I. THERMAL SCATTERING OF X-RAYS BY A CLOSE-PACKED HEXAGONAL LATTICE.

II. ON THE FINE STRUCTURE IN THE INFRA-RED SPECTRUM OF IONIC CRYSTALS.

Thesis

Submitted by

NOEL KYNASTON POPE
B.Sc., M.Sc.,

University of NEW ZEALAND.

For the Degree of

Doctor of Philosophy

University of Edinburgh

November 1948.

TABLE OF CONTENTS.

PART ONE

PART TWO

LIST OF FIGURES.

I. THERMAL SCATTERING OF X-RAYS BY A CLOSE-PACKED HEXAGONAL LATTICE.

1. INTRODUCTION

The first theoretical investigation of the influence of the thermal motion on the scattering of X-rays in crystals was given by Debye (1913). The main result of his calculation was the prediction of a decrease in the intensity, but no influence on the sharpness of the Laue spots, or Bragg reflections and a general diffuse background. In actual fact, the general background of Laue photographs is not structureless, but consists of more or less well-defined spots and streamers. These extra spots differ from the Laue spots in that they do not depend on definite positions of the crystal relative to a monochromatic incident beam, but exist for a continuous range of angles, though with decreasing intensity for increasing distance from the Laue spots. A characteristic feature of the spots is the decrease of intensity as the temperature is lowered. A full account of the experimental material has appeared in "Reports on Progress in Physics," (Lonsdale 1942-43).

Since Debye's first theoretical investigation, many researches have been made into the problem, of which the most important is due to Waller (Uppsala

1925). A condensed presentation of this theory appeared in "Reports on Progress in Physics," (Born, 1942-43), which contains a bibliography of the subject and an account of its development. The main point of this report is that the scattering by a molecule or a crystal, instead of being expressed in terms of the frequencies of its normal modes of vibration, is given in terms of the "dynamical matrix" of the system. The latter is the matrix of the coefficients of the quadratic terms in the expansion of the potential energy in powers of small displacements of the particles from their equilibrium positions. In particular, for crystals where the normal modes of vibration have the form of waves, the result is a function of the transformed dynamical matrix (in wave vector space.)

In the case in which the wave vector tends to zero, i.e. elastic waves, the transformed dynamical matrix can be expressed in terms of the elastic constants (Waller, 1925, Born and Sarginson, 1941, Jahn, 1942). This allows one to write the scattering in the region of the reciprocal lattice points, (Laue spots), as a function of the elastic constants - the so-called Jahn approximation.

To investigate the intermediate region of reciprocal space, one has to know the value of the transformed dynamical matrix for all wave vectors, or use a model, for which it may be calculated. Begbie and Born (1947), have proposed a model in which only neighbouring particles act on one another, while the law of force is quite arbitrary, except in so far as it has to satisfy the symmetry of the lattice. In this case, the elements of the dynamical matrix can be expressed in terms of a small number of constants, (the atomic constants). The application to a face-centred cubic lattice has been carried out by Begbie (1947). In this case, the atomic constants, being equal in number to the elastic constants, can be expressed in terms of the latter. Thus the dynamical matrix, its transform in wave vector space and the scattering for all reciprocal space are functions of the elastic constants. The final result shows that a considerable intensity of scattering, with a quite definite structure can be expected in the region between the Laue spots.

This method fails when it is applied to the close-packed hexagonal lattice, because in this case, the number of independent atomic constants (seven) is greater than the elastic constants (five). In these circumstances, Begbie limited his calculation to the regions in the neighbourhood of the reciprocal lattice points. Results were given for beryl. The purpose of the present investigation is to extend the work of Begbie into the regions of reciprocal space between the lattice points, by the assumption of central forces. The effect of this assumption is to reduce both the number of independent atomic and elastic constants to one. The elastic constants for a close-packed hexagonal lattice under the assumption of central forces have been calculated by Born (1942). Beryl is the only hexagonal crystal for which the complete set of elastic constants is known, and in this case, the ratio between the constants agrees quite well with that calculated by Born. This suggests that the assumption of central forces is quite a reasonable approximation.

2. LATTICE DYNAMICS.

This section summarizes briefly the results already obtained by Born (1942-43), and Born and Begbie, (1947). The lattice cell is described by three elementary vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$. Then the position vector of the particle at the vertex of any cell is

$$\underline{r}^l = l_1 \underline{a}_1 + l_2 \underline{a}_2 + l_3 \underline{a}_3 \tag{2.1}$$

where l_1 , l_2 , l_3 , are integers. If there are S particles in the unit cell with masses m_k, $(k = 1, 2 \cdots s)$ and $\underline{r}_k$ is the position vector of the k^{th} particle from the cell vertex, then

$$\underline{r}\binom{l}{k} = \underline{r}^l + \underline{r}_k \tag{2.2}$$

defines the position of the particle $\binom{l}{k}$ in equilibrium. The rectangular components of $\underline{r}\binom{l}{k}$ are $x_\alpha\binom{l}{k}$ $(\alpha = 1, 2, 3)$.

Now consider small arbitrary displacements $\underline{u}\binom{l}{k}$ of the particles from equilibrium. The potential energy Φ of the deformed lattice can be expanded in powers of the rectangular components $u_\alpha\binom{l}{k}$ $(\alpha = 1, 2, 3)$ of $\underline{u}\binom{l}{k}$. The whole domain of the values of α, l, k is $3SN$, where N is the number of cells and S the number of particles in each cell. The linear terms of Φ vanish in equilibrium and the second order terms are

$$\Phi_2 = \frac{1}{2} \sum_{lk} \sum_{l'k'} \sum_{\alpha\beta} \Phi_{\alpha\beta}\binom{l\,l'}{k\,k'} u_\alpha\binom{l}{k} u_\beta\binom{l'}{k'} \qquad (\alpha, \beta = 1, 2, 3) \tag{2.3}$$

where

$$(2.4)\quad \Phi_{\alpha\beta}\binom{l\,l'}{k\,k'} = \left[\frac{\partial^2 \Phi}{\partial x_\alpha\binom{l}{k}\,\partial x_\beta\binom{l'}{k'}}\right]_0 \qquad \binom{l}{k} \neq \binom{l'}{k'}$$

For the case $\binom{l}{k} = \binom{l'}{k'}$ see (2.7).

These second derivatives in equilibrium depend only on the difference of cell indices $(l-l')$, and satisfy the condition.

$$(2.5)\quad \Phi_{\alpha\beta}\binom{l}{k\,k'} = \Phi_{\beta\alpha}\binom{-l}{k'\,k}$$

The equation of motion of a particle of type k, mass m_k is then

$$(2.6)\quad m_k\,\ddot{u}_\alpha\binom{l}{k} + \sum_{l'k'}\sum_{\beta} \Phi_{\alpha\beta}\binom{l-l'}{k\,k'}\,u_\beta\binom{l'}{k'} = 0 .$$

From this one sees that the quantities $\Phi_{\alpha\beta}\binom{l}{k\,k'}$ represent the quasi-elastic forces between any point $\binom{l}{k}$ and a point of the base $\binom{0}{k'}$. In particular, the so-called "force of a point $\binom{l}{k}$ on itself" $\Phi\binom{0}{k\,k}$, can be determined from all the other forces, for if the whole lattice is subjected to a translation $u_\alpha\binom{l}{k} = \text{const.},\ \ddot{u}_\alpha\binom{l}{k} = 0$ then from (2.6) one obtains

$$(2.7)\quad \sum_{l'k'} \Phi_{\alpha\beta}\binom{l'}{k\,k'} = 0 \quad \text{or} \quad \Phi_{\alpha\beta}\binom{0}{k\,k} = -\sum_{l'k'}{}' \,\Phi_{\alpha\beta}\binom{l'}{k\,k'},$$

where a dash on the summation sign denotes that the term in which $l'=0$, $k=k'$ is to be omitted from the summation. One can remove the mass factor in

(2.6) by introducing the reduced displacement vector

(2.8) $$\underline{V}\binom{l}{k} = \sqrt{m_k}\,\underline{u}\binom{l}{k}$$

and the coefficients

(2.9) $$D_{\alpha\beta}\binom{l}{kk'} = \frac{1}{\sqrt{m_k m_{k'}}}\,\Phi_{\alpha\beta}\binom{l}{kk'}$$

which satisfy

(2.5a) $$D_{\alpha\beta}\binom{l}{kk'} = D_{\beta\alpha}\binom{-l}{kk'}$$

Then the equations of motion become

(2.6a) $$\ddot{V}_\alpha\binom{l}{k} = -\sum_{\beta l' k'} D_{\alpha\beta}\binom{l-l'}{kk'}\,V_\beta\binom{l'}{k'} .$$

$D_{\alpha\beta}\binom{l-l'}{kk'}$ considered as a function of the two triads (α, l, k) and (β, l', k') is an element of the dynamical matrix. It is now easy enough to show that the equations of motion can be satisfied by plane waves. An alternative procedure is the following. The kinetic energy of the particles, T, is

(2.10) $$T = \frac{1}{2}\sum_{lk\alpha} m_k\,\dot{u}_\alpha\binom{l}{k}^2 = \frac{1}{2}\sum_{lk\alpha}\dot{V}_\alpha\binom{l}{k}^2$$

It is well known that both Φ_2 and T can be transformed into sums of squares, by introducing normal co-ordinates. Only the results will be given. Let $q(J)$ be the complex normal co-ordinates, where the index J assumes the same number of values $3sN$ as the domains of α, l, k together. Then one has

(2.11) $$V_\alpha\binom{l}{k} = \sqrt{m_k}\,u_\alpha\binom{l}{k} = \sum_J e_\alpha\left(\binom{l}{k}\middle| J\right) q(J)$$

$$q(J) = \sum_{\alpha l k} e^{*}_{\alpha}\left(\left.\begin{smallmatrix} l \\ k \end{smallmatrix}\right| J\right) \sqrt{m_k}\, u_{\alpha}\binom{l}{k} = \sum_{\alpha l k} e^{*}_{\alpha}\left(\left.\begin{smallmatrix} l \\ k \end{smallmatrix}\right| J\right) v_{\alpha}\binom{l}{k} \tag{2.12}$$

The coefficients are the solutions of the linear equations for free vibrations of waves. In consequence of the periodicity of the lattice, these can be split into N sets of $3S$ equations,

$$\omega^2\binom{q}{j}\, e_{\alpha}\left(k \left| \begin{smallmatrix} q \\ j \end{smallmatrix}\right.\right) = \sum_{\beta k'} D_{\alpha\beta}\binom{q}{k k'}\, e_{\beta}\left(k' \left| \begin{smallmatrix} q \\ j \end{smallmatrix}\right.\right) \tag{2.13}$$

where $D_{\alpha\beta}\binom{q}{k k'}$, the transformed dynamical matrix in reciprocal space, is given by

$$D_{\alpha\beta}\binom{q}{k k'} = \sum_{l} D_{\alpha\beta}\binom{l}{k k'}\, e^{-i(l,q)} \;, \qquad (l,q) = \underline{r}^{l} . \underline{q} = l_1 q_1 + l_2 q_2 + l_3 q_3 \tag{2.14}$$

Since

$$D_{\alpha\beta}\binom{-q}{k k'} = D^{*}_{\alpha\beta}\binom{q}{k k'} \tag{2.15}$$

it follows that

$$e_{\alpha}\left(k \left| \begin{smallmatrix} -q \\ j \end{smallmatrix}\right.\right) = e^{*}_{\alpha}\left(k \left| \begin{smallmatrix} q \\ j \end{smallmatrix}\right.\right) \tag{2.16}$$

