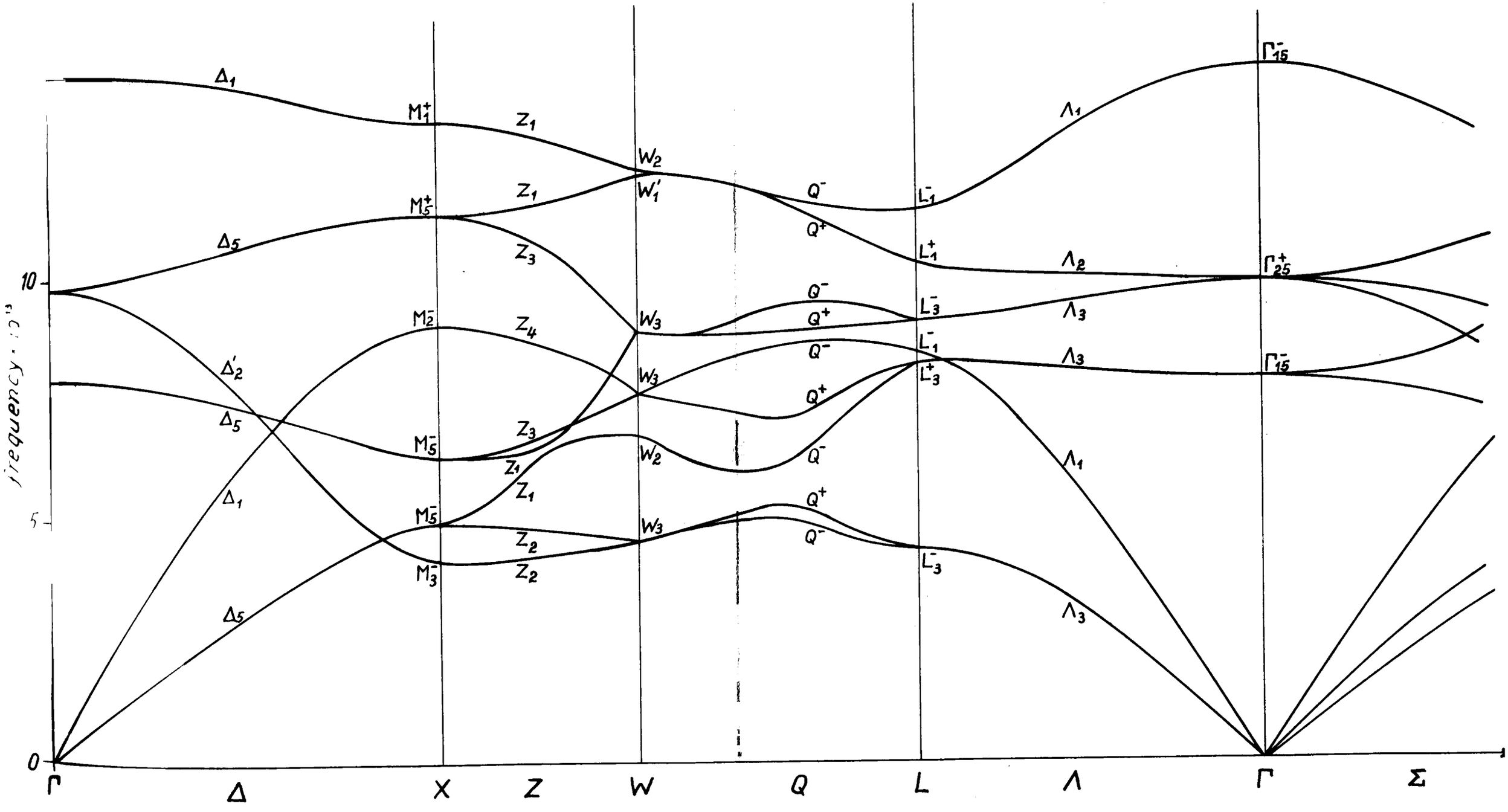

Frequency · 10¹³
10
5
0
Γ
Δ
X
Z
W
Q
L
Λ
Γ
Σ
Δ1
Δ5
Δ'2
Δ5
Δ1
Δ5
M1+
M5+
M2−
M5−
M5−
M3−
Z1
Z1
Z3
Z4
Z3
Z1
Z1
Z2
Z2
W2
W'1
W3
W3
W2
W3
Q−
Q+
Q−
Q+
Q−
Q+
Q−
Q+
Q−
L1−
L1+
L3−
L1−
L3+
L3−
Γ15−
Λ1
Λ2
Λ3
Λ3
Λ1
Λ1
Λ3
Γ25+
Γ15−

Fig.-1

agree with the present calculations to within the experimental error, thus representing a slight improvement over the calculations of Ganesan and Srinivasan.

It is hoped to make the present calculation the basis for a more accurate model when more experimental data are available.

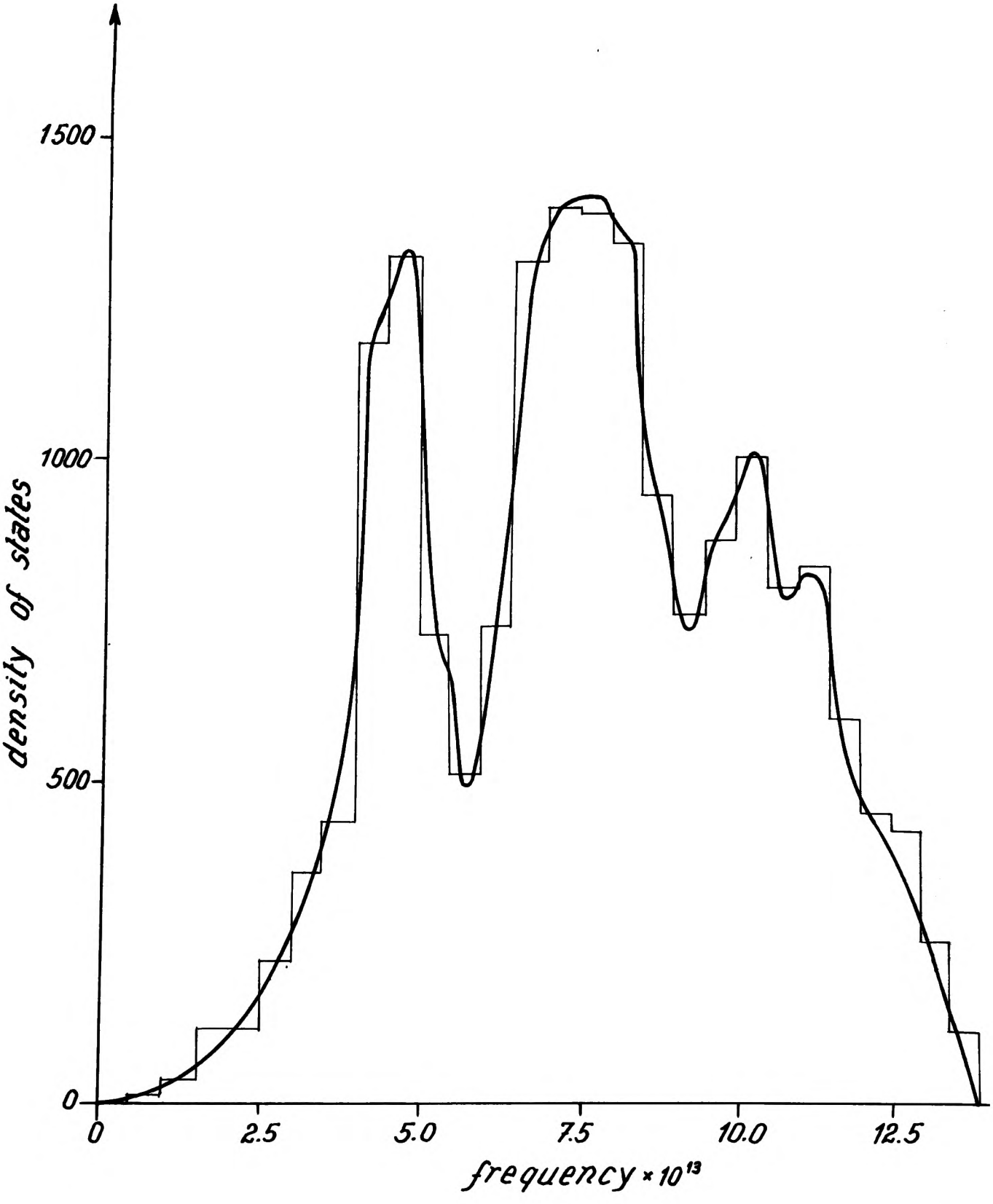

1500
1000
500
0
density of states
0
2.5
5.0
7.5
10.0
12.5
frequency × 10^13

Fig.-2

CHAPTER III.

The Theory of Defects in Crystal Lattices.

In recent years, a considerable interest has attached to the solution of the equations of motion of slightly perturbed lattices. Because of the mathematical difficulty, much of this work has been restricted to one dimensional, or simple model lattices. A review and detailed exposition may be found in the book by Maradudin, Montroll and Weiss (1963). The object of the present chapter is to show how the defect equations may be solved for more realistic crystal models, while keeping the numerical solution within the capabilities of present day computers.

As indicated in the Introduction, Chapter I, the physical quantities which it is required to calculate are (a) the frequencies of localised modes, if any occur and (b) the perturbation of the normal modes, in particular the change in amplitude, near the defect. To do this, the equations of motion are written down with the perfect lattice equations on the LHS and the deviation from the perfect lattice, introduced by the defect, is written on the right. This is then treated as a source function, and the equations solved by the Green function for the perfect lattice.

The fundamental equations are therefore:

$$M_\alpha \ddot{u}_\alpha(l) + \sum K_{\alpha\beta}(l,l')\, u_\beta(l') = -\left(\Delta M_\alpha(l)\ddot{u}_\alpha(l) + \sum \Delta K_{\alpha\beta}(ll')\, u_\beta(l')\right) \quad \ldots(3.1)$$

in terms of the mass and force constant increases ΔM and ΔK. Within the framework of the harmonic approximation this equation may be exactly resolved into normal co-ordinates which are introduced by means of a similar transformation to equation (2.2):-

$$u_\alpha(l) = \sum \chi_\alpha(f,l)\, Q(f) \quad \ldots(3.2)$$

where the quantum number f takes on 3s N values as do the previous j and k together. As in the unperturbed case, the χ's satisfy the closure and orthonormality relations:-

$$\sum_f \chi_\alpha(f,l)\,\chi_\beta(f,l') = \frac{\delta_{\alpha\beta}\delta_{ll'}}{M_\alpha} \quad \ldots(3.3)$$

$$\sum M_\alpha \chi^*_\alpha(f,l)\chi_\alpha(f'l) = \delta_{ff'} \quad \ldots(3.4)$$

In second quantisation, the normal modes are

$$Q(f) = \sqrt{\frac{\hbar}{2\omega_f}}\left(a_f + a^+_f\right) \quad \ldots(3.5)$$

and the χ's are determined from the equations of motion:-

$$-\omega^2(f) M_\alpha \chi_\alpha(f,l) + \sum K_{\alpha\beta}(ll')\chi_\beta(l') = \sum C^{\omega(f)}_{\alpha\beta}(ll')\chi_\beta(fl') \quad \ldots(3.6)$$

where the matrix

$$C^{\omega}_{\alpha\beta}(ll') = \Delta M_\alpha(l)\omega^2 1\delta_{\alpha\beta}\delta_{ll'} - \Delta K_{\alpha\beta}(ll') \quad \ldots(3.7)$$

has been introduced.

The solutions of (3.6) are written in terms of the Green's function for the perfect lattice, which in turn is defined from

$$-\omega^2 M_\alpha g^{\omega}_{\alpha\beta}(ll') + \sum K_{\alpha\gamma}(ll'')g_{\gamma\beta}(l''l') = 1\delta_{\alpha\beta}\delta_{ll'} \quad \ldots(3.8)$$

so that

$$\chi_\alpha(fl) = \sum g^{\omega(f)}_{\alpha\beta}(ll')C^{\omega(f)}_{\beta\gamma}\chi_\gamma(fl'') \quad \ldots(3.9)$$

The Green's function is well known to be

$$g^{\omega}_{\alpha\beta}(ll') = \sum_{j,k} \frac{\sigma^j_\alpha(k)\sigma^{j+}_\beta(k)e^{2\pi i \underline{k}.\underline{v}_{\alpha\beta}(l-l')}}{N(\omega_j^2(k) - \omega^2)} \quad \ldots(3.10)$$

so that once the eigenvectors $\sigma^j_\alpha(k)$ and eigenvalues $\omega^2_j(k)$ are known, and the form of $C_{\alpha\beta}(ll')$, the problem is in principle solved.

The G – matrix only connects cells perturbed by the defect; considering then only those equations (3.9) which involve these cells gives an eigenvalue condition for the implicit determination of the $\omega(f)$:-

$$\mathrm{Det}\left| \sum_{\alpha\gamma} g^{\omega}_{\alpha\gamma}(ll')C_{\gamma\gamma}(l'l'') - \delta_{\alpha\gamma}\delta_{ll''} \right| = 0 \qquad \ldots(3.11)$$

and this equation has $3sN$ solutions, which apart from any localised modes differ from the unperturbed frequencies only to order $O\left(\frac{1}{N}\right)$, as pointed out in Chapter I.

For a mass change only, G becomes proportional to a $3s \times 3s$ unit matrix; typical solutions for which case have been calculated by Dawber and Elliott (1963). However, for force constant changes, also, a $3sn \times 3sn$ matrix has to be diagonalised, where n is the number of cells perturbed. This however, may be very much simplified if, once more, the methods of group theory are applied to the problem. Equation (3.9) may be rewritten in the significant abbreviated notation

$$gCx = x \qquad \ldots(3.12)$$

where χ is a 3sn dimensional vector representing the displacements of the sn perturbed particles, and g and C are 3sn x 3sn matrices, whose elements are those elements corresponding to equations (3.9) and (3.7) respectively, with indices representing the perturbed particles.

The form of (3.12) shows that the symmetry properties of the χ-vectors may be used to perform the diagonalisation of gC: only χ-vectors of the same symmetry type will be mixed by gC. A well known example of this classification is the case of a mass change in the linear chain. The symmetry group in this case is reflection in the plane perpendicular to the chain, at the defect, with the two representations odd and even. In this case the odd vibrations are perturbed by the mass change, but the even ones are not.

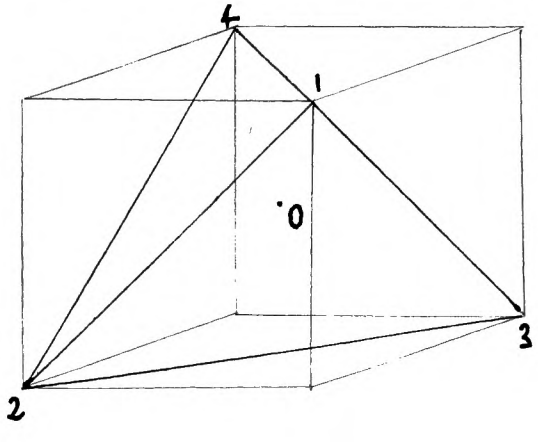
It is necessary therefore, to derive the transformation properties of the g and C-matrices. The Green function of course, has the symmetry of the unperturbed lattice, and the transformation properties may be derived from the symmetry of the eigenvectors and eigenvalues. On substituting equations (2.16) to (2.18) of Chapter II there results the relation

$$g_{\alpha\rho}(l_1 l_2) = \tilde{\sum} g_{\alpha'\rho'}(l'l_2') S \qquad \ldots(3.13)$$

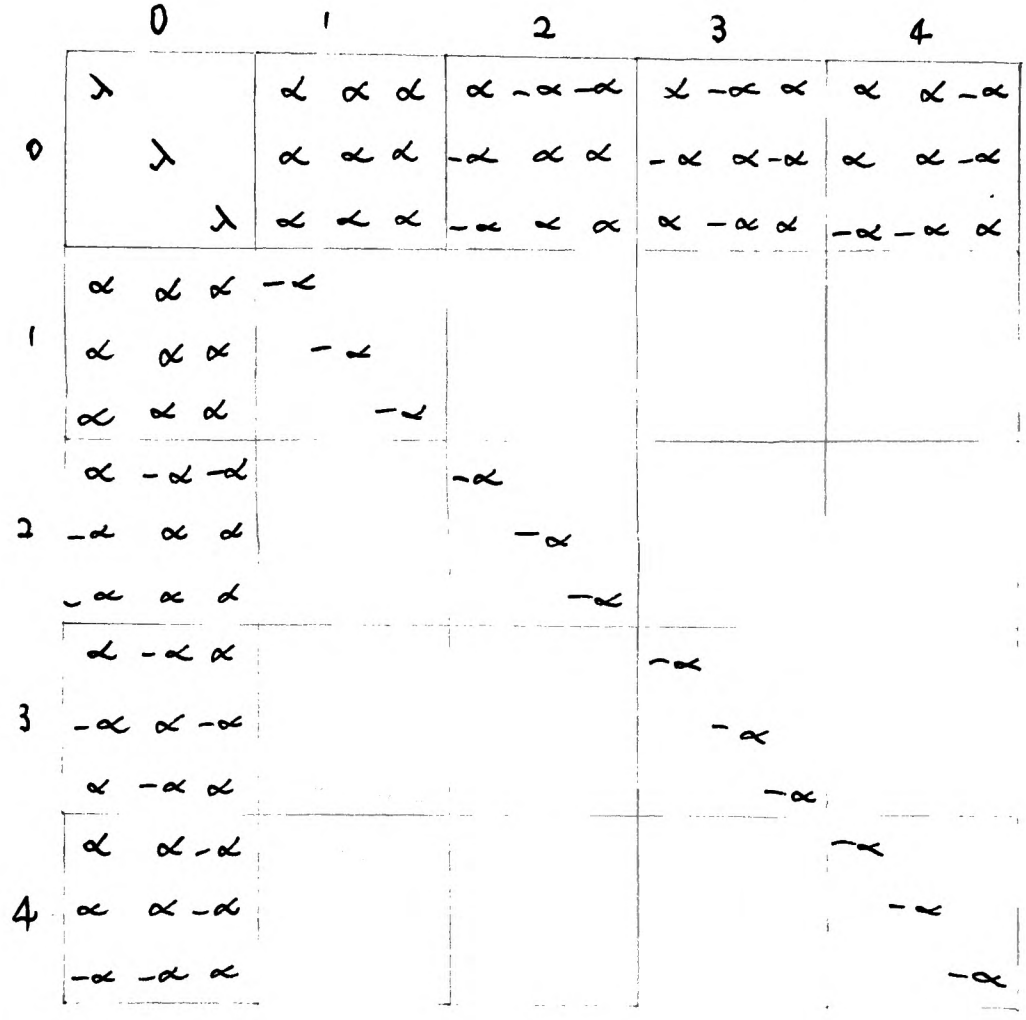
where $(\alpha', l'| = (S|v(S)|(\alpha, l)$. It is not really surprising that the g matrix should transform in the same way as a force constant matrix. The G matrix of course transforms in a similar way, except that the operation S must now be a member of the site group at the defect rather than the full group of the unit cell.

In order to clarify these ideas, they will be applied to a problem which will be of interest later in this thesis, namely a defect at a fluorine site in calcium fluoride. To simplify this problem as much as possible only changes in central force constants will be considered; thus the matrix G will contain only 2 constants, the mass change and the single force constant change.

Rather than use 2 indices α, l to locate each atom the central defect will be called 0 and the 4 nearest neighbour calcium ions, arranged in a tetrahedron around 0 are labelled 1 - 4 as follows:



and the C-matrix is of the form:



$$\lambda = -4\alpha + \Delta M\omega^2$$

The g-matrix will not be written out explicitly as it is rather too complicated to be interesting. The number of independent submatrices may however be found by referring back to Chapter II when it will be seen that g_{01} is for example

$$\underline{g}_{01} = \begin{vmatrix} g_1 & g_2 & g_2 \\ g_2 & g_1 & g_2 \\ g_2 & g_2 & g_1 \end{vmatrix}$$

$$g_1 = \sum \frac{\sigma_{2x}^{*j}(k)\,\sigma_{1x}^{j}(k)\, e^{2\pi i \underline{k}.\underline{r}_{01}}}{N(\omega_j^2(k) - \omega^2)}$$

$$g_2 = \sum \frac{\sigma_{2x}^{j*}(k)\,\sigma_{1y}^{j}(k)\, e^{2\pi i \underline{k}.\underline{r}_{01}}}{N(\omega_j^2(k) - \omega^2)} \qquad \ldots(3.14)$$

because the g matrices must have an identical form to the force constant matrices previously calculated.

Possible symmetry types for the χ's may be obtained by placing displacement vectors on the calcium ions and analysing the resultant space. The symmetry types are of the form:-

Γ_{1S}^{-} : motion of O

Γ_{1C}^{-} : 'acoustic' motion of 1, 2, 3, 4.

Γ_{1S}^{-} : rhombic distortions of tetrahedron.

Γ_{2S}^{-} : rotation of tetrahedron

Γ_{2}^{-} : compression of tetrahedron along opposite edges.

Γ_2^-: dilation of tetrahedron.

In other words, in this case the solutions of (3.12) are of 6 types, 3 arising from the solution of a cubic equation involving the first 3 modes and 3 from linear equations involving the last 3 modes. To take the simplest case of the Γ_2^- dilation mode, the eigenvalue condition (3.12) reduces to

$$-\gamma\alpha = 1 \qquad \ldots(3.15)$$

where

$$C\chi(\Gamma_i) = -\alpha\chi(\Gamma_i)$$

and

$$g\chi(\Gamma_i) = \gamma\chi(\Gamma_i) \qquad \ldots(3.16)$$

and γ is the function

$$\gamma = \int \frac{1}{N(w_j^2(k)-\omega^2)} \left\{ |\sigma_{1x}^j(k)|^2 + 2\sigma_{1x}^j(k)\sigma_{1y}^{j*}(k) \right.$$

$$+ |\sigma_{1x}^j(k)|^2 e^{2\pi i \underline{k}\cdot\underline{r}_{12}} - 4\sigma_{1x}^j(k)\sigma_{1y}^{j*}(k) e^{2\pi i \underline{k}\cdot\underline{r}_{12}}$$

$$\left. + 2|\sigma_{1x}^j(k)|^2 e^{2\pi i \underline{k}\cdot\underline{r}_{13}} + 2\sigma_{1x}^j(k)\sigma_{1y}^{j*}(k) e^{2\pi i \underline{k}\cdot\underline{r}_{14}} \right\} \qquad \ldots(3.17)$$

This is not quite so alarming as it might appear at first sight. The equation may be re-written

$$\gamma = \int \frac{f_j(k)}{N(w_j^2(k)-\omega^2)} \qquad \ldots(3.18)$$

and using the methods of Appendix II it is possible to define a function $f(\omega)$ such that

$$\gamma = \int_{j,k} \frac{f(\omega_j(k))}{N(\omega_j^2(k) - \omega^2)} \qquad \ldots(3.19)$$

For α positive, one of the solutions of (3.15) is given by $\omega^2 > \omega_j^2(k)$, that is, a localised mode: in this case, the summation in (3.19) may be replaced by an integral in a straightforward way to give

$$-\alpha \int \frac{3s f(\mu) \nu(\mu)\, d\mu}{\mu - z} = 1 \qquad \ldots(3.20)$$

as a condition determining the frequency of the localised mode. The variables μ and z are the squared frequencies $\omega_j^2(k)$ and ω^2 respectively, and $\nu(\mu)$ is the density of states normalised to unity:-

$$\int \nu(\mu)\, d\mu = 1 \qquad \ldots(3.21)$$

It is unfortunate that the localised mode, which is of most interest, namely the actual vibrations of a light defect, is always complicated: this localised mode has symmetry Γ_{15}^-: i.e., it transforms like a polar vector. But there is always at least one other mode of this symmetry

type, corresponding to the uniform motion of all the nearest neighbours. The corresponding $f(\omega)$ is derived from at least a quadratic, or as in the case of the CaF_2 crystal hitherto considered as an example, a cubic equation. However, the next most interesting mode, the dilation mode, is quite often the simplest.