The index J has been split into two indices $\binom{q}{j}$ where $j = 1, 2, \cdots 3S$ represents the different branches of the spectrum, and $\underline{q}\ (q_1, q_2, q_3)$ the different waves of each branch. The choice of possible wave vectors $\underline{q}$ is restricted by the "cyclic lattice" condition (Born, 1923). The basic vectors $\underline{b}_{\alpha}$ of the reciprocal lattice (Ewald, 1923) are given by

$$\underline{a}_\alpha \cdot \underline{b}_\beta = \begin{cases} 1 & \alpha = \beta \\ 0 & \alpha \neq \beta \end{cases}$$

(2.17) $$\underline{b}_1 = \frac{\underline{a}_2 \times \underline{a}_3}{(\underline{a}_1 \cdot \underline{a}_2) \times \underline{a}_3}, \quad \underline{b}_2 = \frac{\underline{a}_3 \times \underline{a}_1}{(\underline{a}_1 \cdot \underline{a}_2) \times \underline{a}_3}, \quad \underline{b}_3 = \frac{\underline{a}_1 \times \underline{a}_2}{(\underline{a}_1 \cdot \underline{a}_2) \times \underline{a}_3}.$$

The vector

(2.18) $$\underline{Q}^h = Q_1^h \underline{b}_1 + Q_2^h \underline{b}_2 + Q_3^h \underline{b}_3$$

where $Q_1^h/2\pi$, $Q_2^h/2\pi$, $Q_3^h/2\pi$ are integers, determines the reciprocal lattice points. Then if $\underline{r}^l = l_1 \underline{a}_1 + l_2 \underline{a}_2 + l_3 \underline{a}_3$ the scalar product

(2.19) $$\underline{Q}^h \cdot \underline{r}^l = Q_1^h l_1 + Q_2^h l_2 + Q_3^h l_3$$

is an integral multiple of 2π. The cyclic lattice condition postulates that the lattice deformations have a period large compared with the dimensions of the cell, so that any function

$$f(\underline{r}^L) = f(\underline{r}^l) \quad \text{if} \quad L^\alpha = l^\alpha + n \qquad (\alpha = 1, 2, 3) \quad ;$$

hence for $e^{i(\underline{Q}^h \cdot \underline{r}^l)}$ to be periodic in this way the permitted values of $\underline{Q}^h$ must be such that

(2.20) $$Q_1^h = \frac{2\pi h_1}{n}, \quad Q_2^h = \frac{2\pi h_2}{n}, \quad Q_3^h = \frac{2\pi h_3}{n}. \qquad (h_1, h_2, h_3 = 0, 1, 2 \cdots n-1)$$

The coefficients in (2.11) and (2.12) are the elements of a unitary matrix and can be written

(2.21) $$e_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix} \middle| J\right) = e_\alpha\left(\begin{smallmatrix} l \\ k \end{smallmatrix} \middle| \begin{smallmatrix} q \\ j \end{smallmatrix}\right) = e_\alpha\left(k \middle| \begin{smallmatrix} q \\ j \end{smallmatrix}\right) e^{i(l, q)}$$

where the $e_\alpha\left(k \middle| \begin{smallmatrix} q \\ j \end{smallmatrix}\right)$ must satisfy the identities

(2.22) $$\sum_{\alpha k} e_\alpha\left(k \middle| \begin{smallmatrix} q \\ j \end{smallmatrix}\right) e_\alpha^*\left(k \middle| \begin{smallmatrix} q \\ j' \end{smallmatrix}\right) = \delta_{jj'}, \quad \sum_j e_\alpha\left(k \middle| \begin{smallmatrix} q \\ j \end{smallmatrix}\right) e_\beta^*\left(k' \middle| \begin{smallmatrix} q \\ j \end{smallmatrix}\right) = \delta_{\alpha\beta} \delta_{kk'}$$

Since the $\underline{u}\binom{l}{k}$ are real, one has

$$q\binom{-Q}{j} = q^{*}\binom{Q}{j} \qquad (2.23)$$

Now each complex $q\binom{Q}{j}$ represents two real normal co-ordinates, but on account of the last relation, the number of these can be reduced to the correct value again by restricting the Q values to the points in half the unit cellof reciprocal space.

The elements of the matrix $D\binom{l-l'}{kk'}$ are related to one another through the symmetry of the lattice, in the following way:

A lattice point is defined by the vector $\underline{r}\binom{l}{k}$, referred to rectangular axes. A symmetry operation of the lattice is represented by a transformation matrix T_{ρ} such that some other lattice point $\binom{L}{K}$ exists for which

$$\underline{r}\binom{L}{K} = T_{\rho}\,\underline{r}\binom{l}{k} \qquad (2.24)$$

The elements of the matrix will then have the transformation law

$$D\binom{L-L'}{KK'} = T_{\rho}\, D\binom{l-l'}{kk'}\, \widetilde{T_{\rho}} \qquad (2.25)$$

where $\widetilde{T_{\rho}}$ is the transpose of T_{ρ} and the change of indices $\binom{l}{k}$, is obtained from (2.24).

3. THE EXPRESSION FOR THE THERMAL SCATTERING OF X-RAYS.

Let it be assumed that a beam of X-rays is passing through a crystal and let $\underline{K}$ be the wave vector of the incident beam and K' be the wave vector of the scattered beam. Then, if the scattering power is defined as the ratio of the scattered intensity in any direction to the incident intensity, and if $\underline{K} - \underline{K}' = \underline{Q}$ it can be shown, (Born, 1942-43), that the scattering produced by the thermal motion is given by

$$\sigma = \sigma_0 N \sum_{k\alpha} \sum_{k'\beta} S_{\alpha\beta}\binom{Q}{kk'} w_\alpha(k)\, w^*_\beta(k') \tag{3.1}$$

where $S_{\alpha\beta}\binom{Q}{kk'}$ are the elements of a matrix, the scattering matrix, which in first approximation is proportional to the reciprocal of the transformed dynamical matrix,

$$S(Q) = kT\ D(Q)^{-1} \tag{3.2}$$

Here k is Boltzmann's constant[x] and T is the absolute temperature.

The other symbols have the following meanings:

$$\underline{w}(k) = \frac{f_k}{\sqrt{m_k}}\, e^{i\,\underline{Q}\cdot\underline{r}_k}\, \underline{Q} \tag{3.3}$$

---

[x] the fact that k is also used as a suffix is not likely to cause confusion.

f_k , the modified scattering factor dependent on T ;

N , the number of cells in the crystal;

(3.4) $\sigma_0 = \left(\frac{e^2}{mc^2}\frac{1}{r}\right)^2 \frac{1}{2}\left(1+\cos^2\chi\right)$ the Thomson factor

e , the electronic charge;

m , the mass of the electron;

c , the velocity of light;

r , the distance of the small scattering volume from the point of observation;

χ , the angle of deflection of the X-ray beam.

4. THE DYNAMICAL MATRIX.

In the work of Born and Begbie, all the elements of the dynamical matrix were assumed to be arbitrary constants and then relations were found between them, by applying symmetry transformations described in (2.25).

In the case of central forces, the elements of the dynamical matrix are given explicitly in terms of the atomic constants, and hence already satisfy the necessary symmetry relations. The dynamics of a crystal lattice under the assumption of central forces have been completely worked out by Born, (Atomtheorie des festen Zustandes, 1923). Here it is assumed that the potential energy between any two particles $\varphi\binom{l}{kk'}$ depends only on the nature of the particles, and $r\binom{l}{kk'} = \left|\underline{r}\binom{l}{kk'}\right|$ the distance between them. Accordingly, the elements of the dynamical matrix are given by

$$(4.1) \quad -\Phi_{\alpha\beta}\binom{l}{kk'} = \delta_{\alpha\beta} P\binom{l}{kk'} + x_\alpha\binom{l}{kk'} x_\beta\binom{l}{kk'} Q\binom{l}{kk'}$$

where

$$(4.2) \quad P\binom{l}{kk'} = \left[\frac{1}{r\binom{l}{kk'}} \frac{d\varphi\binom{l}{kk'}}{dr\binom{l}{kk'}}\right]_0 \qquad Q\binom{l}{kk'} = \left[\frac{1}{r\binom{l}{kk'}} \frac{d}{dr\binom{l}{kk'}} \left\{\frac{1}{r\binom{l}{kk'}} \frac{d\varphi\binom{l}{kk'}}{dr\binom{l}{kk'}}\right\}\right]_0$$

and $\left[\quad\right]_0$ means the values of the variables are to be taken at the equilibrium position.

The condition for equilibrium is

$$(4.3) \quad \sum_{k'l} P\binom{l}{kk'} x_\alpha\binom{l}{kk'} = 0 \qquad (\alpha = 1, 2, 3.) .$$

$$\sum_{kk'l} P\binom{l}{kk'} x_\alpha\binom{l}{kk'} x_\beta\binom{l}{kk'} = 0$$

Now, in the special case where only first neighbours are considered to act on one another, and all the particles are the same, one has

(4.4) $P\binom{l}{kk'}\sum_{k'l} x_{\alpha}^{2}\binom{l}{kk'} = 0$ ($\alpha = 1,2,3$, l restricted to first neighbours.)

So it follows that if P' represents $P\binom{l}{kk'}$ for first neighbours

(4.5) $P' = 0$

and the elements of the dynamical matrix reduce to

(4.6) $\Phi_{\alpha\beta}\binom{l}{kk'} = -x_{\alpha}\binom{l}{kk'}\, x_{\beta}\binom{l}{kk'}\, Q\binom{l}{kk'}$

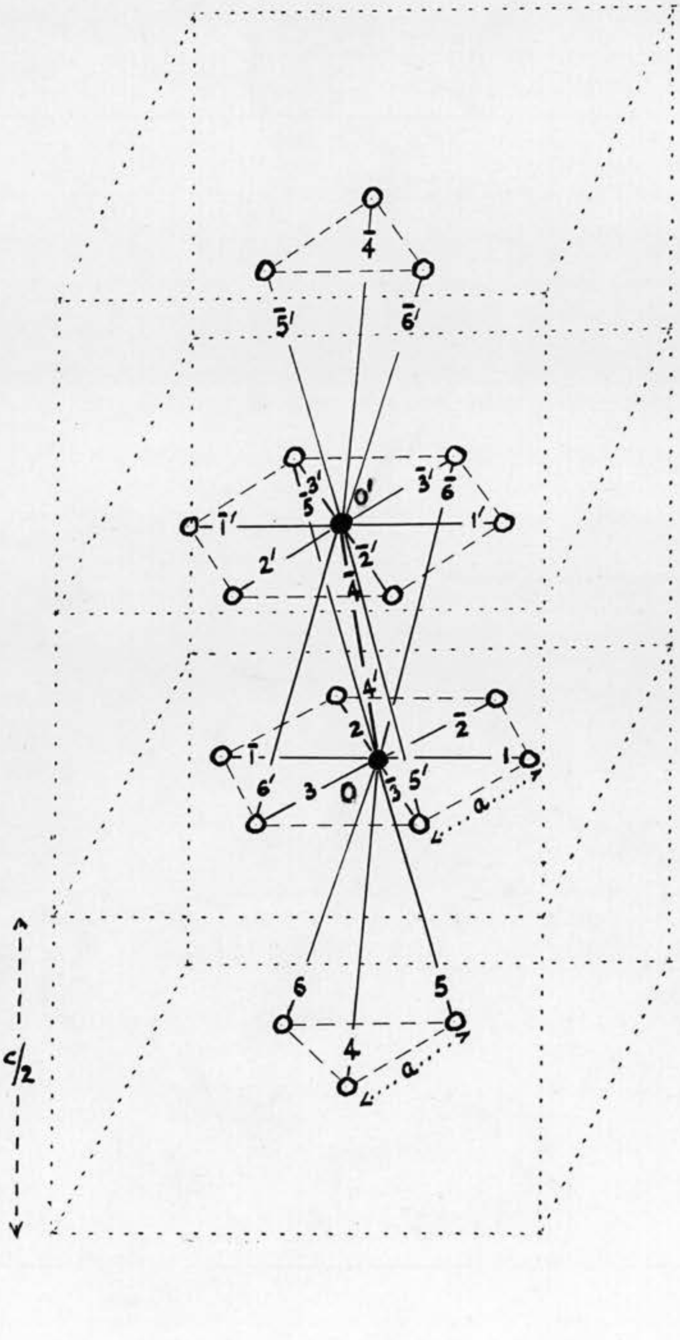
(l restricted to first neighbours).