The other solutions of (3.15) have values of ω^2 interspersed between the unperturbed $\omega_j^2(k)$ and so differ to order $O(\frac{1}{N})$ from the unperturbed values. Consequently a few of the terms in (3.19) will be of $O(1)$ and equal to the sum of the rest, which individually are of order $\frac{1}{N}$. The method of Lifshitz (1952) may be applied to the calculation of this sum, assuming an essentially non-singular distribution of unperturbed $\omega_j^2(k)$ these are written as $\omega^2(\rho) = \mu(\rho)$ where ρ increases from 1 to 3sN. A continuous variable $\rho(z)$ can then be defined by $\mu(\rho) = z$. The arguments reproduced in Appendix 2 show that

$$S_1 = \sum_{\mu} \frac{f(\mu)}{N(\mu - z)}$$

$$= -3s\pi\nu(z) f(z) \cot(\pi\rho(z)) + \mathcal{P}\int \frac{3sf\nu\, d\mu}{\mu - z} \qquad \ldots(3.22)$$

a principal valued integral together with a contribution from those terms in the sum near the perturbed eigenvalue.

In actual fact, for these band modes, the interesting physical property is not the frequency but the change in the amplitude of the normal mode near the defect. This may be derived from the orthogonality relation (3.4):

$$\sum_{\alpha l} M_\alpha(l) \chi_\alpha^+(f,l) \chi_\alpha(f,l) = 1 \qquad \ldots(3.4)$$

On substituting (3.9) for the values of χ not in the neighbourhood of the defect, one obtains an equation for the amplitude of the χ-vectors of equation (3.12) as

$$\sum_{\alpha l} \Delta M_\alpha(l) |\chi_\alpha(f,l)|^2 + \sum_{\alpha l} M_\alpha \chi^+ C^+ g^+ g C \chi = 1 \qquad \ldots(3.13)$$

The first term need not necessarily contribute: for the dilation mode for example, if $\Delta M_\alpha(l) \neq 0$, $\chi_\alpha(f,l) = 0$ In any case, except for the localised modes, it gives rise to a contribution only $O(\frac{1}{N})$ of the second term.

The sum on α and l in this second term may be performed as follows:

$$\left(\sum_{\alpha\ell} M_\alpha\, g^+ g\right) = \sum_{\alpha\ell} M_\alpha \sum_{j,k} \frac{\sigma_\beta^j(k)\,\sigma_\alpha^{j+}(k)\, e^{2\pi i \underline{k}\cdot \underline{r}_{\beta\alpha}(\ell'-\ell)}}{N\left(\omega_j^2(k) - \omega^2\right)}$$

$$\times \sum_{j'k'} \frac{\sigma_\alpha^{j'}(k')\,\sigma_\gamma^{j'+}(k')\, e^{2\pi i k'\cdot \underline{r}_{\alpha\gamma}(\ell-\ell'')}}{N\left(\omega_{j'}^2(k') - \omega^2\right)}$$

$$= \sum_{j,k} \frac{\sigma_\beta^j(k)\,\sigma_\gamma^{j+}(k)\, e^{2\pi i k\cdot \underline{r}_{\beta\gamma}(\ell'-\ell'')}}{N\left(\omega_j^2(k) - \omega^2\right)^2} \qquad \ldots(3.24)$$

where the closure property of the unperturbed eigenvectors has been used. Equation (3.24) is symbolically written

$$\sum_{\alpha\ell} M_\alpha\, g^+ g = \frac{\partial g}{\partial \omega^2} \qquad \ldots(3.25)$$

It is immediately obvious that $\frac{\partial g}{\partial \omega^2}$ has the same transformation properties as g; and furthermore, for the particular dilation mode so far considered

$$|\chi|^2 = \left\{ \alpha^2 \sum \frac{f(\omega_j(k))}{N\left(\omega_j^2(k) - \omega^2\right)^2} \right\}^{-1} \qquad \ldots(3.26)$$

For a mode which has a unique symmetry, the f of equation (3.26) is the same as the f of equation (3.19); but for modes of repeated symmetry type the two f's will differ.

The evaluation of S_2 in the former case is performed using the methods of Appendix 2 to give

$$S_2 = \sum_{j,k} \frac{f(\omega_j^2(k))}{N(\omega_j^2(k) - \omega^2)^2}$$

$$= N\left[9\pi^2 s^2 f(z) v(z) + \left(\frac{1}{\alpha} - \mathcal{P}\int \frac{3sf\nu}{\mu - z}\, d\mu\right)^2\right] \frac{1}{f(z)} \quad \ldots(3.27)$$

and $$|\chi|^2 = \frac{1}{\alpha^2 S_2} \quad \ldots(3.28)$$

which is $O(\frac{1}{N})$ as expected for a band mode. For a softening of the force constants, $\alpha < 0$ the amplitude will show a maximum due to the zero of the second term in (3.27). These are frequencies at which a localised mode would like to appear, but the unperturbed lattice will now accept these frequencies and consequently they have a finite width $\frac{1}{3\pi s f(z) v(z)}$. Thus the main outlines of the defect problem with force constant changes are broadly similar to that of a simple mass change, except that in this case the properties are determined by the function $f(z)v(z)$ rather than the density of states alone.

CHAPTER IV

Anharmonic Effects in Impurity Absorption.

Although the existence of localised vibrations in crystals has been known theoretically for many years, only in recent years have such vibrations been experimentally observed; the U-centre, i.e. hydrogen ions substituted in alkali halide crystals has been observed by this method by Pick (1959), Schaefer (1960) and Fritz (1962). It was shown by Hall and Schumacher (1962) that hydrogen and deuterium will dissolve readily in calcium fluoride if the crystals are heated in the presence of the gas at 800°C in the presence of aluminium, and crystals so treated have been the subject of experimental investigations by Hayes and Jones (1963). They have observed the infra-red spectrum of hydrogen and deuterium ions dissolved in calcium barium and strontium fluorides, and have measured the effect of temperature on these spectra. They observe four lines, two singlets and a doublet of rapidly diminishing intensity which are attributed to the fundamental and second and third harmonics of the localised vibrations of the substituted ions. The deuterium doped crystals show absorption lines whose squared frequency bears the ratio 1.92^{-1} to that of the hydrogen lines. The closeness of this ratio to 2 is an indication of the extent to which the defect ions vibrate independently of the rest of the lattice. Both

the position and width of the lines are strongly temperature dependent; as the temperature increases from liquid helium temperature to room temperature, the width of the second harmonic line in CaF_2:H increases from 1 - 20 cm^{-1}.

In the case of the U-centre in the alkali halides Fritz (1963) has also observed two side bands on either side of the fundamental absorption. These have a temperature dependent intensity proportional to $n(\omega)$ and $n(\omega) + 1$ on the low and high energy sides of the fundamental respectively, where $n(\omega)$ is the function $\{\exp\frac{\hbar\omega}{kT} - 1\}^{-1}$. All of these experimental observations may be explained by invoking anharmonic effects: These anharmonicities mix the otherwise pure normal co-ordinates: mixtures of local modes correspond to the formation of harmonics, while the admixture of band modes gives rise to the temperature dependent effects. Evidence will be given to support the view that these defects are in fact situated at fluorine sites, and on the basis of the Debye approximation all of the temperature dependent effects will be given an explanation. Although physically this is not a very good model, and the final parameters calculated do not have a very great deal of physical significance, the temperature

variation is so smooth as not to distinguish between the various models. However, initially, a lattice picture will be used to show more clearly the precise nature of the approximations made.

1. Approximate calculation of the localised mode frequency.

The correct calculation of the localised mode eigenvalue using the methods of Chapter III, is rather too complicated to be worth the effort. However, if, as seems likely from the experimental results with the deuterium defects, these very light defects vibrate independently of the rest of the lattice in the potential well formed at the defect site, then the eigenvalue may be computed directly from the force constant at the defect site. These force constants for the unperturbed lattice may be calculated from the data of Chapter II for the fluorine and calcium sites which shows that the unperturbed harmonic potentials are isotropic, although of course, for fluorine defects this is not necessarily the case with the perturbed potential. There are two parts to the force constant matrices, the short range and the Coulomb interactions. In the notation of Chapter II these are written

$$ {}^{c}K_{oo}(0\,0) + {}^{s}K_{oo}(0\,0) = \xi 1 $$

and the fundamental absorption frequency is then given by

$$m\Omega^2 = \xi \qquad \ldots(4.1)$$

where m is the mass of the hydrogen ion and Ω is its localised frequency of vibration. The short range part ${}^{s}K_{\omega}(0$ is the constant α of Chapter II for the calcium site and β for the fluorine site. The coulomb part may be calculated by putting an effective charge Z on the hydrogen ion. When this is done and the unknown constants substituted from Chapter II, there results for the frequency:

	Ca Site	F Site	Experimental value = 965.6
Born model	1770 cm^{-1}	1060 cm^{-1}	
Shell model	1790 cm^{-1}	1237 cm^{-1}.	

All the predictions result in too high a frequency, so apparently there is some softening of the force constant on the substitution of the defect.

4. Symmetry restriction of the anharmonic force constants.

The potential in which the nuclei move may be expanded in a Taylor series of successive powers of the displacements, retaining terms up to and including the fourth order:

$$V = V_0 + \sum K^{ij}_{\alpha\beta}(ll')\, u^i_\alpha(l)\, u^j_\beta(l')$$
$$+ \sum h^{ijk}_{\alpha\beta\gamma}(ll'l'')\, u^i_\alpha(l)\, u^j_\beta(l')\, u^k_\gamma(l'')$$
$$+ \sum M^{ijkm}_{\alpha\beta\gamma\delta}(ll'l''l''')\, u^i_\alpha(l)\, u^j_\beta(l')\, u^k_\gamma(l')\, u^m_\delta(l''')$$
$$+ \ldots$$

The symmetry properties of these force constant tensors may be derived using the arguments of Chapter II, and are an obvious extension of equation (2.11):-

$$L^{i'j'k'}_{\alpha'\beta'\gamma'}(l_1'l_2'l_3') = \sum_{ijk} L^{ijk}_{\alpha\beta\gamma}(l_1l_2l_3)\,S_{ii'}\,S_{jj'}\,S_{kk'} \quad \ldots(4.3)$$

with a similar relation for the M tensors. In addition, the tensors are invariant under interchange of any pair of sets of indices α, i, l.

The force constants at the origin will be considered first of all. Each component of the tensor transforms like a product of x,y or z, so the number of independent constants is given in the usual way by the number of times the identity representation is contained in the space spanned by the product of three polar vectors, (or four in the case of quartic terms). The complete symmetry group is the direct product of the permutation group of the three indices and the point group at the site, so only the character of that part of the space which transforms like the identity representation of the permutation group will be considered. The projection operator is

$$\Pi_{P_i} = \frac{1}{N!}\sum \begin{pmatrix} i & j & k & \ldots \\ l & m & \sim & \ldots \end{pmatrix}$$

which projects into the identity representation of the group of permutation of N objects. If then $\chi(S)$ is the character of the polar vector representation of the operator S in the point group under consideration, then the symmetric characters are

$$\chi_3 = \frac{1}{3!}\left[\chi^3(S) + 3\chi(S)\chi(S^2) + 2\chi(S^3)\right]$$

$$\chi_4 = \frac{1}{4!}\left[\chi^4(S) + 6\chi^2(S)\chi(S^2) + 8\chi(S)\chi(S^3) + 3\chi^2(S^2) + 6\chi(S^4)\right] \qquad \ldots(4.4)$$

The coefficients in front of each of the terms are just the number of operations in each class of the permutation group, and as the permutation groups $\mathfrak{P}_3$ and $\mathfrak{P}_4$ are respectively isomorphic to O_{3v} and T_d these are easily found from tables.

In the case of T_d this gives a character table as follows:

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
$\chi(\Gamma_4)$	3	0	-1	1	-1
χ_3	10	1	-2	2	0
χ_4	15	0	3	3	1

The other point group of interest, O_h is formed from T_d by taking the direct product with the inversion. The number of times the identity representation is contained in these

spaces is then given by the character orthonormality theorem:

$$n_3 = \frac{1}{24}(10 + 8.1 - 3.2 + 6.2 + 6.0) = 1$$
$$n_4 = \frac{1}{24}(15 + 8.0 + 3.3 + 6.2 + 6.1) = 2 \qquad \ldots(4.5)$$

The results for O_h are easily derived from these using the fact that the polar vector representation is odd, so that in this case,

$$n_3 = \frac{1}{48}(n_3(T_d) + n_3(T_d)) = 0$$
$$n_4 = \frac{1}{48}(n_4(T_d) + n_4(T_d)) = 2 \qquad \ldots(4.6)$$

Thus the defect on a fluorine site introduces some cubic anharmonicity, which it is unable to do on a calcium site, or an interstitial site. It is to be noted that the unperturbed crystal has no cubic anharmonicity at either site. The non-zero components of the tensors may be found by operating with the elements of the site group. Clearly $\lambda^{xyz}_{222}(000)$ is the only one which survives in the cubic cases, while in the quartic terms, 3_z^2 kills off terms odd in x, y, or z and O_h guarantees the equivalence of x, y, and z, so

$$\mu^{xxxx}_{2222}(0000) = \mu^{yyyy}_{2222}(0000) = \mu^{zzzz}_{2222}(0000);$$
$$\mu^{xxyy}_{2222}(0000) = \mu^{yyzz}_{2222}(0000) = \mu^{zzxx}_{2222}(0000)$$

$\ldots.(4.7)$

with similar relations for the other quartic terms.

The other anharmonic force constants are treated by an obvious extension of this procedure. Instead of considering $\Lambda^{ijk}_{\alpha\beta\gamma}(l_1 l_2 l_3)$ and $\Lambda^{jik}_{\beta\alpha\gamma}(l_2 l_1 l_3)$ as separate but equal entities, they are thought to be the same, thus dispensing with the factor $\frac{1}{N!}$ in equation (4.4). The group of the bond is generated from the unit cell group by operating with this latter group on an invariant set of bonds: a procedure less liable to error than guessing the group of the bond. One then obtains the formula

$$n_g = \frac{1}{g} \sum \left\{ N_1(S)\chi^2(S) + 2N_2(S)\chi(S)\chi(S^2) + 2N_3(S)\chi(S^3) \right\} \qquad \ldots(4.8)$$

an extension of (4.15). Here $N_1(S)$ is the number of bonds left invariant by S, $N_2(S)$ is the number of bonds in which S brings about a reversal of a pair of lattice points and $N_3(S)$ is the number in which S performs a cyclic interchange. It is interesting to note in passing that a bond possessing no symmetry whatsoever must be one of a star of g bonds generated by the group. In this case $N_2(S) = N_3(S) = 0$ for all S and $N_1(S) = g$ for $S = E$ and is otherwise zero. Consequently the number of components in this tensor is

$$n_g = \frac{1}{g} \times g \times 27 = 27$$

as $\chi(E) = 3$, the dimensionality of the polar vector representation. Evidently in such a case every element of the tensor is different.

With the introduction of a defect into the unit cell some of the symmetry is frequently lost; in this case the site group operations must be used rather than the full unit cell group. For $K_{Fm}(ccc)$ for example, from a defect on a fluorine site, the symmetry is T_d rather than O_h. This gives, for this set of four bonds

$$n_3(K_{Fm}(ccc)) = \frac{1}{24}(4\times 2 + 6\times 1\times 1) = 5 \text{ constants} \qquad \ldots(4.9)$$

These results will be used later to list the possibilities for the defect motion in calcium fluoride.

3. Discussion of the normal modes.

The Hamiltonian of the lattice with a defect is written

$$\mathcal{H} = \sum \tfrac{1}{2} M_{(l)} \dot{u}^2_{(l)} + V \qquad \ldots(4.10)$$

where V is given by (4.2). The first two terms of this Hamiltonian may be diagonalised exactly using the methods of Chapter III and the other terms are then treated by perturbation theory. Thus

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_3 + \mathcal{H}_4 \qquad \ldots(4.11)$$

where $$H_0 = \sum \hbar\omega(f)\left(a^+(f)a(f) + a(f)a^+(f)\right) \quad \ldots(4.12)$$

and $$H_3 = \sum L^{ijk}_{\alpha\beta\gamma}(l_1 l_2 l_3)\, u^i_\alpha(l_1)\, u^j_\beta(l_2)\, u^k_\gamma(l_3)$$

$$= \sum L(f_1 f_2 f_3)\, a(f_1)\, a(f_2)\, a(f_3)$$

$$\ldots(4.13)$$

on performing the transformation to normal co-ordinates. There is a similar expression for H_4. Here

$$L(f_1 f_2 f_3) = \sum L^{ijk}_{\alpha\beta\gamma}(l_1 l_2 l_3)\, X^i_\alpha(f_1 l_1)\, X^j_\beta(f_2 l_2)\, X^k_\gamma(f_3 l_3) \quad \ldots(4.14)$$

In the first instance terms involving two or three local mode operators will be considered and then simplified expressions approximating to these will be derived. Throughout the discussion it will be assumed that the local mode may be decoupled from the other modes because of its high frequency and highly localised state. The estimate already made indicates a softening of the force constant by up to a third, whereas the squared frequency of the localised mode is about 10 times larger than the higher calcium fluoride vibration frequencies. Accordingly the part of the G matrix of Chapter III referring to the defect motion is 20 - 30 times larger than the parts which couple this motion to the other

modes. The corresponding elements of the Green function matrix are also falling off for this localised mode, so it seems that the amount of local mode vibration on the nearest neighbours would be at the most a few percent of the vibration due to other modes.

Terms involving three local mode operators.

In this case (4.13) becomes

$$L(fefefe) = \sum L^{ijk}_{\rho\rho'\rho''}(l_1 l_2 l_3)\, g^{ii'}_{\kappa 0}(l_1 0)\, g^{jj'}_{\rho 0}(l_2 0)\, g^{kk'}_{\rho 0}(l_3 0)$$
$$X^{i'}_0(fe,0)\, X^{j'}_0(fe,0)\, X^{k'}_0(fe,0) \qquad \ldots(4.15)$$

and the defect site has been labelled (0.0). The sum over all lattice sites (4.15) can only depend on the co-ordinates of the defect atom, and it is easy to see that it involves exactly the same number of independent constants as $L_{000}(000)$ does. This leads to the very important result that, no matter what the localisation, a defect ion situated at a calcium or an interstitial site can have no cubic anharmonic term involving three local mode operators. This is a consequence of equation (4.6) which shows that under the group at these sites $U_h . N_g = 0$. The importance of this result lies in the fact that these are the terms responsible for mixing the first excited

state of the local mode oscillator into the second, which lights up the second harmonic. Harmonics therefore, will only be observed when the defect site symmetry is less than O_h: which seems to rule out the possibility of the defect being situated at the calcium or interstitial sites in this case. This is also in agreement with the non-observation of harmonics for the F-centre in alkali halides as in this case the hydrogen ion is situated at a halide site of symmetry O_h.

In actual fact the term will be written down directly as a function of the defect displacements, in order to facilitate the calculation:-

$$L(f_\ell\ f_\ell\ f_\ell)\,d^3(f) = \sum L^{ijk} x_i x_j x_k \qquad \ldots(4.16)$$

The physical meaning to be attached to the constant L^{ijk} is that

$$L^{ijk} \simeq L^{ijk}_{\ell\ell\ell}\ (000) \qquad \ldots(4.17)$$

This approximation is probably quite accurate as the sum (4.15) involves the cube of the localised function $\lambda(r,l)$.

Terms involving two local mode operators

Following the philosophy of treating the hydrogen vibration as a highly localised vibration, the anharmonic

terms contributing mostly to (4.15) are of the type

$$L_{\alpha\beta}(\cos\theta)$$

that is assuming the greatest contribution comes from the nearest neighbour forces. As has been shown in (4.9) this tensor involves 3 independent constants which couple to the five symmetry types discussed in Chapter III. Thus (4.15) may be written

$$\sum_{\beta} \omega(\beta\beta\beta)\, d^2\beta_1)\, d\beta| = \sum_{\beta} |\chi(\beta_2)|^2\, d^2\beta_2| \{ a|\chi(\Gamma_2\beta)|d\beta| + b|\chi(\Gamma_{15}\beta)|d\beta| + c|\chi(\Gamma_{25}\beta)||d\beta| + d|\chi(\Gamma_{15,1},\beta)|d\beta| + e|\chi(\Gamma_{15,2},\beta)|d\beta\} \quad (\ldots(4.18)$$

For no change in these force constants these modes are unperturbed; for change in central force constants they all become perturbed with the exception of the Γ_{25} mode. However, the point of interest here is that the Γ_2 mode, for example, is entirely independent of the localised mode. If only the mass were changed, although the individual vibrations of the atoms would be perturbed, the symmetric combination implied by $\chi(\Gamma)$ would be as for the unperturbed lattice.

The expression (4.18) already contains more parameters than it is possible to fix from the experimental data, so evidently it must be simplified further. Two approximations are therefore made.

1. The expression within curly brackets in (4.18) is approximated by the corresponding expression which would be derived for a Debye solid, containing an isolated point mass defect. In this picture the force constants are coalesced into one, proportional to the local strain induced by each mode.

2. The expression $|\chi(f_e)|^2$ is approximated by the asymptotic value for extremely light masses. This may be obtained from equation (3.23):

$$\Delta M |\chi|^2 + \chi^+ C^+ \frac{\partial g}{\partial \omega^2} C \chi = 1 \qquad \ldots(4.19)$$

for this case and

$$|\chi|^2 = \left\{ \Delta M + (\Delta M \Omega^2)^2 \sum \frac{|\sigma_{2\lambda}(k)|^2}{N(\omega_\lambda^2(k) - \Omega^2)^2} \right\}^{-1} \qquad \ldots(4.20)$$

On putting $M_g + \Delta M_g = m$ the mass of the defect, substituting in (4.20) and dropping terms of second order in $\frac{m}{M_g}$ and using the closure relation (3.8), the asymptotic value

$$m |\chi(f_e)|^2 \to 1 \qquad \ldots(4.21)$$

is obtained.

Thus (4.18) is now replaced by the expression

$$A_3 = \sum_k \alpha^2 k \, d^2(f_e) \, d(k) \frac{1}{m\sqrt{M}} \qquad \ldots(4.22)$$

The final factor of (4.22) is somewhat arbitrary and comes from replacing the $|\chi(l)|$ by $\left|\frac{e^{ik.r}k}{\sqrt{M}}\right|$ for a Debye solid. To approximate to the acoustic modes of Ca F_2 the constant M should be equal to the cell mass. Finally the normal co-ordinate operators in (4.22) are replaced by the second quantised expressions (3.5) thus transforming (4.22) to the form

$$\mathcal{H}_3 = \sum_k \alpha \left\{\frac{\hbar}{2m\Omega}\sqrt{\frac{\hbar}{2MW(k)}}\right\} k\,(b+b^+)^2(a(k)+a(k')) \quad \ldots(4.23)$$

where the creation and annihilation operators for a local mode are written b^+ and b respectively.