The value of the remaining atomic constant Q' say, can be obtained by comparison with the matrix (c_{rs}) of the elastic constants (see(4.11)). Now the elements of the dynamical matrix can be written down, as soon as the form of the lattice is known.

In the close packed hexagonal lattice, there are two identical particles of mass m in the unit cell, distinguished by $k=1$, $k=2$. The cell vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$ can be chosen in such a way that the angle between $\underline{a}_1$ and $\underline{a}_2$ is $2\pi/3$ and $\underline{a}_3$ is at right-angles to the plane of $\underline{a}_1$ and $\underline{a}_2$ in the direction that makes the system of axes right-handed. The lengths of lattice vectors are given by

FIGURE I

First Neighbours of the Two Points in the Unit Cell of the Close-Packed Hexagonal Lattice.



$$|\underline{a}_1| = |\underline{a}_2| = a \qquad |\underline{a}_3| = c = \sqrt{8/3}\; a$$

(4.7)

The Cartesian co-ordinate system used is so orientated that x_1 lies along the positive direction of $\underline{a}_2$ and x_3 along the positive direction of $\underline{a}_3$. (Fig. II)

For simplicity, it is assumed that the base vector of particles of the type $k=1$ is zero, while that of the type $k=2$ is given by

(4.8) $$\underline{r}_2 = \underline{r}_{21} = \tfrac{2}{3}\underline{a}_1 + \tfrac{1}{3}\underline{a}_2 + \tfrac{1}{3}\underline{a}_3$$

or, in rectangular co-ordinates by

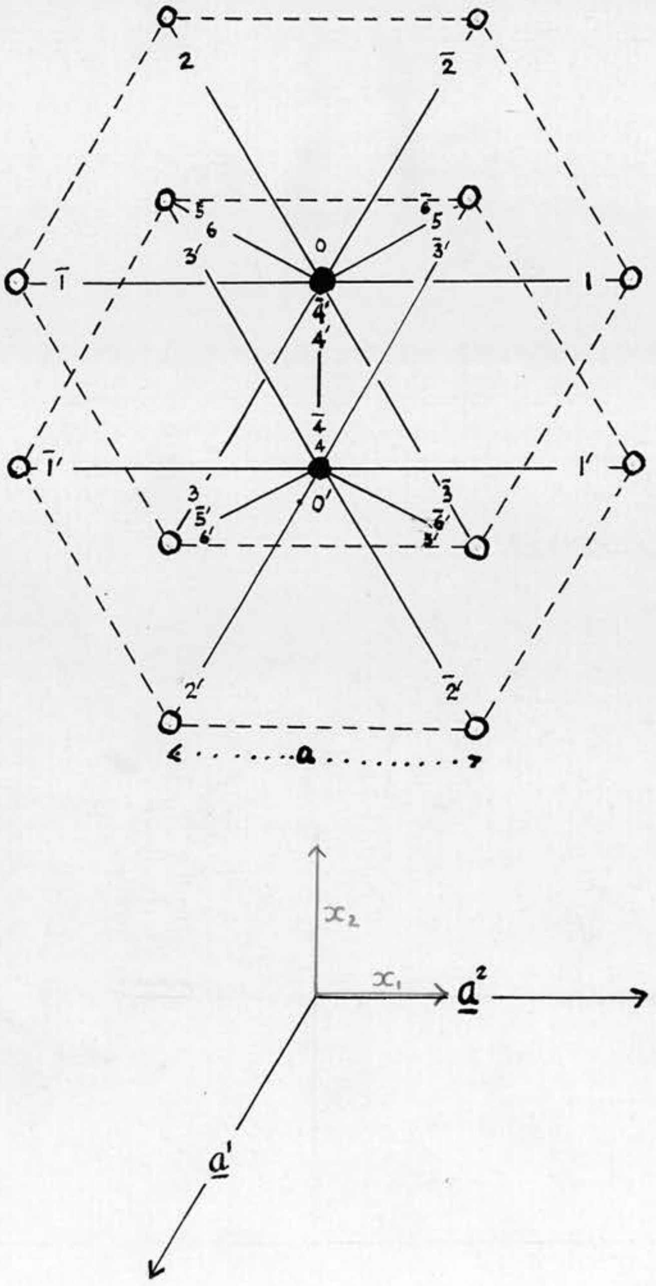
(4.9) $$\underline{r}_{21} = \left(0, -\tfrac{a}{\sqrt{3}}, \tfrac{c}{2}\right)$$

Particles of the same type lie in alternate planes, perpendicular to the $\underline{a}_3$ axis.

It is only necessary to consider those matrices $D\binom{l}{kk'}$ which arise from the first neighbours of the two particles in a chosen unit cell. These two particles are labelled O and O' in figs. 1 and 2. Each point has twelve first neighbours, six in a plane containing the point, and three above and three below this plane. The line joining O or O' to a neighbouring point $\binom{l}{kk'}$ is labelled by the letter h and D^h is written for $D\binom{l}{kk'}$. The twelve neighbours of O are again split into two groups $h, \bar{h}$ those of O' into h', $\bar{h}'$ as indicated by the following scheme.

FIGURE II

Projection of the Structure in Figure I on to a Plane Perpendicular to the Lattice Vector $\underline{a}_3$.



$$\left.\begin{array}{l} p \to 1, 2, 3, 4, 5, 6 \\ p \to \bar{1}, \bar{2}, \bar{3}, \bar{4}, \bar{5}, \bar{6} \end{array}\right\} \text{ Neighbours of } O$$

$$\left.\begin{array}{l} p' \to 1', 2', 3', 4', 5', 6' \\ p' \to \bar{1}', \bar{2}', \bar{3}', \bar{4}', \bar{5}', \bar{6}' \end{array}\right\} \text{ Neighbours of } O'$$

The connection between the symbols p and $\binom{l}{kk'}$ is given in Table 1.

TABLE 1.

l \ p	1	2	3	4	5	6	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$
l_1	0	-1	1	0	-1	-1	0	-1	1	0	-1	-1
l_2	1	-1	0	0	0	-1	-1	0	1	0	-1	0
l_3	0	0	0	-1	-1	-1	0	0	0	0	0	0
(kk')	(11)	(11)	(11)	(21)	(21)	(21)	(11)	(11)	(11)	(21)	(21)	(21)

l \ p	$1'$	$2'$	$3'$	$4'$	$5'$	$6'$	$\bar{1}'$	$\bar{2}'$	$\bar{3}'$	$\bar{4}'$	$\bar{5}'$	$\bar{6}'$
l_1	0	1	-1	0	1	1	0	1	-1	0	1	1
l_2	1	0	-1	0	1	0	-1	1	0	0	0	1
l_3	0	0	0	0	0	0	0	0	0	1	1	1
(kk')	(22)	(22)	(22)	(12)	(12)	(12)	(22)	(22)	(22)	(12)	(12)	(12)

The notation is due to Begbie (1947).

The components of x_{α}^{p} in the Cartesian system are given in Table 2.

TABLE 2.

r^h \ h	1	2	3	4	5	6	$\bar{1}$	$\bar{2}$	$\bar{3}$	$\bar{4}$	$\bar{5}$	$\bar{6}$
x_1^h	a	$-\frac{a}{2}$	$-\frac{a}{2}$	0	$\frac{a}{2}$	$-\frac{a}{2}$	$-a$	$\frac{a}{2}$	$\frac{a}{2}$	0	$-\frac{a}{2}$	$\frac{a}{2}$
x_2^h	0	$\frac{\sqrt{3}a}{2}$	$-\frac{\sqrt{3}a}{2}$	$-\frac{a}{\sqrt{3}}$	$\frac{a}{2\sqrt{3}}$	$\frac{a}{2\sqrt{3}}$	0	$\frac{\sqrt{3}a}{2}$	$-\frac{\sqrt{3}a}{2}$	$-\frac{a}{\sqrt{3}}$	$\frac{a}{2\sqrt{3}}$	$\frac{a}{2\sqrt{3}}$
x_3^h	0	0	0	$-\frac{c}{2}$	$-\frac{c}{2}$	$-\frac{c}{2}$	0	0	0	$\frac{c}{2}$	$\frac{c}{2}$	$\frac{c}{2}$
(kk')	(11)	(11)	(11)	(21)	(21)	(21)	(11)	(11)	(11)	(21)	(21)	(21)

r^h \ h	$1'$	$2'$	$3'$	$4'$	$5'$	$6'$	$\bar{1}'$	$\bar{2}'$	$\bar{3}'$	$\bar{4}'$	$\bar{5}'$	$\bar{6}'$
x_1^h	a	$-\frac{a}{2}$	$-\frac{a}{2}$	0	$\frac{a}{2}$	$-\frac{a}{2}$	$-a$	$\frac{a}{2}$	$\frac{a}{2}$	0	$-\frac{a}{2}$	$\frac{a}{2}$
x_2^h	0	$-\frac{\sqrt{3}a}{2}$	$\frac{\sqrt{3}a}{2}$	$\frac{a}{\sqrt{3}}$	$-\frac{a}{2\sqrt{3}}$	$-\frac{a}{2\sqrt{3}}$	0	$-\frac{\sqrt{3}a}{2}$	$\frac{\sqrt{3}a}{2}$	$\frac{a}{\sqrt{3}}$	$-\frac{a}{2\sqrt{3}}$	$-\frac{a}{2\sqrt{3}}$
x_3^h	0	0	0	$-\frac{c}{2}$	$-\frac{c}{2}$	$-\frac{c}{2}$	0	0	0	$\frac{c}{2}$	$\frac{c}{2}$	$\frac{c}{2}$
(kk')	(22)	(22)	(22)	(12)	(12)	(12)	(22)	(22)	(22)	(12)	(12)	(12)

The elements of the dynamical matrix being given by

$$D^h_{\alpha\beta} = \frac{-1}{m} x^h_\alpha x^h_\beta \varphi' \tag{4.10}$$

can be read off immediately from the above table. They are given in Table 3. All the elements have to be multiplied by the factor $-a^2\varphi/m$.

TABLE 3.

$$D^{1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = D^{\bar{1}'} \qquad D^{\bar{1}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = D^{1'}$$

$$D^{2} = \begin{bmatrix} \frac{1}{4} & -\frac{\sqrt{3}}{4} & 0 \\ -\frac{\sqrt{3}}{4} & \frac{3}{4} & 0 \\ 0 & 0 & 0 \end{bmatrix} = D^{\bar{2}'} \qquad D^{\bar{2}} = \begin{bmatrix} \frac{1}{4} & \frac{\sqrt{3}}{4} & 0 \\ \frac{\sqrt{3}}{4} & \frac{3}{4} & 0 \\ 0 & 0 & 0 \end{bmatrix} = D^{2'}$$

$$D^{3} = \begin{bmatrix} \frac{1}{4} & \frac{\sqrt{3}}{4} & 0 \\ \frac{\sqrt{3}}{4} & \frac{3}{4} & 0 \\ 0 & 0 & 0 \end{bmatrix} = D^{\bar{3}'} \qquad D^{\bar{3}} = \begin{bmatrix} \frac{1}{4} & -\frac{\sqrt{3}}{4} & 0 \\ -\frac{\sqrt{3}}{4} & \frac{3}{4} & 0 \\ 0 & 0 & 0 \end{bmatrix} = D^{3'}$$

$$D^{4} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \frac{1}{3} & \frac{\sqrt{2}}{3} \\ 0 & \frac{\sqrt{2}}{3} & \frac{2}{3} \end{bmatrix} = D^{\bar{4}'} \qquad D^{\bar{4}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & \frac{1}{3} & -\frac{\sqrt{2}}{3} \\ 0 & -\frac{\sqrt{2}}{3} & \frac{2}{3} \end{bmatrix} = D^{4'}$$

$$D^{5} = \begin{bmatrix} \frac{1}{4} & \frac{1}{4\sqrt{3}} & \frac{-1}{\sqrt{6}} \\ \frac{1}{4\sqrt{3}} & \frac{1}{12} & -\frac{\sqrt{2}}{6} \\ \frac{-1}{\sqrt{6}} & -\frac{\sqrt{2}}{6} & \frac{2}{3} \end{bmatrix} = D^{\bar{5}'} \qquad D^{\bar{5}} = \begin{bmatrix} \frac{1}{4} & \frac{-1}{4\sqrt{3}} & \frac{-1}{\sqrt{6}} \\ \frac{-1}{4\sqrt{3}} & \frac{1}{12} & \frac{\sqrt{2}}{6} \\ \frac{-1}{\sqrt{6}} & \frac{\sqrt{2}}{6} & \frac{2}{3} \end{bmatrix} = D^{5'}$$

$$D^{6} = \begin{bmatrix} \frac{1}{4} & \frac{-1}{4\sqrt{3}} & \frac{1}{\sqrt{6}} \\ \frac{-1}{4\sqrt{3}} & \frac{1}{12} & -\frac{\sqrt{2}}{6} \\ \frac{1}{\sqrt{6}} & \frac{-\sqrt{2}}{6} & \frac{2}{3} \end{bmatrix} = D^{\bar{6}'} \qquad D^{\bar{6}} = \begin{bmatrix} \frac{1}{4} & \frac{1}{4\sqrt{3}} & \frac{1}{\sqrt{6}} \\ \frac{1}{4\sqrt{3}} & \frac{1}{12} & \frac{\sqrt{2}}{6} \\ \frac{1}{\sqrt{6}} & \frac{\sqrt{2}}{6} & \frac{2}{3} \end{bmatrix} = D^{6'}$$

The elements of $D\binom{l}{kh}$ $(l = 0,0,0)$ obtained from the condition (2.7) are

$$D^{0} = \begin{bmatrix} -4 & 0 & 0 \\ 0 & -4 & 0 \\ 0 & 0 & -4 \end{bmatrix} = D^{0'}$$

The elastic constants of the close-packed hexagonal lattice have been considered by Born (1942) in an investigation of the stability of such a lattice. The matrix (c_{rs}) of the elastic constants, (case of first neighbours only), can be written in the form

$$(c_{rs}) = \frac{a^4 Q'}{12\Delta} \begin{bmatrix} 29 & 11 & 8 & 0 & 0 & 0 \\ 11 & 29 & 8 & 0 & 0 & 0 \\ 8 & 8 & 32 & 0 & 0 & 0 \\ 0 & 0 & 0 & 8 & 0 & 0 \\ 0 & 0 & 0 & 0 & 8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 9 \end{bmatrix}$$

(4.11)

where Voigt's form for the elastic energy per unit volume is

(4.12) $$\Phi_2 = \frac{1}{2} \sum_{\rho\sigma} c_{\rho\sigma} x_\rho x_\sigma$$

and Δ is the volume of the unit cell. Thus Q' can be obtained by a determination of the elastic constants.

5. THE TRANSFORMED DYNAMICAL MATRIX.

The elements of the dynamical matrix in the reciprocal lattice space, (which for a hexagonal lattice is another hexagonal lattice), are obtained from the $D_{\alpha\beta}\binom{l}{kk'}$ by means of (2.14). Before doing this, however, it is convenient to denote the co-ordinates of a wave vector $\underline{Q}$ in reciprocal space by four symbols instead of three. This is done in order to utilize fully the symmetry of the lattice and corresponds to the fact that, in a hexagonal direct lattice, there are three symmetry lines in the plane $l_3 = 0$, any two of which may be taken for the direction of the cell vectors. The co-ordinates of the point $\underline{Q}$ are thus denoted by (Q_1, Q_2, Q_3, Q_4) where Q_3 denotes the new co-ordinate and the one previously called Q_3 now becomes Q_4. As a point is now specified by four co-ordinates instead of three, a relation must hold between them. This is given by

(5.1) $$Q_1 + Q_2 + Q_3 = 0$$

The elements of the matrix are thus given by

(5.2) $$D_{\alpha\beta}\binom{Q}{kk'} = \sum_{l} D_{\alpha\beta}\binom{l}{kk'} e^{-i(\underline{Q}.\underline{r}^{l})} \qquad \left(\underline{Q}.\underline{r}^{l} = Q_1 l_1 + Q_2 l_2 + Q_4 l_3\right)$$

It is not necessary to calculate all the matrices, as certain symmetry relations hold between them. Since from Table 3

(5.3) $$D^{h} = D^{\bar{h}'}$$

and

(5.4) $$D^{\bar{p}} = D^{p'}$$

and as is easily seen from Table 1,

(5.5) $$(\underline{r}^{l})_{p} = -(\underline{r}^{l})_{\bar{p}'}$$

and

(5.6) $$(\underline{r}^{l})_{\bar{p}} = -(\underline{r}^{l})_{p'}$$

it follows that

(5.7) $$D\binom{q}{11} = D\binom{-q}{22}$$

and

(5.8) $$D\binom{q}{21} = D\binom{-q}{12}$$

Thus only the cases $D\binom{q}{11}$ and $D\binom{q}{21}$ are worked out in detail. The corresponding l values are given below in Table 4.

TABLE 4.

$l \backslash p$	1	2	3	$\bar{1}$	$\bar{2}$	$\bar{3}$	4	5	6	$\bar{4}$	$\bar{5}$	$\bar{6}$
l_1	0	-1	1	0	-1	1	0	-1	-1	0	-1	-1
l_2	1	-1	0	-1	0	1	0	0	-1	0	-1	0
l_3	0	0	0	0	0	0	-1	-1	-1	0	0	0
(kk')	(11)	(11)	(11)	(11)	(11)	(11)	(21)	(21)	(21)	(21)	(21)	(21)

The resultant $D\binom{q}{kk'}$ matrices are given by

$$D\binom{q}{11} = D^1 e^{-iQ_2} + D^2 e^{-iQ_3} + D^3 e^{-iQ_1} + D^{\bar{1}} e^{iQ_2} + D^{\bar{2}} e^{iQ_1} + D^{\bar{3}} e^{iQ_3} + D^0$$

(5.9) $$D\binom{q}{21} = D^4 e^{iQ_4} + D^5 e^{i(Q_1+Q_4)} + D^6 e^{i(Q_4-Q_3)} + D^{\bar{4}} + D^{\bar{5}} e^{-iQ_3} + D^{\bar{6}} e^{iQ_1}$$

As in the case of Begbie, the calculation is confined to the plane $Q_4 = 0$. With this condition, the non-vanishing elements reduce to

$$\left.\begin{aligned} D_{11}\binom{q}{11} &= 2c_2 + \tfrac{1}{2}(c_1+c_3) - 4 \\ D_{22}\binom{q}{11} &= \tfrac{3}{2}(c_1+c_3) - 4 \\ D_{12}\binom{q}{11} &= \tfrac{\sqrt{3}}{2}(c_1-c_3) = D_{21}\binom{q}{11} \\ D_{33}\binom{q}{11} &= -4 \end{aligned}\right\} \times \frac{-a^2Q'}{m} \qquad \left.\begin{aligned} D_{11}\binom{q}{21} &= \tfrac{1}{2}\left(e^{iQ_1} + e^{-iQ_3}\right) \\ D_{22}\binom{q}{21} &= \tfrac{2}{3} + \tfrac{1}{6}\left(e^{iQ_1} + e^{-iQ_3}\right) \\ D_{12}\binom{q}{21} &= \tfrac{1}{2\sqrt{3}}\left(e^{iQ_1} - e^{-iQ_3}\right) = D_{21}\binom{q}{21} \\ D_{33}\binom{q}{21} &= \tfrac{4}{3}\left(1 + e^{iQ_1} + e^{-iQ_3}\right) \end{aligned}\right\} \times \frac{-a^2Q'}{m}$$

(5.10)

where

(5.11) $$c_\alpha = \cos Q_\alpha$$

6. THE RECIPROCAL OF THE TRANSFORMED DYNAMICAL MATRIX.

The matrix $D(q)$ is of order 6 x 6, corresponding to the six possible values of the pair of indices α, k. If the rows and columns are so ordered that the elements $D_{\alpha\beta}\left(\begin{smallmatrix} q \\ kk' \end{smallmatrix}\right)$ which occur in the fifth and sixth rows and columns have at least one of the indices $\alpha, \beta = 3$, then the matrix can be written in the form

$$\begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix} \tag{6.1}$$

Here the A_{rs} are sub-matrices. A_{11} consists of the sixteen elements for which α and β are equal to 1 or 2, A_{22} the four elements for which both α and β are equal to 3, and A_{12}, A_{21} are composed of the remaining terms for which one of the indices α, β is equal to 3. From the previous section, it follows that the sub-matrices A_{12}, A_{21} are zero matrices.

Now, if the reciprocal matrix is partitioned in a corresponding manner, the sub-matrices being denoted by B_{rs}, it will have the same form as the original matrix, and the sub-matrices B_{11}, B_{22} are the reciprocals of A_{11}, A_{22} respectively.

A glance at the scattering formula, (3.1), shows that the sub-matrix B_{22} always acts on the component Q_3 or, as it is now called Q_4. Since the calculation is confined to the plane $Q_4 = 0$, this sub-matrix will contribute nothing to the scattering. Hence, in the sequel the term transposed dynamical matrix $D(q)$ will be applied to the 4×4 sub-matrix A_{11}.