Terms involving two local modes in the quartic anharmonicity will also be considered; these are written in a similar form as

$$\mathcal{H}_4 = \sum_{kk'} \mathcal{M}\left\{\frac{\hbar}{2m\Omega}\frac{\hbar}{2M\sqrt{W(k)W(k')}}\right\} kk'(b+b^+)^2 \times (a(k)+a^+(k))(a(k')+a^+(k')) \quad \ldots(4.24)$$

Thus the final form chosen for the H amiltonian is

$$\mathcal{H} = \mathcal{H}_0 + V_3 + V_4 + \mathcal{H}_3 + \mathcal{H}_4 \quad \ldots(4.25)$$

where H_3 and H_4 are given by (4.23) and (4.24) and V_3 and V_4 are written

$$V_3 = \sum L^{ijk} X_i X_j X_k = L\,xyz \quad \ldots(4.26)$$

...(

$$V_4 = \sum M^{ijkl} x_i x_j x_k x_l = M_1(x^4+y^4+z^4) + M_2(y^2z^2+z^2x^2+x^2y^2) \quad \ldots(4.27)$$

on substituting the symmetry relations derived earlier. The effect of these two pairs of perturbations will be treated separately, for the sake of clarity.

4. The Vibrations of a Hydrogen Defect in an Anharmonic Potential Well.

The Hamiltonian is now simplified to the form

$$\mathcal{H} = \frac{1}{2m}\left(p^2 + m^2\Omega^2(x^2+y^2+z^2)\right) + Lxyz + M_1(x^4+y^4+z^4) + M_2(x^2y^2+y^2z^2+z^2x^2) \quad \ldots(4.28)$$

The terms V_3 and V_4 will be treated as perturbations on the spherical harmonic oscillator. It simplifies the calculations considerably if the unperturbed Hamiltonian is separated into Cartesian co-ordinates rather than spherical polars, so the unperturbed wave functions are written in the form $|\, N_1\, N_2\, N_3\rangle$ showing the occupation numbers of each of the three independent linear oscillators. The wave function $|210\rangle$ for example can be written in the form

$$\left(x - \frac{\partial}{\partial x}\right)^2 \left(y - \frac{\partial}{\partial y}\right) e^{-\frac{1}{2}r^2}$$

in appropriate units and suitably normalised. The high symmetry of the harmonic oscillator implies a high degeneracy

of the unperturbed wave functions, some examples of which are listed:

	Wave function	Symmetry	Degeneracy
Ground State	$\|000\rangle$	Γ_1	1
1st excited State	$\|100\rangle$	Γ_4	3
2nd excited State	$\|200\rangle$	$\Gamma_1+\Gamma_3$	6
	$\|110\rangle$	Γ_4	
3rd excited State	$\|111\rangle$	Γ_1	10
	$\|210\rangle$	$\Gamma_4+\Gamma_5$	
	$\|300\rangle$	Γ_4	

The anharmonicity lifts some of the degeneracy, splitting the levels into their different symmetry types and mixing levels of the same symmetry type. The observable levels have Γ_4 symmetry type and so one sees the fundamental, the second harmonic and two third harmonics.

We use perturbation theory to second order in V_3 and first order in V_4 to give the following results:

$$\Delta E_{000} = \langle 000|V_4|000\rangle + \sum \frac{|\langle 000|V_3|i\rangle|^2}{E_0 - E_i}$$

$$= (9M_1 + 3M_2)\lambda^2 - \frac{L^2\lambda^3}{3\omega^2} \qquad \ldots(4.29)$$

Here λ is the mean square particle displacement $\lambda = \frac{t\nu}{2m\Omega}$

$$\Delta E_{100} = (21M_1 + 7M_2)\lambda^2 - \frac{5L^2\lambda^3}{3t\nu\Omega} \qquad \ldots(4.30)$$

$$\Delta E_{110} = (33M_1 + 15M_2)\lambda^2 - \frac{13}{3}\frac{L^2\lambda^3}{t\nu\Omega} \qquad \ldots(4.31)$$

The third energy level is treated by degenerate perturbation theory and involves the diagonalisation of a 2x2 matrix, the eigenvalues of which are,

$$\Delta E_{300/210} = \frac{1}{2}\left\{(138M_1 + 40M_2)\lambda^2 - \frac{40}{3}\frac{L^2\lambda^3}{t\nu\Omega}\right.$$

$$\left. \pm \sqrt{\left[\left\{(24M_1 - 10M_2)\lambda^2 - \frac{14}{3}\frac{L^2\lambda^3}{t\nu\Omega}\right\}^2 + 96\frac{L^4\lambda^6}{t^2\nu^2\Omega^2}\right]}\right. \qquad \ldots(4.32)$$

The frequencies actually observed in the case of CaF_2:H are the fundamental $\Omega_1 = 965.6\,cm^{-1}$ the second harmonic $\Omega_2 = 1919.8\,cm^{-1}$ and the two third harmonics Ω_3' and Ω_3'' at $2912.2\,cm^{-1}$ and $2825.6\,cm^{-1}$ respectively. These four results serve to determine the four constants L M_1 M_2 and Ω as follows:

$$\begin{aligned} L &= 4.31 \times 10^{12} \ ergs/cm^3 \\ M_1 &= 1.29 \times 10^{21} \ ergs/cm^4 \\ M_2 &= -1.768 \times 10^{21} \ ergs/cm^4 \\ \Omega &= 952 \ cm^{-1}. \end{aligned} \qquad \ldots(4.33)$$

The accuracy is only about 10% as the constants are determined from the small differences $\Omega_2 - 2\Omega_1$, $\Omega_3' - \Omega_3''$, $\frac{\Omega_3' + \Omega_3''}{2} - 3\Omega_1$ However, the order of magnitude of these terms is what one would expect for anharmonic force constants, which may be seen as follows. When the potential is expanded as a power series in the displacements, the actual expansion parameter is x/a = (atomic displacement)/(lattice spacing), so that

$$V = V_0 + m\Omega^2 a^2 \left(\frac{x^2}{a^2} + \alpha \frac{x^3}{a^3} + \beta \frac{x^4}{a^4} + \dots \right)$$

where α and β are of order unity. Thus one expects $L \sim 10^{12}$ and $M \sim 10^{20}$.

The splitting of the third harmonic line is largely due to the cubic anharmonic term in (4.32) due to its large co-efficient, so the splitting is proportional to

$$\Delta\Omega_3 \propto \frac{\lambda^3}{\Omega} \propto \frac{1}{m^3\Omega^9} \qquad \dots(4.34)$$

If the force constant is constant $m\Omega^2$ remains the same for mass changes so

$$\Delta\Omega \propto \frac{1}{m} \qquad \dots(4.35)$$

For the hydrogen defect in CaF_2. $\Delta\Omega_3 = 86.6\ cm^{-1}$ whereas on substituting deuterium $\Delta\Omega_3 = 45\ cm^{-1}$ in rough agreement with (4.35)

The intensity of the absorption may also be calculated using perturbation theory. The optical matrix element involved in the second harmonic absorption is

$$\langle 0|\epsilon.p|2\rangle = \frac{\langle 000|V_3|111\rangle}{E_0 - E_3}\langle 111|\epsilon.p|110\rangle + \langle 0|\epsilon.p|001\rangle\frac{\langle 001|V_3|110\rangle}{E_2 - E_1} \qquad \ldots(4.36)$$

and so the absorption differs from the fundamental by a factor

$$\frac{L^2\lambda^3}{\hbar^2\Omega^2}\left(-\tfrac{1}{3}+1\right)^2 = \frac{4L^2\lambda^3}{9\hbar^2\Omega} \sim \frac{1}{360} \qquad \ldots(4.37)$$

The third harmonic absorption is more complicated involving terms of second order in V_3 and first order in V_4. The matrix element to the perturbed 10037 state will be calculated to show both the simplicity of the calculation in the Cartesian quantisation, and also to indicate a curious cancellation effect:

$$\langle 0|\epsilon.p|3\rangle = \frac{\langle 0|V_3|111\rangle\langle 111|V_3|002\rangle\langle 002|\epsilon.p|003\rangle}{(E_0-E_1)(E_0-E_2)} + \frac{\langle 0|V_3|111\rangle\langle 111|\epsilon.p|112\rangle\langle 112|V_3|003\rangle}{(E_0-E_3)(E_3-E_4)}$$
$$+ \frac{\langle 0|\epsilon.p|001\rangle\langle 001|V_3|112\rangle\langle 112|V_3|003\rangle}{(E_3-E_4)(E_3-E_1)}$$
$$+ \frac{\langle 0|V_4|004\rangle\langle 004|\epsilon.p|003\rangle}{E_0-E_4} + \langle 0|\epsilon.p|001\rangle\frac{\langle 001|V_4|003\rangle}{E_3-E_1}$$

$$= \frac{L^2\lambda^3}{\hbar^2\Omega^2}\langle 0|\epsilon.p|1\rangle\left\{\frac{\sqrt{2}.\sqrt{3}}{(-3)(-2)} + \frac{\sqrt{2}.\sqrt{3}}{(-4)(-1)} + \frac{\sqrt{2}.\sqrt{2}}{(-1)2}\right\}$$
$$+ \frac{M_1\lambda^2}{\hbar\Omega}\langle 0|\epsilon.p|1\rangle\left\{\frac{\sqrt{1.2.3.4.4}}{-4} + \frac{1}{2}\left(\sqrt{2.3.4.3} + \sqrt{2.1.3.3} + \sqrt{2.2.3.3}\right)\right\}$$

$$= \frac{M_1\lambda^2}{\hbar\Omega}\langle 0|\epsilon.p|1\rangle\sqrt{6}\left(\tfrac{1}{2} + \sqrt{3} + \tfrac{1}{2}\sqrt{6}\right) \qquad \ldots(4.38)$$

All the V_3 contributions cancel out, presumably due to the existence of some other symmetry operator of the harmonic oscillator Hamiltonian. A similar effect cancels out the matrix element from the ground state to the fourth harmonic via V_3 in first order; this means that each successive harmonic decreases in intensity. Knowing therefore, the two matrix elements and the amount of admixture to the $|2_1 0_4^2\rangle$ state, one can calculate the ratio of the intensities of the two lines and the intensity of one of these lines to the fundamental. These two numbers are respectively 5.5 and 3×10^{-4}.

In actual fact the experimental results indicate intensity ratios much larger than these, that is the harmonics are much more intense than would be expected from the frequency shifts. A discussion of a possible reason for this will be given later.

5. The effect of anharmonic terms involving the band modes.

The effect of the terms $\mathcal{H}_3$ and $\mathcal{H}_4$ will now be calculated. The Hamiltonian is written:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_3 + \mathcal{H}_4 \qquad \ldots(4.39)$$

where $\mathcal{H}_0$ now includes N harmonic oscillator Hamiltonians and $\mathcal{H}_3$ and $\mathcal{H}_4$ are as defined previously.