The reciprocal of the 4×4 sub-matrix can be written

$$D^{-1}(q) = \frac{1}{\Delta} \begin{bmatrix} \Delta_{11} & -\Delta_{21} & \Delta_{31} & -\Delta_{41} \\ -\Delta_{12} & \Delta_{22} & -\Delta_{32} & \Delta_{42} \\ \Delta_{13} & -\Delta_{23} & \Delta_{33} & -\Delta_{43} \\ -\Delta_{14} & \Delta_{24} & -\Delta_{34} & \Delta_{44} \end{bmatrix}$$

(6.2)

where Δ is the determinant

$$\begin{vmatrix} D_{11}\binom{q}{11} & D_{12}\binom{q}{11} & D_{11}\binom{q}{12} & D_{12}\binom{q}{12} \\ D_{21}\binom{q}{11} & D_{22}\binom{q}{11} & D_{21}\binom{q}{12} & D_{22}\binom{q}{12} \\ D_{11}\binom{q}{21} & D_{12}\binom{q}{21} & D_{11}\binom{q}{22} & D_{12}\binom{q}{22} \\ D_{21}\binom{q}{21} & D_{22}\binom{q}{21} & D_{21}\binom{q}{22} & D_{22}\binom{q}{22} \end{vmatrix}$$

(6.3)

and Δ_{rs} are the minors of the elements in the r^{th} row and the s^{th} column. They satisfy the relations

(6.4) $$\Delta_{rs} = \Delta^*_{sr}$$

and

(6.5) $$\Delta_{11} = \Delta_{33} \qquad \Delta_{22} = \Delta_{44} \qquad \Delta_{12} = \Delta^*_{34} \qquad \Delta_{23} = \Delta^*_{41}$$

For ease in writing, the determinant Δ is written

$$\Delta = \begin{vmatrix} a & b & x^* & y^* \\ b & c & y^* & z^* \\ x & y & a & b \\ y & z & b & c \end{vmatrix}$$

(6.6)

where the values of the constants obtained from (5.10) (omitting for the present the factor $-\frac{a^2 Q'}{m}$) are

$$a = 2c_2 + \tfrac{1}{2}(c_1+c_3) - 4 \qquad b = \tfrac{\sqrt{3}}{2}(c_1 - c_3) \qquad c = \tfrac{3}{2}(c_1+c_3) - 4$$

$$x = \tfrac{1}{2}(e^{iQ_1} + e^{-iQ_3}) \qquad y = \tfrac{1}{2\sqrt{3}}(e^{iQ_1} - e^{-iQ_3}) \qquad z = \tfrac{2}{3} + \tfrac{1}{6}(e^{iQ_1} + e^{-iQ_3})$$

$$|x|^2 = \frac{1+c_2}{2} \qquad |y|^2 = \frac{1-c_2}{6} \qquad |z|^2 = \frac{1}{9}\left\{2(c_1+c_3) + \frac{c_2}{2} + 4\tfrac{1}{2}\right\}$$

(6.7)

Instead of working out the elements of the reciprocal matrix in detail, the calculation is simplified by taking certain linear combinations, which, being related to the symmetry of the lattice, simplify the expression of the scattering power. This will be shown in detail in the next section. In the next paragraph, combinations of Δ_{11} , Δ_{22} , Δ_{12} are evaluated, then combinations of Δ_{31} , Δ_{41} Δ_{42} and finally the determinant Δ .

The explicit expressions for the first set of minors are

$$\Delta_{11} = \begin{vmatrix} c & y^* & z^* \\ y & a & b \\ z & b & c \end{vmatrix} = -a|z|^2 + b(y^*z + yz^*) - c|y|^2 + c(ac - b^2)$$

(6.8)

$$\Delta_{22} = \begin{vmatrix} a & x^* & y^* \\ x & a & b \\ y & b & c \end{vmatrix} = -a|y|^2 + b(x^*y + xy^*) - c|x|^2 + a(ac - b^2)$$

(6.9)

$$\Delta_{12} = \begin{vmatrix} b & x^* & y^* \\ y & a & b \\ z & b & c \end{vmatrix} = -a\,y^*z + b(|y|^2 + x^*z) - c\,x^*y + b(ac - b^2)$$

(6.10)

The first two expressions are real. If the real part of the last one is called Δ^{r}_{21} it is given by

$$\Delta^{r}_{21} = -\frac{a}{2}(y^*z+yz^*)+b\left(|y|^2+\frac{1}{2}x^*z+\frac{1}{2}xz^*\right)-\frac{c}{2}(x^*y+xy^*)+b(ac-b^2) \tag{6.11}$$

In the following, the symbol R before a quantity means that the real part of that quantity has to be taken. Now three quantities Δ_1, Δ_2, Δ_3 are introduced as follows.

$$\begin{aligned}\Delta_1 &= R(\sqrt{3}\Delta_{21}-\Delta_{22})\\ &= -a\left\{-\frac{\sqrt{3}}{2}(y^*z+yz^*)+|y|^2\right\}+b\left\{x^*y+xy^*-\frac{\sqrt{3}}{2}(x^*z+xz^*)-\sqrt{3}|y|^2\right\}-c\left\{-\frac{\sqrt{3}}{2}(x^*y+xy^*)+|x|^2\right\}\\ &\qquad +(a-\sqrt{3}b)(ac-b^2).\end{aligned} \tag{6.12}$$

$$\begin{aligned}\Delta_2 &= \frac{1}{2}(3\Delta_{11}-\Delta_{22})\\ &= \frac{1}{2}\left\{a(|y|^2-3|z|^2)+b(3y^*z+3yz^*-x^*y-xy^*)+c(|x|^2-3|y|^2)+(3c-a)(ac-b^2)\right\}\end{aligned} \tag{6.13}$$

$$\begin{aligned}\Delta_3 &= R(\sqrt{3}\Delta_{21}+\Delta_{22})\\ &= -a\left\{\frac{\sqrt{3}}{2}(y^*z+yz^*)+|y|^2\right\}+b\left\{x^*y+xy^*+\frac{\sqrt{3}}{2}(x^*z+xz^*)+\sqrt{3}|y|^2\right\}-c\left\{\frac{\sqrt{3}}{2}(x^*y+xy^*)+|x|^2\right\}\\ &\qquad +(a+\sqrt{3}b)(ac-b^2).\end{aligned} \tag{6.14}$$

From (6.7) it follows that

$$\begin{aligned}x^*y+xy^* &= 0\\ y^*z+yz^* &= \frac{2}{3\sqrt{3}}(c_1-c_3)\\ z^*x+zx^* &= \frac{1}{3}\left\{2(c_1+c_3)+c_2+1\right\}\end{aligned} \tag{6.15}$$

and that the quantities α_1, α_2, α_3 and γ can be introduced as follows:

$$\begin{aligned}\alpha_1 &= a-\sqrt{3}b = 2(c_2+c_3)-c_1-4\\ \alpha_2 &= \frac{3c-a}{2} = 2(c_1+c_3)-c_2-4\\ \alpha_3 &= a+\sqrt{3}b = 2(c_1+c_2)-c_3-4\end{aligned} \tag{6.16}$$

$$\gamma = 3(ac-b^2) = 9(c_1c_2+c_2c_3+c_3c_1)-24(c_1+c_2+c_3)+48 \tag{6.17}$$

If the substitutions (6.15), (6.16), (6.17) are put into (6.12), (6.13), (6.14) Δ_1, Δ_2, Δ_3, reduce to

$$\Delta_1 = \alpha_1\gamma - c_1^2 + c_2^2 + c_3^2 - 4c_2c_3 + 3(c_2+c_3) - 8c_1 + 8$$

$$\Delta_2 = \alpha_2\gamma + c_1^2 - c_2^2 + c_3^2 - 4c_3c_1 + 3(c_3+c_1) - 8c_2 + 8$$

$$\Delta_3 = \alpha_3\gamma + c_1^2 + c_2^2 - c_3^2 - 4c_1c_2 + 3(c_1+c_2) - 8c_3 + 8$$

(6.18)

The second set of minors is given by

$$\Delta_{31} = \begin{vmatrix} b & x^* & y^* \\ c & y^* & z^* \\ z & b & c \end{vmatrix} = -x^*c^2 + 2y^*bc - z^*b^2 + z(x^*z^* - y^{*2})$$

(6.19)

$$\Delta_{41} = \begin{vmatrix} b & x^* & y^* \\ c & y^* & z^* \\ y & a & b \end{vmatrix} = -x^*bc + y^*(b^2+ac) - z^*ab + y(x^*z^* - y^{*2})$$

(6.20)

$$\Delta_{42} = \begin{vmatrix} a & x^* & y^* \\ b & y^* & z^* \\ x & a & b \end{vmatrix} = -x^*b^2 + 2y^*ab - z^*a^2 + x(x^*z^* - y^{*2})$$

(6.21)

and the required linear combinations by

$$\Delta_{42}-\sqrt{3}\Delta_{41}=-b(b-\sqrt{3}c)x^*+(2ab-\sqrt{3}b^2-\sqrt{3}ac)y^*-a(a-\sqrt{3}b)z^*+(x-\sqrt{3}y)(x^*z^*-y^{*2})$$

$$\tfrac{1}{2}(3\Delta_{31}-\Delta_{42})=\tfrac{1}{2}\left\{(b^2-3c^2)x^*+2b(3c-a)y^*+(a^2-3b^2)z^*+(3z-x)(x^*z^*-y^{*2})\right\}$$

$$\Delta_{42}+\sqrt{3}\Delta_{41}=-b(b+\sqrt{3}c)x^*+(2ab+\sqrt{3}b^2+\sqrt{3}ac)y^*-a(a+\sqrt{3}b)z^*+(x+\sqrt{3}y)(x^*z^*-y^{*2})$$

(6.22)

Now the factor

$$x^*z^*-y^{*2}=\tfrac{1}{6}\left\{e^{-iQ_1}+e^{iQ_3}\right\}\left\{2+\tfrac{1}{2}(e^{-iQ_1}+e^{iQ_3})\right\}-\tfrac{1}{12}\left(e^{-iQ_1}-e^{iQ_3}\right)^2$$

$$=\tfrac{1}{3}\left(e^{-iQ_1}+e^{iQ_3}+e^{i(Q_3-Q_1)}\right)$$

(6.23)

Substituting for this and x, y, z **in (6.22) gives**

$$\Delta_{42}-\sqrt{3}\Delta_{41}=-\frac{b}{2}(b-\sqrt{3}c)(e^{-iQ_1}+e^{iQ_3})+\left(\frac{ab}{\sqrt{3}}-\frac{b^2+ac}{2}\right)\left(e^{-iQ_1}-e^{iQ_3}\right)-\frac{a}{3}(a-\sqrt{3}b)\left\{2+\tfrac{1}{2}(e^{-iQ_1}+e^{iQ_3})\right\}$$
$$+\tfrac{1}{3}e^{-iQ_3}\left(e^{-iQ_1}+e^{iQ_3}+e^{i(Q_3-Q_1)}\right).$$

$$\tfrac{1}{2}(3\Delta_{31}-\Delta_{42})=\tfrac{1}{2}\left[\frac{b^2-3c^2}{2}\left(e^{-iQ_1}+e^{iQ_3}\right)+\frac{b}{\sqrt{3}}(3c-a)(e^{-iQ_1}-e^{iQ_3})+\left(\frac{a^2-3b^2}{3}\right)\left\{2+\tfrac{1}{2}(e^{-iQ_1}+e^{iQ_3})\right\}\right.$$
$$\left.+\tfrac{2}{3}\left(e^{-iQ_1}+e^{iQ_3}+e^{i(Q_3-Q_1)}\right)\right]$$

$$\Delta_{42}+\sqrt{3}\Delta_{41}=-\frac{b}{2}(b+\sqrt{3}c)(e^{-iQ_1}+e^{iQ_3})+\left(\frac{ab}{\sqrt{3}}+\frac{b^2+ac}{2}\right)\left(e^{-iQ_1}-e^{iQ_3}\right)-\frac{a}{3}(a+\sqrt{3}b)\left\{2+\tfrac{1}{2}(e^{-iQ_1}+e^{iQ_3})\right\}$$
$$+\tfrac{1}{3}e^{iQ_1}\left(e^{-iQ_1}+e^{iQ_3}+e^{i(Q_3-Q_1)}\right)$$