There is still a variety of processes implied in these terms, but to account for the temperature dependent width and shift, terms involving products like $b^+b\,a^+(k')a(k)$ in $\mathcal{H}_4$ will be considered. This term represents the scattering of a phonon from k to k' by means of the defect, thus changing the crystal state from one of zero crystal momentum to one of momentum $-\underline{k}+\underline{k}'$, while at the same time conserving energy. This gives a finite lifetime to the optically observed state, and a broadening proportional to the transition probability. This process may be achieved either by $\mathcal{H}_4$ in first order or $\mathcal{H}_3$ in second, leading to a total half width,

$$\Gamma = \frac{2\pi}{\hbar}\left\{\left|\langle n(k)n(k')|\mathcal{H}_4|n(k)-1,\, n(k')+1\rangle\right|^2 + \left|\sum_i \frac{\langle n(k)n(k')|\mathcal{H}_3|i\rangle\langle i|\mathcal{H}_3|n(k)-1\; n(k')+1\rangle}{\epsilon_1-\epsilon_i}\right|^2\right\} \times \delta\left(\hbar\omega(k)-\hbar\omega(k')\right)d\underline{k}\,d\underline{k}' = \Gamma_1+\Gamma_2 \qquad \ldots(4.40)$$

Using the Debye approximation, $\omega = sk$ where s is the velocity of sound, and

$$\Gamma_1 = \frac{2\bar{a}}{\hbar} \int_{kk'} |\langle n(k)n(k')|\mathcal{H}_4|n(k)-1\,n(k')+1\rangle|^2 \delta(\hbar\omega(k)-\hbar\omega(k'))$$

$$= \frac{2\pi}{\hbar^2}\iint e\mathcal{M}^2 \left\{\frac{\hbar^4}{16m^2M^2\Omega^2}\right\} \frac{k^2k'^2}{\omega(k)\omega(k')} \cdot 3^2 \cdot n(k)(n(k')+1)\,dk\,dk' \; \delta(\omega(k)-\omega(k'))$$

$$= \frac{18\pi e\mathcal{M}^2\hbar^2}{16(Mm\Omega)^2} 16\pi^2 \cdot \frac{V^2}{(2\pi)^6} \cdot \frac{\omega_{max}^{10}}{s^{10}} \left(\frac{\hbar}{k\Theta}\right)^3 \left(\frac{T}{\Theta}\right)^7 \int_0^{\Theta/T} \frac{z^6 e^z dz}{(e^z-1)^2}$$

$$= \frac{9^5\pi^3(9\pi^2)^{\frac{1}{3}}}{8v_0^4} \frac{e\mathcal{M}^2\hbar^2}{(Mm\Omega)^2 v_0^4} \left(\frac{\hbar}{k\Theta}\right)^3 \left(\frac{T}{\Theta}\right)^7 \int_0^{\Theta/T} \frac{z^6 e^z dz}{(e^z-1)^2} \quad \ldots(4.41)$$

following the usual notation of the Debye theory (cf. Ziman 1960).

Similarly,

$$\Gamma_2 = \frac{9^6\pi^3(9\pi^2)^{\frac{1}{3}}}{32v_0^4} \frac{\mathcal{L}^4\hbar^2}{m^4M^2\Omega^4} \left(\frac{T}{\Theta}\right)^5 \left(\frac{\hbar}{k\Theta}\right)^5 \int_0^{\Theta/T} \frac{z^4 e^z dz}{(e^z-1)^2} \times 2 \quad \ldots(4.42)$$

for $T > \Theta$ the high temperature limits of the integrals may be taken, so that

$$\Gamma = \Gamma_1 + \Gamma_2 = \frac{9^5\pi^3(9\pi^2)^{\frac{1}{3}}}{8v_0^4} \frac{\hbar^2}{(mM\Omega)^2} \left(\frac{\hbar}{k\Theta}\right)^3 \left(\frac{T}{\Theta}\right)^2$$

$$\times \left[\frac{1}{5}e\mathcal{M}^2 + \frac{3\mathcal{L}^4}{2m^2\Omega^2}\left(\frac{\hbar}{k\Theta}\right)^2\right] \quad \ldots(4.43)$$

giving a width proportional to T^2. In actual fact, owing to the smoothness of the Debye integrals this T^2 behaviour becomes apparent for quite low temperatures, the T^5 and T^7 behaviour being confined to the region $T < \Theta_H/5_0$

The diagonal terms of this perturbation give rise to an energy shift, which, for high temperatures is linear in T:

$$\Delta E = \langle 1, n(k)|\mathcal{H}_4|1, n(k)\rangle + \sum \frac{|\langle 1, n(k)|\mathcal{H}_3|i\rangle|^2}{E_1 - E_i}$$

...(4.44)

This is evaluated in an exactly similar way, so that

$$\Delta E = \Delta E_1 + \Delta E_2$$

$$\Delta E_1 = \frac{3^5\pi(3\pi)^{\frac{1}{3}}}{4r_0^2}\,\frac{\mathcal{M}\hbar^2}{mM\Omega}\left(\frac{T}{\Theta_H}\right)^4\left(\frac{\hbar}{k\Theta_H}\right)\int_0^{\Theta_H/T} z^3\left(n(z)+\tfrac{1}{2}\right)dz$$

$$\Delta E_2 = \frac{3^5\pi(3\pi)^{\frac{1}{3}}}{8r_0^2}\,\frac{\mathcal{L}^2\hbar^2}{m^2\Omega^2 M}\left(\frac{\hbar}{k\Theta_H}\right)^2$$

...(4.45)

The linear shift with temperature is, therefore

$$\Delta E = \frac{3^4\pi(3\pi)^{\frac{1}{3}}}{4r_0^2}\,\frac{\mathcal{M}\hbar^2}{mM\Omega}\left(\frac{\hbar}{k\Theta_H}\right)\frac{T}{\Theta_H} \qquad \text{...(4.46)}$$

With the experimental results for CaF_2 M, we obtain

$$\mathcal{L} = 2.20 \times 10^4 \quad \text{ergs/cm}^2$$
$$\mathcal{M} = -3.33 \times 10^4 \quad \text{ergs/cm}^2 \qquad \ldots(4.47)$$

If the residual shift implied by equations (4.45) is now calculated one can recalculate the constants L, M_1 and M_2, assuming that the effect on each level of the local mode oscillator is given by $\left(\frac{2n+1}{3}\right)^2 \Delta\epsilon_1$ etc. These are then

$$L = 7.66 \times 10^{12} \quad \text{ergs/cm}^3$$
$$M_1 = 4.2 \times 10^{19} \quad \text{ergs/cm}^4$$
$$M_2 = 1.7 \times 10^{20} \quad \text{ergs/cm}^4$$
$$\mathcal{R} = 975.6 \text{ cm}^{-1}$$

In comparing these constants $\mathcal{L}$ and $\mathcal{M}$ ought to be multiplied by a mean k or k^2 say of order 10^8 or 10^{16}, when they are seen to be in very reasonable agreement.

A further check consists in calculating the widths of the second harmonic line and of the line in the deuterium substituted crystals. These results are:-

Line	CaF_2:H 2nd Harmonic	CaF_2:D 2nd Harmonic
Experimental width	21.2 cm^{-1}	11.6 cm^{-1}
Calculated width	25.0 cm^{-1}	8.0 cm^{-1}

In view of the approximations made, the agreement is reasonably satisfactory. Also in the case of the deuterium defect, there are other processes which contribute to the width, as will be explained in the next section.

6. Other Anharmonic Processes.

(i) An interaction of the type $b_z^+ b_y a(k)$ enables a transition from the state $|110\rangle$ to the non-visible state $|00k\rangle$ to be made by creating a phonon. This again leads to a

finite lifetime and a broadning of the second harmonic proportional to the number of phonons having an energy equal to the energy difference between these two states. This limits this contribution to the line width to a negligible quantity. However, the quartic term $C M b_z^+ b_y a^+(k) a(k')$ can scatter phonons and conserve energy at the same time. For a small energy difference between the two states the resulting contribution is of the same order as the scattering involving no change in the state of the localised mode.

(ii) Probability for three phonon decay.

For the case of the hydrogen substituted crystals the 2 phonon decay is forbidden by energy conservation. Three phonon decay is possible however, and takes place via the quartic anharmonic matrix element:

$$\langle 0, n(k)+1, n(k')+1, n(k'')+1 | H_4' | 1, n(k), n(k') n(k'') \rangle$$

with

$$H_4' = \sum_{kk'k''} C M' b\, a^+(k) a^+(k') a^+(k'') \left\{ \frac{\hbar^2}{4M^{3/2}(m\Omega)^{1/2}} \right\} \times \frac{k\, k'\, k''}{\sqrt{\omega(k)\,\omega(k')\,\omega(k'')}} \qquad \ldots(4.48)$$

The contribution to the broadening is made up of two parts: the probability for the decay is equal to the difference between the probability for the localised mode to decay into three phonons and the probability for the reverse process. Thus, the probability for decay is

$$\frac{1}{\tau} = \frac{2\pi}{\hbar}\left(\frac{V}{(2\pi)^3}\right)^3 \int\int\int \frac{\hbar^4}{16M^3 m\Omega}\Big[(n(k)+1)(n(k')+1)(n(k'')+1) - n(k)n(k')n(k'')\Big] C M'^2 \frac{(kk'k'')^2}{\omega(k)\omega(k')\omega(k'')} \delta\big(\hbar(\Omega-(\omega(k)+\omega(k')+\omega(k'')))\big)\, dk\, dk'\, dk'' \quad \ldots(4.49)$$

$$= \frac{2\pi}{\hbar^2}\frac{\Omega V^3}{(2\pi)^6}\left\{\frac{\hbar^4 C M'^2}{16M^3 m\Omega}\right\}\frac{1}{5^{1/2}}\int\int\int \omega^3 d\omega\, \omega'^3 d\omega'\, \omega''^3 d\omega''\, \delta(\Omega-\omega-\omega'-\omega'') \quad \ldots(4.50)$$

on taking the low temperature limit when $n(\omega) \simeq 0$. The integral is really a surface integral, the surface being the triangle formed by the intersection of the plane $\Omega = \omega+\omega'+\omega''$ with the cube $0 \le \omega, \omega', \omega'' \le \omega_m$. The maximum value of this integral is obtained by multiplying the maximum value of the integrand on the triangle by the area of the triangle. The transition probability comes out to be

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2}\frac{\Omega V^2}{(2\pi)^6}\left\{\frac{\hbar^4 C M'^2}{16M^3 m\Omega}\right\}\frac{1}{5^{1/2}}\frac{\sqrt{3}}{2}(3\omega_m-\Omega)^2\left(\frac{\Omega}{\omega_m}\right)^9$$

$$= \frac{2(3\pi)^5}{r_0^6}\left\{\frac{C M'^2 \hbar^2}{16M^3 m\Omega}\right\}\left(\frac{\hbar\omega}{k\Theta}\right)^4 \frac{1}{2.39}\left(3-\frac{\Omega}{\omega_m}\right)^2\left(\frac{\Omega}{\omega_m}\right)^9 \quad \ldots(4.51)$$

Estimating the magnitude of from the previous calculations gives a zero temperature half width of 0.15 cm^{-1}. The variation of this width with temperature is roughly $\{3n^2(\omega)+3n(\omega)+1\}$ where is some suitably averaged frequency, approximately equal to a third of that of the localised mode. When $kT>\hbar\omega$ the temperature variation is again like T^2 and drops exponentially to one at low temperatures.

This calculation, although at somewhat greater length, has also been performed by Hanamura and Imui (1963) who used this process as an explanation of the half width of the U-centre in the alkali halides. Certainly in the case of the defects here considered, when, even at room temperature $n(\omega)\sim 0.2$ and the temperature variation is probably less than linear, it seems unlikely that this process is a major contribution. Furthermore, the phonon scattering mechanism described in Section 5 appears to be always greater than the three phonon decay: even if the latter were not limited by the density of three phonon states it is only proportional to the amplitude of the defect motion, and not its square as is the case with the former; the amplitude of the defect motion is of course greater than that of the lattice.

However, it should be pointed out that the Debye lattice is hardly appropriate in this calculation as it is mainly the optical modes which take part, so that the calculated value of the zero temperature half width is likely to be rather more approximate than the other calculations.

The case of the deuterium substituted crystals, is however, somewhat different, for the increased mass of the defect lowers the frequency of the localised mode until it lies within the two phonon spectrum. A decay via cubic anharmonic term is now possible, the one concerned being:

$$\mathcal{H}_3' = \sum \mathcal{L}' \delta a^+(k) a^+(k') \left\{ \frac{\hbar^{\frac{3}{2}}}{\sqrt{m \Omega M \sqrt{8}}} \right\} \frac{kk'}{\sqrt{\omega(k)\omega(k')}}$$

leading to a transition probability

$$\frac{1}{\tau} = \frac{2\pi}{\hbar} \left(\frac{V}{(2\pi)^3}\right)^2 \iint \frac{\hbar^3 k^2 k'^2}{8m\Omega M \omega(k)\omega(k')} \mathcal{L}'^2 \left[(n(k)+1)(n(k')+1) - n(k)n(k') \right] \delta\left(\hbar(\Omega - (\omega(k)+\omega(k')))\right) dk\, dk'$$

$$= \frac{\mathcal{L}'^2 \hbar}{8M^2 m \Omega} \frac{(3\pi^2)^{\frac{4}{3}}}{V_0^4} \frac{9\pi}{2} \left(\frac{\hbar}{k\Theta}\right)^3 \frac{1}{128} F\left(\frac{\Omega}{\omega_m}\right)$$

...(4.5)

where

$$F(x) = \left[x^6 - x^4 + \tfrac{3}{5} x^2 - \tfrac{1}{7} \right]$$

An order of magnitude calculation shows that this half width is of order 1 cm^{-1}.

It is to be noted however, that this has a linear variation with temperature. At present results are not available to say whether this is observed or not.

7. Combination bands.

In the case of the perfect lattice, the existence of anharmonic terms gives rise to the possibility of observing summation and difference bands in the infra-red absorption. With the addition of a defect, combination bands in which one of the phonons involved is a localised mode, occur which are different from the unperturbed lattice. Such absorption arises both from anharmonic terms in the potential as well as second order terms in the electric moment. Both these effects will be discussed here, using the theory of Burstein and Lax (1955).

The intensity of absorption of light of frequency in the crystal is proportional to Lax (1952)

$$I(\omega) = A \sum_m \{ \sum_n k_n |M(\omega)|_{nm}|^2 \delta(E_m - E_n - h\nu) \} \quad \ldots(4.53)$$

a thermal average over the initial vibrational states of the crystal, of the matrix element squared of the electronic dipole moment, multiplied by an energy conserving δ-function and summed over the final vibrational states. In the Born-Oppenheimer approximation $\underline{M}$ may be written in terms of the nuclear displacements and the electronic wave functions $\varphi(r_j)$ as follows:

$$M(u,\nu) = \sum_{\alpha,l} \exp\{i\nu.r_\alpha(l)\}\left[Z_\alpha u_\alpha(l) + \int \varphi^*(r_j,u)\, e r_j\, \varphi(r_j,u)\, dr_j\right] \qquad \ldots(4.54)$$

As the wave vector of light is very small compared with the reciprocal lattice vectors, it is possible to put $\nu \simeq 0$ and then, expanding the integral in a power series of the displacements up to terms of second order, the dipolemoment operator becomes

$$\underline{M}(u) = \sum B_\alpha u_\alpha(l) + \sum \underline{\underline{e}}_{\alpha\beta}(l-l')\, u_\alpha(l)\, u_\beta(l') \qquad \ldots(4.55)$$

On transforming to normal co-ordinate operators,

$$\underline{M} = \sum B_j\, d_j(k=0) + \sum e_{j,j'}(k)\, d_j(k)\, d_{j'}(k) \qquad \ldots(4.56)$$

B_j represents the dipole moment induced in one cell by the j'th mode at $\underline{k} = 0$ and consequently is non zero only for transverse modes which polarise the lattice. In terms of

the quantities defined in Chapter II

$$B_j d_j = \sum_{\alpha\rho} (Z_\alpha \delta_{\rho\beta} + Y_\alpha (D^{-1}C)_{\alpha\rho}) U^j_\rho(0) \qquad \ldots(4.57)$$

and the quantities D and C are calculated without the macroscopic field contribution.

For the harmonic lattice the linear term gives rise to a series of δ-function absorption lines. This is also the case for the lattice with defects; here, the only effect is to introduce an absorption of $O(\frac{1}{N})$ compared to the main reststrahlen band at the localised mode frequency. The frequency of the mode which, in the limit when the perturbation due to the defect tends to zero, becomes the T.O. mode is only changed to $O(\frac{1}{N})$, and similarly the amplitude of this mode is only altered in a small region of the crystal, of $O(\frac{1}{N})$ of the whole crystal, all of which contributes to the reststrahlen absorption, and so the reststrahlen absorption is not greatly different from that of the perfect crystal.

The introduction of anharmonicity leads to a finite lifetime for the normal modes and a consequent broadening of the previous δ-function optical absorption. The linear term in (4.55) is also now able to induce transitions between

vibrational states other than those previously considered: the matrix element for the second harmonic absorption process considered in Section 6 is thus:

$$\langle 0,n|\mathcal{B}\sqrt{\frac{E}{2\omega}}(a(0)+a^{+}(0))|2,n\rangle \qquad \ldots(4.58)$$

where the n refers to the population of reststrahl phonons and the 0 and 2 to the localised mode. In first order perturbation theory these wave functions are

$$|0,n\rangle' = |0\,n\rangle + |2,n+1\rangle\frac{\langle 2,n+1|\mathcal{H}_3|0,n\rangle}{-(2\hbar\Omega+\hbar\omega)}$$

$$+|2,n-1\rangle\frac{\langle 2,n-1|\mathcal{H}_3|0,n\rangle}{-(2\hbar\Omega-\hbar\omega)}$$

$$|2,n\rangle' = |2,n\rangle + |0,n+1\rangle\frac{\langle 0,n+1|\mathcal{H}_3|2,n\rangle}{2\hbar\Omega-\hbar\omega}$$

$$+|0,n-1\rangle\frac{\langle 0,n-1|\mathcal{H}_3|2,n\rangle}{2\hbar\Omega+\hbar\omega} \qquad \ldots(4.59)$$

As the interaction is with an optic mode the form of $\mathcal{H}_3$ differs somewhat from the forms previously used:

$$\mathcal{H}_2'' = \mathcal{L}'' b^+ b^+ (a(0) + a^+(0)) \frac{\hbar}{2m\Omega} \sqrt{\frac{\hbar}{2M\omega}} \qquad \ldots(4.60)$$

Using this, the matrix element becomes

$$\langle 0, n | \mathcal{B} \sqrt{\frac{\hbar}{2\omega}} (a(0) + a^+(0)) | 2, n \rangle = \mathcal{B} \mathcal{L}'' \sqrt{2} \frac{\hbar}{2m\Omega} \frac{\hbar}{2\sqrt{M\omega}} \frac{2\omega}{\hbar(4\Omega^2 - \omega^2)}$$

$$= \frac{\sqrt{2}\,\mathcal{B}\mathcal{L}''\hbar}{2m\sqrt{M}\,\Omega(4\Omega^2 - \omega^2)} \qquad \ldots(4.61)$$

which is independent of n as expected. The matrix element for the fundamental absorption to the localised mode is

$$\langle 0 | \mathcal{B}' \sqrt{\frac{\hbar}{2\Omega}} (b + b^+) | 1 \rangle = \mathcal{B}' \sqrt{\frac{\hbar}{2\Omega}}$$

where, apart from factors of N $\mathcal{B}/\mathcal{B}' \sim 1$. The ratio of the fundamental absorption to the second harmonic absorption via the process is therefore:

$$\frac{\dfrac{2\mathcal{B}^2\mathcal{L}''^2\hbar^2}{4m^2M\Omega^2(4\Omega^2 - \omega^2)^2}}{\dfrac{\mathcal{B}'^2\hbar}{2\Omega}} \sim \frac{\mathcal{L}''^2\hbar}{m^2M\Omega(4\Omega^2 - \omega^2)^2}$$

Putting $\mathcal{L}^{12}\hbar^3/\rho(M\omega)^3 \sim \frac{(\hbar\omega)^2}{100}$ reduces this fraction to the form

$$\left(\frac{M}{m}\right)^2 \frac{\rho\omega^5 10^{-2}}{\Omega(4\Omega^2-\omega^2)^2} \sim \frac{1}{50}$$

on putting M = 30 m and Ω = 3ω, which is in reasonable agreement with the observed intensity ratio.

In the perfect lattice without a defect, the second order electric moment does not contribute a summation band in which both phonons come from the same branch. This follows from the inversion symmetry, which requires:

$$C_{\alpha\beta}(k) = \sum_{l}{}' C_{\alpha\beta}(l) e^{2\pi i \underline{k}.\underline{r}_{\alpha\beta}(l)}$$

$$= - C_{\alpha\beta}(-k) = C_{\beta\alpha}(-k) \qquad \ldots(4.62)$$

as the $C_{\alpha\beta}(l)$ are symmetrical in the lattice indices. Thus

$$\sigma_{00}(k) = -\sigma_{00}(-k) = \sigma_{00}(-k) = 0.$$
$$\sigma_{1\bar{1}}(k) = -\sigma_{\bar{1}1}(-k) = \sigma_{\bar{1}1}(-k) = 0.$$

and

$$C_{jj'} = \sum_{\alpha\beta} C_{\alpha\beta}\sigma_{\alpha}^{j}(k)\sigma_{\beta}^{j'}(k) = C_{11}\left(\sigma_{1}^{j}(k)\sigma_{1}^{j'}(k) - \sigma_{\bar{1}}^{j}(k)\sigma_{\bar{1}}^{j''}(k)\right)$$

which vanishes when $j = j'$.

However, the introduction of the defect destroys the inversion symmetry and it is possible for L local modes to be made via this second order term. It might be expected however, that this term would be small as the process is forbidden in the perfect lattice case.

The second order moment does contribute more strongly however to the combination bands arising from a local mode and another mode. In this case

$$C(fe,f) = \sum b_{\alpha\beta}(l-l_2)\chi_\alpha(l,fe)\chi_\beta(l_2 f) \qquad \ldots(4.63)$$

This is written, in the abbreviated notation of Chapter II.

$$C(fe\,f) = \sum X^+(fe,0)C^+ g^+ b\, g\, C X(f,0)$$

$$= \sum_{\alpha\beta} X^+_\alpha(fe,0)\,\mathbb{C}_{\alpha\beta}\,X_\beta(f,0) \qquad \ldots(4.64)$$

where now α and β label the perturbed lattice sites. The summation bands have been observed for the U-centre in the alkali-halides by Fritz (1963) so we shall confine our attention to this case. Labelling the nearest neighbours of the defect, 1, 2, 3 and I, II, 3 for

nearest neighbours along the x, y, and z directions respectively with 0 for the defect, we have the following independent components for $\mathbb{C}_{01}$:

$$\mathbb{C}^{x}_{01xx}\ ;\ \mathbb{C}^{x}_{01yz} = -\mathbb{C}^{x}_{01zy}\ ;\ \mathbb{C}^{y}_{01xx} = \mathbb{C}^{z}_{01xx}\ ;\ \mathbb{C}^{y}_{01yy} = -\mathbb{C}^{z}_{01zz}$$

The general symmetry relation $\mathbb{C}_{\alpha\alpha} = -\mathbb{C}_{\alpha z}$ ensures that only the positive parity modes contribute to this sum: there are four of these, so that equation (4.64) now becomes

$$\sum \mathbb{C}(f_e f) \, d(f_e) \, d(f) = \sum_{f} |X(f_e)| \, d(f_e) \left\{ a|X(\Gamma_1, f)| \, d(f) + b|X(\Gamma_{12} f)| \, d(f) \right.$$

$$\left. + c|X(\Gamma_{15}^{+} f)| \, d(f) + d|X(\Gamma_{25}, f)| \, d(f) \right\} \qquad \ldots(4.65)$$

This operator has matrix elements to the 1 phonon states as follows:

$$\langle 0 | M | 1 \text{ localmode}, 1 \text{ bandmode} \rangle$$

$$= |X(f_e)| \sqrt{\frac{\hbar}{2\Omega}} a|X(\Gamma_1, f)| \sqrt{\frac{\hbar}{2\omega(f)}} (n(f) + 1) \qquad \ldots(4.66)$$

for absorption to the combination band of localised modes plus Γ_1^+-type band modes. The strength of the absorption is just this matrix element squared multiplied by the density of states at that frequency.