(6.24)

Rearranging (6.24) according to the exponentials leads to

$$\Delta_{42}-\sqrt{3}\Delta_{41}=\left\{-b^2+\frac{\sqrt{3}}{2}bc+\frac{ab}{\sqrt{3}}-\frac{ac}{2}-\frac{a}{6}(a-\sqrt{3}b)\right\}e^{-iQ_1}+\left\{\frac{\sqrt{3}}{2}bc-\frac{ab}{2\sqrt{3}}+\frac{ac}{2}-\frac{a^2}{6}\right\}e^{iQ_3}-\frac{2a}{3}(a-\sqrt{3}b)$$
$$+\tfrac{1}{3}\left(e^{-i(Q_1+Q_3)}+1+e^{-iQ_1}\right)$$

(6.25)

$$\tfrac{1}{2}(3\Delta_{31}-\Delta_{42})=\tfrac{1}{2}\Big[\Big\{-\tfrac{3c^2}{2}+\tfrac{b}{\sqrt{3}}(3c-a)+\tfrac{a^2}{6}\Big\}e^{-iQ_1}+\Big\{-\tfrac{3c^2}{2}-\tfrac{b}{\sqrt{3}}(3c-a)+\tfrac{a^2}{6}\Big\}e^{iQ_3}+2(a^2-3b^2)$$
$$+\tfrac{2}{3}\left(e^{-iQ_1}+e^{iQ_3}+e^{i(Q_3-Q_1)}\right)\Big]$$

$$\Delta_{42}+\sqrt{3}\Delta_{41}=\Big\{\tfrac{ab}{2\sqrt{3}}-\tfrac{\sqrt{3}}{2}bc+\tfrac{ac}{2}-\tfrac{a^2}{6}\Big\}e^{-iQ_1}+\Big\{-b^2-\tfrac{\sqrt{3}}{2}bc-\tfrac{\sqrt{3}}{2}ab-\tfrac{ac}{2}-\tfrac{a^2}{6}\Big\}e^{iQ_3}-\tfrac{2a}{3}(a+\sqrt{3}b)$$
$$+\tfrac{1}{3}\left(1+e^{i(Q_1+Q_3)}+e^{iQ_3}\right)$$

(6.25)

The coefficients of the exponentials can be factorized thus:

$$\Delta_{42}-\sqrt{3}\Delta_{41}=(a-\sqrt{3}b)\left(\tfrac{b}{\sqrt{3}}-\tfrac{c}{2}-\tfrac{a}{6}\right)e^{-iQ_1}+\tfrac{1}{3}\tfrac{(3c-a)}{2}(a+\sqrt{3}b)e^{iQ_3}+\left(\tfrac{-2a}{3}\right)(a-\sqrt{3}b)$$
$$+\tfrac{1}{3}\left(e^{-i(Q_1+Q_3)}+1+e^{-iQ_1}\right)$$

$$\tfrac{1}{2}(3\Delta_{31}-\Delta_{42})=\left(\tfrac{a-3c}{2}\right)\left(\tfrac{a}{6}-\tfrac{b}{\sqrt{3}}+\tfrac{c}{2}\right)e^{-iQ_1}+\left(\tfrac{a-3c}{2}\right)\left(\tfrac{a}{6}+\tfrac{b}{\sqrt{3}}+\tfrac{c}{2}\right)e^{iQ_3}+(a+\sqrt{3}b)(a-\sqrt{3}b)$$
$$+\tfrac{1}{3}\left(e^{-iQ_1}+e^{iQ_3}+e^{i(Q_3-Q_1)}\right)$$

$$\Delta_{42}+\sqrt{3}\Delta_{41}=\tfrac{1}{3}\left(\tfrac{a-3c}{2}\right)(\sqrt{3}b-a)e^{-iQ_1}-\tfrac{1}{3}(a+\sqrt{3}b)\left(\tfrac{a}{2}+\sqrt{3}b+\tfrac{3c}{2}\right)e^{iQ_3}-\tfrac{1}{3}(2a)(a+\sqrt{3}b)$$
$$+\tfrac{1}{3}\left(1+e^{i(Q_1+Q_3)}+e^{iQ_3}\right).$$

(6.26)

But

$$\tfrac{a}{2}+\sqrt{3}b+\tfrac{3c}{2}=4c_1+c_2+c_3-8 \qquad 2a=c_1+4c_2+c_3-8 \qquad \tfrac{a}{2}-\sqrt{3}b+\tfrac{3c}{2}=c_1+c_2+4c_3-8$$

(6.27 $\quad=\alpha_2+\alpha_3 \qquad\qquad =\alpha_1+\alpha_3 \qquad\qquad =\alpha_1+\alpha_2$

On substituting (6.27), (6.26) reduces to

$$\Delta_{42}-\sqrt{3}\Delta_{41}=\tfrac{1}{3}\left[-\alpha_1(\alpha_1+\alpha_2)e^{-iQ_1}+\alpha_2\alpha_3e^{iQ_3}-\alpha_1(\alpha_1+\alpha_3)+e^{-i(Q_1+Q_3)}+1+e^{-iQ_1}\right]$$

$$\tfrac{1}{2}(3\Delta_{31}-\Delta_{42})=\tfrac{1}{3}\left[-\alpha_2(\alpha_1+\alpha_2)e^{-iQ_1}-\alpha_2(\alpha_2+\alpha_3)e^{iQ_3}+\alpha_1\alpha_3+e^{-iQ_1}+e^{iQ_3}+e^{i(Q_3-Q_1)}\right]$$

$$\Delta_{42}+\sqrt{3}\Delta_{41}=\tfrac{1}{3}\left[\alpha_1\alpha_2e^{-iQ_1}-\alpha_3(\alpha_2+\alpha_3)e^{iQ_3}-\alpha_3(\alpha_1+\alpha_3)+1+e^{i(Q_1+Q_3)}+e^{iQ_3}\right]$$

(6.28)

From (6.28) it follows that

$$\left(\Delta_{42}-\sqrt{3}\Delta_{41}\right)e^{i\frac{(\varphi_1-\varphi_3)}{3}}=\frac{1}{3}\Big[-\alpha_1(\alpha_1+\alpha_2)e^{i\left(\frac{\varphi_2-\varphi_1}{3}\right)}+\alpha_2\alpha_3 e^{i\left(\frac{\varphi_3-\varphi_2}{3}\right)}-\alpha_1(\alpha_1+\alpha_3)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}+e^{i\left(\frac{\varphi_2-\varphi_1}{3}\right)}+e^{i\frac{\varphi_1-\varphi_3}{3}}+e^{i\frac{2}{3}(\varphi_2-\varphi_3)}\Big]$$

$$\frac{1}{2}\left(3\Delta_{31}-\Delta_{42}\right)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}=\frac{1}{3}\Big[-\alpha_2(\alpha_1+\alpha_2)e^{i\left(\frac{\varphi_2-\varphi_1}{3}\right)}-\alpha_2(\alpha_2+\alpha_3)e^{i\left(\frac{\varphi_3-\varphi_2}{3}\right)}+\alpha_1\alpha_3 e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}+e^{i\left(\frac{\varphi_3-\varphi_2}{3}\right)}+e^{i\left(\frac{\varphi_2-\varphi_1}{3}\right)}+e^{i\frac{2}{3}(\varphi_3-\varphi_1)}\Big]$$

$$\left(\Delta_{42}+\sqrt{3}\Delta_{41}\right)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}=\frac{1}{3}\Big[\alpha_1\alpha_2 e^{i\left(\frac{\varphi_2-\varphi_1}{3}\right)}-\alpha_3(\alpha_2+\alpha_3)e^{i\left(\frac{\varphi_3-\varphi_2}{3}\right)}-\alpha_3(\alpha_1+\alpha_3)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}+e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}+e^{i\left(\frac{\varphi_3-\varphi_2}{3}\right)}+e^{i\frac{2}{3}(\varphi_1-\varphi_2)}\Big]$$

(6.29)

Now the quantities Δ_1' . Δ_2' . Δ_3' . are introduced by

$$\Delta_1'=R\left(\Delta_{24}-\sqrt{3}\Delta_{23}\right)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}=R\left(\Delta_{42}-\sqrt{3}\Delta_{41}\right)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}$$

$$\Delta_2'=R\left(\frac{3}{2}\Delta_{13}-\frac{1}{2}\Delta_{24}\right)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}=R\frac{1}{2}\left(3\Delta_{31}-\Delta_{42}\right)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}$$

$$\Delta_3'=R\left(\Delta_{24}+\sqrt{3}\Delta_{23}\right)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}=R\left(\Delta_{42}+\sqrt{3}\Delta_{41}\right)e^{i\left(\frac{\varphi_1-\varphi_3}{3}\right)}$$

(6.30)

The values of these quantities are obtained from (6.29).

$$3\Delta_1'=-\alpha_1(\alpha_1+\alpha_2)\cos\frac{\varphi_2-\varphi_1}{3}+\alpha_2\alpha_3\cos\frac{\varphi_3-\varphi_2}{3}-\alpha_1(\alpha_1+\alpha_3)\cos\frac{\varphi_1-\varphi_3}{3}+\cos\frac{\varphi_2-\varphi_1}{3}+\cos\frac{\varphi_1-\varphi_3}{3}+\cos\frac{2(\varphi_2-\varphi_3)}{3}$$

$$3\Delta_2'=-\alpha_2(\alpha_1+\alpha_2)\cos\frac{\varphi_2-\varphi_1}{3}-\alpha_2(\alpha_2+\alpha_3)\cos\frac{\varphi_3-\varphi_2}{3}+\alpha_1\alpha_3\cos\frac{\varphi_1-\varphi_3}{3}+\cos\frac{\varphi_3-\varphi_2}{3}+\cos\frac{\varphi_2-\varphi_1}{3}+\cos\frac{2(\varphi_3-\varphi_1)}{3}$$

$$3\Delta_3'=\alpha_1\alpha_2\cos\frac{\varphi_2-\varphi_1}{3}-\alpha_3(\alpha_2+\alpha_3)\cos\frac{\varphi_3-\varphi_2}{3}-\alpha_3(\alpha_1+\alpha_3)\cos\frac{\varphi_1-\varphi_3}{3}+\cos\frac{\varphi_1-\varphi_3}{3}+\cos\frac{\varphi_3-\varphi_2}{3}+\cos\frac{2(\varphi_1-\varphi_2)}{3}.$$

(6.31)

From (6.6.) it follows that the determinant Δ is given by

$$\Delta=(ac-b^2)^2-2R(ay-bx)(cy^*-bz^*)-|az-by|^2-|by-cx|^2+|xz-y^2|^2$$

$$=(ac-b^2)^2-c^2x^2-2(b^2+ac)|y|^2-a^2|z|^2+2bR\{2ayz^*+2cxy^*-bz^*x\}+|xz-y^2|^2$$

(6.32)

Elimination of x, y, **and** z **from (6.32) gives**

$$\Delta=\frac{1}{9}\gamma^2-\frac{1}{2}c^2(1+c_2)-\frac{1}{3}(b^2+ac)(1-c_2)-\frac{1}{9}a^2\left\{4+2(c_1+c_3)+\frac{1+c_2}{2}\right\}+\frac{4ab}{3\sqrt{3}}(c_1-c_3)$$
$$-\frac{2b^2}{3}\left(c_1+c_3+\frac{1+c_2}{2}\right)+\frac{1}{9}\{3+2(c_1+c_2+c_3)\}.$$