The linear term in the electric moment, in combination with the anharmonicity also gives rise to absorption in this band. The interaction Hamiltonian involved is proportional to $b^+ b\, a(k)$ and so derives mainly from the anharmonic force constants like $L^{zzi}_{00\alpha}(00l)$; that is, it must have 2 indices on the defect and one on the nearest neighbours, assuming nearest neighbour forces only are important. There are 6 bonds like these described by

$$n = \frac{1}{48}\{6x27 + 6x2x1 + 3x1x(-1) + 3x4x1 + 6x2x1\}$$

$$= 4 \text{ independent constants.}$$

This is exactly the same as for the similar tensor describing the second order moment, as both tensors transform like triads of polar vectors, the only difference being that the anharmonic force constant is symmetrical under all its indices, whereas the second order moment is symmetrical in two only.

Applying the group operations in succession shows that only components like xxx, xyz, xxy and xyy are non zero for x oriented bonds and consequently there are 2 constants which describe the 18 components $L^{zzi}_{00\alpha}(00l)$.

These two constants couple the Γ_1 and the Γ_{12} modes to the two local mode operators and in exactly the same way, so that the interaction is written

$$H_3''' = \int_f h''' \frac{t}{2m\Omega} (b+b^+)^2 \sqrt{\frac{t}{2w(f)}} (a(f)+a^+(f)) \times \{|X(\Gamma_1, f)| + |X(\Gamma_{12}, f)|\} \quad \ldots(4.67)$$

and accordingly the absorption to the summation band differs from the absorption to the fundamental by a factor

$$\frac{3 h'''^2 t}{\rho m^3 \Omega^2} \frac{n(w)+1}{\omega^3} \{|X(\Gamma_1, f)|^2 + |X(\Gamma_{12}, f)|^2\} \nu(\omega) \quad \ldots(4.68)$$

where $\nu(\omega)$ is the density of states at that frequency. Putting $h''' \sim \frac{m\Omega^2}{a}$ makes the first factor in (4.68) of order

$$\frac{m^2 \Omega^4 t}{a^2 2m^2 \Omega^2 \omega^3 M} = \frac{t}{2M\omega a^2} \frac{\Omega^2}{\omega^2} \sim 10^{-1} - 10^{-2}$$

which is of the correct order of magnitude.

Both the processes represented by (4.68) and (4.66) have summation and difference bands with temperature dependences $n(\omega)+1$ and $n(\omega)$ respectively. In actual fact,

as Frits points out the bands he observes flanking the main defect absorption do not have this variation of intensity with temperature, but the ratio is fairly accurately proportional to exp $\frac{\pm\hbar\omega}{kT}$. It appears that there are other contributing processes which cancel out of the ratio.

In both cases, too, the absorption is peaked at the density of states and at the peaks in the $|\chi|$ functions, that is the resonant modes. The absorption extends only over a range of frequencies corresponding roughly to the acoustic modes of the alkali halide lattices, indicating that perhaps the anharmonic process is the greater contributor because the high frequency modes are cut off by the $\frac{1}{\omega^3}$ factor in (4.68). Otherwise it would be necessary to assume that the absorption was cut off by the $|\chi|$ functions, which would imply a large change in the force constants.

APPENDIX I.

The Notation Used on the Text.

1. The description of the crystal lattice.

N = number of unit cells in the crystal.

S = number of particles in a unit cell.

α, β etc. labels the basis.

i, j etc. labels the cartesian co-ordinates.

l_1, l_2 etc. labels the cell position.

2. The notation of Chapter II.

Whenever possible, a vector associated with each atom in the unit cell is represented by one 3s dimensional vector for the whole cell.

u represents the displacements of the atoms, which individually are $u_\alpha^i(\ell)$ etc.

U(k) represents the amplitude of the normal co-ordinates.

w represents the fictitious 'shell' displacement.

W(k) represents its amplitude.

P(k) represents the amplitude of the total dipole moment associated with the cell, so that

$$P_\alpha^i(k) = Y_\alpha^i(k) + Z_\alpha U_\alpha^i(k)$$

E represents the amplitude of the macroscopic electric field.

M is a diagonal matrix such that $M_{\alpha\alpha}$ is the mass of the αth particle.

Z is a similar matrix for the ionic charge.

Y is a similar matrix for the shell charge.

$K^{(1)}$, $K^{(2)}$, etc. are force constant matrices.

A B C D are the Fourier transforms of these.

3. The Notation of Chapter III.

The matrices here have dimensionality equal to the number of particles perturbed multiplied by the number of directions with respect to the crystal axes in which they are perturbed. Thus for example, for an alkali-halide crystal containing a substitutional defect changing central forces only the dimensionality is 6 (nearest neighbours) x 1 (direction) + 1(defect) x 3(directions) = 9.

Δ is a matrix representing the change in masses and force constants.

g is the Green function matrix.

χ represents the amplitude of the normal co-ordinate near the defect.

4. The notation of Chapter IV.

$L_{\alpha\beta\gamma}(l_1\ l_2\ l_3)$ are cubic anharmonic force constants.

$M_{\alpha\beta\gamma\delta}(l_1\ l_2\ l_3\ l_4)$ are quartic anharmonic force constants.

APPENDIX II.

The evaluation of certain lattice sums.

Sums of the form

$$S_1 = \sum_{j,k} \frac{f_j(k)}{N(\omega_j^2(k) - \omega^2)} \qquad \ldots(A.1)$$

will first be considered. The procedure followed is to convert the sum over j and $\underline{k}$ in A.1 into a sum over $\omega_j^2(k)$; that is, find a function $f(\omega_j^2(k))$ such that

$$S_1 = \sum \frac{f(\omega_j^2(k))}{N(\omega_j^2(k) - \omega^2)} \qquad \ldots(A.1)$$

The sum is then transformed into an integral which is calculated numerically. The actual calculation is, of course, performed in a computer, so part of the procedure is aimed at making the calculation easy to programme.

The eigenvalues and eigenvectors for crystals of cubic symmetry are computed for the section of the Brillouin Zone

$$0 \leq k_x \leq k_y \leq k_z \leq \pi/a$$

that is $\frac{1}{48}$ of the whole. The eigenvectors from outside this segment are generated using equation (2.18)

$$S\sigma_\alpha^j(k) = e^{ik.v(S)} \sigma_{\alpha'}^j(Sk) \qquad \ldots(2.18)$$

which equally enables values of $f_j(k)$ to be calculated. The eigenvalues corresponding to the star of $\underline{k}$ generated by (2.18) are all degenerate; therefore, defining the function

$$f_J(\omega_j^2(k)) = \frac{1}{h} \sum_{k^*} f_J(k) \qquad \ldots(A.3)$$

where h is the number of vectors in the star, the sum becomes

$$S_1 = \sum_{J,k} \frac{f_J(\omega_j^2(k))}{N(\omega_j^2(k)-\omega^2)} \qquad \ldots(A.4)$$

For ease of computation the function $f_J(\omega_j^2(k))$ is preferably defined from

$$f_J(\omega_j^2(k)) = \frac{1}{g} \sum_{G} \$ f_J(k) \qquad \ldots(A.5)$$

where the action of an operator $\$$, in the unit cell group G, (g elements), acting according to (2.13) in $f_j(k)$ is written symbolically

$$\$ f_j(k) = f_j'(\$k)$$

The summation over j is now eliminated by replacing $f_j(\omega_j^2(k))$ by $f(\omega_j^2(k))$ an average of fj weighted according to the density of states in each branch:

$$f(\omega_j^2(k)) = \frac{1}{\nu(\omega)} \sum_j \nu_j(\omega^2) f_j(\omega_j^2(k)) \qquad \ldots(A.6)$$

To perform this calculation it is not necessary to know the ν_j explicitly. In the computer $f(\omega^2)$ is calculated as a histogram; the height of any ordinate is then the average of the values of $f_j(\omega^2)$ falling within a histogram cell. In terms of the notation of the text, S_1 is now given by

$$S_1 = \sum_{jk} \frac{f(\omega_j^2(k))}{N(\omega_j^2(k) - \omega^4)} = \sum \frac{f(\mu)}{N(\mu - z)} \qquad \ldots(A.7)$$

This sum is now in the form already considered by Dawber & Elliott (1963) who evaluate this sum in the following way:-

Define a variable ϕ to take 3SN integral values for each of the 3SN values of $\omega_j^2(k)$, so that

$$S_1 = \sum_{\phi} \frac{f(\phi)}{N(\mu(\phi) - z)} \qquad \ldots(A.8)$$

and $$\frac{d\rho}{d\mu} = 3sN\nu(\mu) \qquad \text{...(A. 9)}$$

in terms of the density of states, $\nu(\mu)$ per unit squared frequency range, normalised to 1:

$$\int_0^\infty \nu(\mu)\, d\mu = 1 \qquad \text{...(A.10)}$$

The sum is now replaced by a contour integral in the usual way

$$S_1 = \frac{1}{2\pi i N}\left[\int_C \frac{\pi \cot(\pi\rho) f(\rho)}{\mu(\rho) - z}\, d\rho - 2\pi^2 i \cot(\pi\rho(z)) f(\rho(z)) \left.\frac{d\rho}{d\mu}\right)_{\mu=z}\right]$$

...(A.11)

and the contour C enclosed the 3sN poles along the real axis of the complex ρ plane. The second term in (A.11) cancels out the residue caused by the vanishing of the denominator in the integrand and the value of $\rho(z)$ is defined by

$$\mu(\rho) = z \qquad \text{...(A.12)}$$

It can then be shown that the contour integral reduces to a principal valued integral, and

$$S_1 = -3s\pi\, \nu(z) f(z) \cot(\pi\rho(z)) + \mathcal{P}\int \frac{3sf(\mu)\nu(\mu)}{\mu - z}\, d\mu \qquad \text{...(A.13)}$$

which is equation (3.12).

The other sum of interest,

$$S_2 = \sum \frac{f_j(k)}{N(\omega_j^2(k) - \omega^2)^2} \qquad \ldots(A.14)$$

may be found by differentiating with respect to z in equation (A.13) to give

$$S_2 = -3s\pi \frac{\partial}{\partial z}(v(z) f(z) \cot(\pi p(z)) + \mathcal{P}\int \frac{3s f(\mu) v(\mu)}{(\mu - z)^2} d\mu$$

$$+ 3s\pi f(z) v(z) (1 + \cot^2(\pi p(z))) 3s N \pi v(z)$$

The first 2 terms are of order 1 and therefore negligible compared to the last, which may be evaluated from the eigenvalue condition

$$\alpha S_1 = 1 \qquad \ldots(A.15)$$

$$S_2 = N[9s^2\pi^2 v^2(z) f(z)(1 + \cot^2(\pi p(z)))]$$

$$= N\left[9s^2\pi^2 v^2(z) f^2(z) + \left(\frac{1}{\alpha} + \mathcal{P}\int \frac{3s f v}{\mu - z} d\mu\right)^2\right] \frac{1}{f(z)}$$

$$\ldots(A.16)$$

which is equation (3.17)

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