(6.33)

or

$$9\Delta=\gamma^2-\frac{1}{2}c_2(a-3c)^2-2(c_1+c_3)(a^2+3b^2)+8ab^2-\frac{9}{2}(a^2+c^2)-3(2b^2+ac)+3+2(c_1+c_2+c_3)$$

(6.34)

The values of the terms in (6.34) are

$$\frac{1}{2}c_2(a-3c)^2=2c_2^3+8c_2(c_1+c_3)^2+32c_2-8c_2^2(c_1+c_3)-32c_2(c_1+c_3)+16c_2^3$$

$$2(c_1+c_3)(a^2+3b^2)=\frac{1}{2}(c_1+c_3)^3+8c_2^2(c_1+c_3)+4c_2(c_1+c_3)^2-32c_2(c_1+c_3)-8(c_1+c_3)^2+\frac{9}{2}(c_1-c_3)(c_1^2-c_3^2)$$
$$+32(c_1+c_3).$$

$$8ab^2 \quad =12c_2(c_1-c_3)^2+3(c_1-c_3)(c_1^2-c_3^2)-24(c_1-c_3)^2$$

$$-\frac{9}{2}(a^2+c^2)-3(2b^2+ac)=-18c_2^2-\frac{27}{2}(c_1+c_3)^2-\frac{9}{2}(c_1-c_3)^2-18c_2(c_1+c_3)+96(c_1+c_2+c_3)-192$$

(6.35)

This yields for the final value of Δ (except for omitted factors)

$$9\Delta=\gamma^2-2(c_1^3+c_2^3+c_3^3)-48c_1c_2c_3-34(c_1^2+c_2^2+c_3^2)+46(c_1c_2+c_2c_3+c_3c_1)+66(c_1+c_2+c_3)-189$$

6.36)

7. THE SCATTERING POWER AND ISODIFFUSION LINES.

Since all the atoms in the hexagonal lattice are of the same kind, the formula for the scattering power (3.1) reduces to

(7.1) $$\sigma = \sigma_0 NkT \frac{|f|^2}{m} \sum_{k\alpha} \sum_{k'\beta} D^{-1}_{\alpha\beta}\binom{Q}{kk'} e^{-iQ\cdot r_{kk'}} Q'_\alpha Q'_\beta$$

In this equation, dashes are placed over the Q_α, in order to show that they are co-ordinates in the Cartesian system. Now write (7.1) in the form

(7.2) $$\sigma = 2\sigma_0 NkT \frac{|f|^2}{m} \sum_{\alpha\beta} A_{\alpha\beta} Q'_\alpha Q'_\beta$$

where $A_{\alpha\beta}$ is given by

(7.3) $$A_{\alpha\beta} = \tfrac{1}{2} \sum_{kk'} D^{-1}_{\alpha\beta}\binom{Q}{kk'} e^{-iQ\cdot r_{kk'}}$$

If the expansion is written out in full, this is found to reduce to

(7.4) $$A_{\alpha\beta} = R\left\{ D^{-1}_{\alpha\beta}\binom{Q}{11} + D^{-1}_{\alpha\beta}\binom{Q}{21} e^{-iQ\cdot r_{21}} \right\}$$

for from (5.7) and (5.8) it follows that

(7.5) $$D^{-1}\binom{Q}{11} = D^{-1}\binom{Q}{22}^{*} \quad \text{and} \quad D^{-1}\binom{Q}{12} = D^{-1}\binom{Q}{21}^{*}$$

The dashed co-ordinates of Q (Q'_1, Q'_2, Q'_3) in the Cartesian system are now replaced by the hexagonal system (Q_1, Q_2, Q_3, Q_4) referred to the basic vectors of the reciprocal lattice by means of the transformation

(7.6) $$Q_1' = \frac{Q_2}{a} \qquad Q_2' = \frac{Q_3 - Q_1}{\sqrt{3}\, a} \qquad (Q_4 = 0)$$

In these co-ordinates, the scattering power becomes

$$\sigma = 2\sigma_0 NkT \frac{|f|^2}{ma^2}\left\{A_{11} Q_2^2 + \frac{2}{\sqrt{3}} A_{12}(Q_1^2 - Q_3^2) + \frac{1}{3} A_{22}(Q_1^2 - 2Q_1Q_3 + Q_3^2)\right\}$$
(7.7)

or, rearranging

(7.8) $$\sigma = \frac{4}{3}\sigma_0 NkT \frac{|f|^2}{ma^2}\left\{(A_{22} + \sqrt{3}A_{12})Q_1^2 + \frac{1}{2}(3A_{11} - A_{22})Q_2^2 + (A_{22} - \sqrt{3}A_{12})Q_3^2\right\}$$

If (7.8) is written in the form *

(7.9) $$\sigma = \frac{4}{3}\sigma_0 NkT \frac{|f|^2}{a^4 Q'} \sum_{\alpha} \frac{-B_\alpha Q_\alpha^2}{\Delta}$$

the coefficients B_α are given by

$$B_1 = R\left\{\Delta_{22} - \sqrt{3}\Delta_{21} + (\Delta_{24} - \sqrt{3}\Delta_{23}) e^{-i\left(\frac{Q_1 - Q_3}{3}\right)}\right\} = \Delta_1 + \Delta_1'$$

$$B_2 = R\left\{\frac{1}{2}(3\Delta_{11} - \Delta_{22}) + \frac{1}{2}(3\Delta_{13} - \Delta_{24}) e^{-i\left(\frac{Q_1 - Q_3}{3}\right)}\right\} = \Delta_2 + \Delta_2'$$

$$B_3 = R\left\{\Delta_{22} + \sqrt{3}\Delta_{21} + (\Delta_{24} + \sqrt{3}\Delta_{23}) e^{-i\left(\frac{Q_1 - Q_3}{3}\right)}\right\} = \Delta_3 + \Delta_3'$$

(7.10)

where use has been made of

(7.11) $$\underline{Q} \cdot \underline{r}_{21} = \frac{Q_1 - Q_3}{3}$$

Introducing the values of Δ_α and Δ_α' from (6.18) and (6.31) the coefficients B_α become

* Where the constant factor $-\frac{a^2 Q'}{m}$ omitted in (6.7) has been re-introduced.

$$3B_1 = \alpha_1\gamma - c_1^2 + c_2^2 + c_3^2 - 4c_2c_3 + 3c_2 + 3c_3 - 8c_1 + 8 - \alpha_1(\alpha_1+\alpha_2)c_{21} + \alpha_2\alpha_3 c_{32} - \alpha_1(\alpha_1+\alpha_3)c_{13}$$
$$+ c_{21} + c_{13} + \cos\frac{2(q_2-q_3)}{3}$$

$$3B_2 = \alpha_2\gamma - c_2^2 + c_3^2 + c_1^2 - 4c_3c_1 + 3c_3 + 3c_1 - 8c_2 + 8 - \alpha_2(\alpha_2+\alpha_3)c_{32} + \alpha_3\alpha_1 c_{13} - \alpha_2(\alpha_2+\alpha_1)c_{21}$$
$$+ c_{32} + c_{21} + \cos\frac{2(q_3-q_1)}{3}$$

$$3B_3 = \alpha_3\gamma - c_3^2 + c_1^2 + c_2^2 - 4c_1c_2 + 3c_1 + 3c_2 - 8c_3 + 8 - \alpha_3(\alpha_3+\alpha_1)c_{13} + \alpha_1\alpha_2 c_{21} - \alpha_3(\alpha_3+\alpha_2)c_{32}$$
$$+ c_{13} + c_{32} + \cos\frac{2(q_1-q_2)}{3}$$

(7.12)

and re-writing (6.36) for Δ

(6.36) $9\Delta = \gamma^2 - 2(c_1^3+c_2^3+c_3^3) - 48c_1c_2c_3 - 34(c_1^2+c_2^2+c_3^2) + 46(c_1c_2+c_2c_3+c_3c_1) + 66(c_1+c_2+c_3) - 189$

and with definitions

$$\gamma = 9(c_1c_2+c_2c_3+c_3c_1) - 24(c_1+c_2+c_3) + 16 \qquad \alpha_\mu = 2(c_1+c_2+c_3) - 3c_\mu - 4$$

(7.13) $c_{\alpha\beta} = \cos\frac{q_\alpha - q_\beta}{3}$ $\qquad c_\alpha = \cos q_\alpha$

the scattering power is given explicitly as a function of $\underline{Q}$.

For the purpose of calculation it is worthwhile to separate the B_α into the parts Δ_α , Δ'_α , because

$$3(\Delta'_1 q_1^2 + \Delta'_2 q_2^2 + \Delta'_3 q_3^2) = \left[q_1^2 + q_2^2 - (\alpha_1 q_1 - \alpha_2 q_2)^2\right]\cos\frac{q_2-q_1}{3} + + q_1^2\cos\frac{2}{3}(q_2-q_3) + \quad +$$

(7.14)

The problem of finding an analytical expression for the "extra spots" or intensity maxima of the background radiation, when the experimental arrange-ments are specified, is rather complicated, (Born and Sarginson, 1941; Sarginson, 1942). On the other hand, the well-known conditions for selective reflections have been shown (e.g. Born, 1942-43) to be equivalent to the statement that the intensity distribution of the Laue scattering has infinitely high and sharp maxima when

(7.15) $$\underline{Q} = \underline{k} - \underline{k}' = \underline{Q}^h$$

where

(7.16) $$\underline{Q}^h \cdot \underline{a}_\alpha = 2\pi h_\alpha \qquad (\alpha = 1, 2, 3)$$

and the h_α are integers. The similarity of this with

(7.17) $$\underline{r}^l \cdot \underline{b}_\alpha = l_\alpha$$

has suggested (Lonsdale and Smith, 1941; Jahn 1941-42; Weigle 1941-42) that the vectors $\underline{Q}/2\pi$ be interpreted as position vectors in the space of the reciprocal lattice. Thus the reciprocal lattice points correspond to selective reflections, which will be surrounded by a distribution $\sigma(\underline{Q})$ of background scattering. It has thus become customary to express the results of observations in the reciprocal space and compare them directly with theory.

If the formula (7.1) for the scattering power is written in the form

(7.18) $$\sigma = \sigma_0 NkT \frac{|f|^2}{m} d(\underline{Q})$$

where

(7.19) $$d(\underline{Q}) = \sum_{k\alpha} \sum_{k'\beta} D^{-1}_{\alpha\beta}\left({\underline{Q} \atop kk'}\right) e^{-i\underline{Q}\cdot\underline{r}_{kk'}} Q'_\alpha Q'_\beta$$

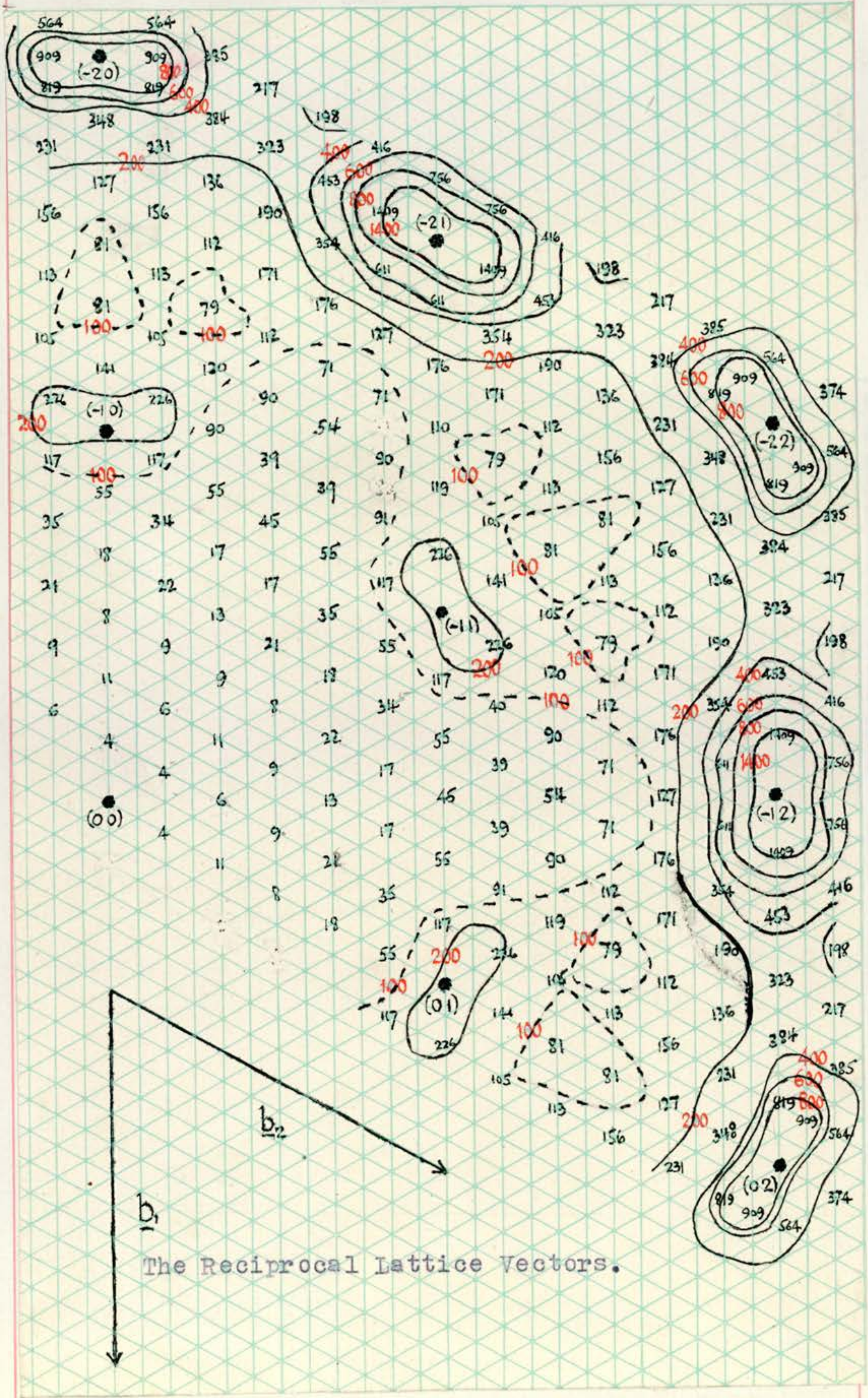
the function $d(Q)$ is known as the "diffusion function" (Born, 1942-43) since it describes the diffusion of scattered intensity about a Laue spot, in virtue of the thermal motion. The so-called "surfaces of isodiffusion" $d(Q) = \text{const.}$, give a graphical representation of the scattering.

In the present case, the isodiffusion function is given from (7.9) by

$$d(Q) = \frac{4m}{3a^4Q'} \sum_{\alpha} \frac{-B_\alpha Q_\alpha^2}{\Delta} \tag{7.20}$$

The process of calculating this function can be considerably reduced on account of various symmetry relations. In the first place, the determinant Δ and the three co-efficients Δ_α are periodic in the Q_α . Then, it is easily shown that replacing the point (Q_1, Q_2, Q_3) by $(-Q_2, -Q_3, -Q_1)$ corresponds to a rotation of 60° in the plane $Q_4 = 0$. Δ is invariant under such substitution and the triad (B_1, B_2, B_3) becomes (B_2, B_3, B_1). Thus it follows that $d(Q)$ is invariant under 60° rotations in the plane $Q_4 = 0$, and so it is only necessary to evaluate it in one sextant. Further, replacing the point $(x - \frac{y}{2}, y, -x - \frac{y}{2})$ by $(-x - \frac{y}{2}, y, x - \frac{y}{2})$ corresponds to a reflection in the line $Q_2 + 2Q_1 = 0$. Inspection shows that (B_1, B_2, B_3) becomes (B_3, B_2, B_1) , so that $d(Q)$ is invariant with respect to reflections in the six lines of the type $Q_2 + 2Q_1 = 0$, and so it is only necessary to calculate it for a sector of 30°.

FIGURE LII. The Isodiffusion Lines of a Close-Packed Hexagonal Lattice in the Plane $Q_4 = 0$.



The Reciprocal Lattice Vectors.

The isodiffusion function $d(Q)$ is calculated from (7.20) for a network of points lying in the plane $Q_4 = 0$. They form a lattice which has unit vectors in the plane $Q_4 = 0$ of magnitude $\frac{1}{6}$th of the reciprocal lattice vectors. In order to check the accuracy of the calculation, the points were taken in a sector of 60^0, so that each value is evaluated twice. The results, which include the nine reciprocal lattice points $(0,0), (0,1), (-1,0), (-1,1), (-1,2), (-2,0), (-2,1), (-2,2), (0,2)$ where the co-ordinates refer to the axes Q_1, Q_2 are shown in Fig. III. The numbers plotted are actually the values of $-\frac{120}{4\pi^2}\sum_{\alpha}\frac{B_\alpha Q_\alpha^2}{\Delta}$ and to get the true diffusion function, have to be multiplied by the factor $\frac{4\pi^2}{120} \times \frac{4m}{3a^4 Q'}$ where, of course, Q' is obtained from the elastic constants in the manner already described. This factor will, naturally, only change the scale of the isodiffusion lines, but not their form. The isodiffusion lines in Fig. III were drawn from the numbers plotted.

From this chart of the isodiffusion lines in the plane $Q_4 = 0$, it is seen that the most intense scattering is represented by those areas which lie close to the points of the reciprocal lattice. These areas of intense scattering are, of course, the so-called "extra spots," which are surrounded by a weak background. Nevertheless, although the background is relatively weak, it possesses a considerable amount of fine structure. The "extra spots" associated with the first ring of reciprocal lattice points are almost isolated by regions of very low scattering power. However, there are ridges of higher scattering power connecting the second ring of reciprocal lattice points.

Further general features of the chart are that it is invariant for 60^0 rotations about the origin, and for reflections in any of the twelve lines joining the second ring of reciprocal lattice points to the origin. Since it can be shown that these features follow from general symmetry considerations, they must be a general consequence of the close-packed arrangement, and not of the particular assumption of central forces. Another feature of the close-packed arrangement is that the isodiffusion function itself apart from the factors Q_α^2, is periodic for displacements of three cells in the reciprocal lattice.

It is rather difficult to see what features are general consequences of the assumption of central forces. In the general case, the equation for an isodiffusion line will contain the seven atomic constants. By the assumption of central forces, these seven atomic constants can be expressed in terms of one independent constant φ'. Thus, the particular form of the isodiffusion lines within the general framework of the features discussed above, is a direct result of the assumption of central forces.

The innermost contour around each reciprocal lattice point of the chart approximates very closely to the isodiffusion lines obtained by Begbie (1947) for the limiting case of the Jahn approximation. This is only to be expected, since Begbie used the elastic constants of Beryl, which as has been stated earlier, satisfy approximately the conditions required for central forces. The general shape of the contours changes as one proceeds outwards from a reciprocal lattice point.

There are no signs of the very strong streaks connecting the Laue spots, which have been reported by Dr. Lonsdale (1946) for the case of ice and ammonium fluoride. This would suggest that the origin of these streaks (Born, 1946) is not due to the ordinary thermal motion, but that there exist in these crystals, atoms, which have two possible positions of equilibrium. In the case of ice, the hydrogen atoms are assumed to lie on a line joining two oxygen atoms. The equilibrium position of the hydrogen atom is not at the mid point of this line, but at a position which is nearer to either one or the other of the oxygen atoms. A survey of the evidence for this is given in a paper by Miss Penny, (1947). If it is assumed that the oxygen atoms can exchange hydrogen atoms, this would lead to a statistical distribution of the hydrogen atoms. Professor Born has shown that this would give rise to a continuous distribution of scattering power in reciprocal space.

It is to be noted that the chart cannot be extended indefinitely in Q-space, for the general formula (3.1), for the scattering power, is valid only for points of Q-space which are not too far from the origin. This distance depends on the temperature. A full discussion of the validity of the general theory is given in the report by Born (1942-43).

Finally, it should be remembered that the calculation has been made using a model in which only the forces between next neighbours are considered. The neglect of long-range forces will be of little influence for long waves (corresponding Q vectors will lie near a reciprocal lattice point.), but will be very essential for waves of the same order of length as the lattice constant. Thus, in the case of an ionic lattice, where long-range forces are important, the value obtained above for the isodiffusion function for those wave vectors which lie in the region between the reciprocal lattice points can be regarded only as a first approximation. As has been stated by Begbie (1947) the reason for using a model, which certainly is not a good picture of reality is that the method of next neighbours can be generalised; it can be used for all kinds of substances, and all kinds of symmetry.

SUMMARY.

The dynamical properties of a crystal for small vibrations can be described by the set of coefficients of the potential energy forming the dynamical matrix. The elastic constants and many other observable quantities can be calculated in terms of the elements of the dynamical matrix, but, in general, the reverse does not hold. On the assumptions that only central forces need to be considered, and that only next-neighbour atoms act on one another, the dynamical matrix for a close-packed hexagonal lattice is expressed in terms of one atomic constant, which can be determined by comparing the expressions for the elastic constants with experiment. The Fourier transform of the dynamical matrix and its reciprocal, which in first approximation is proportional to the scattering matrix, are then calculated. A diagram of the equidiffusion lines, which covers a part of reciprocal space containing nine lattice points, is drawn. The diagram shows that the "extra spots" are surrounded by a weak background, which exhibits considerable fine structure. The equidiffusion lines constructed for the vicinity of the selective reflections (Jahn case) agree with those calculated by Begbie for Beryl. No trace is found of the intense star pattern observed by Lonsdale for ice and ammonium fluoride.

REFERENCES (PART ONE).

Begbie, 1947. Proc. Roy. Soc. A 188, 189.

Begbie and Born, 1947. Proc. Roy. Soc. A 188, 179.

Born, 1923. Atomtheorie des festen Zustandes. Leipzig, Teubner.

Born, 1942. Proc. Camb. Phil. Soc. 38, 82.

Born, 1942-43. Rep. Progr. Phys. 9, 294.

Born, 1946. Nature, Lond. 158, 830.

Born and Oppenheimer, 1927. Ann. Phys., Lpz., 84, 551.

Born and Sarginson, 1941. Proc. Roy. Soc. A 179, 69.

Debye, 1913. Verh. dtsch. phys. Ges. 15, 678, 738, 857.

Ewald, 1923. Kristalle und Rontgenstrahlen. Berlin. Springer.

Jahn, 1941. Nature, Lond., 147, 511.

Jahn, 1942. Proc. Roy. Soc. A 179, 320.

Lonsdale, 1942-43. Rep. Progr. Phys., 9, 256.

Lonsdale, 1946. Nature, Lond. 158, 582.

Lonsdale and Smith, 1941. Proc. Roy. Soc. A 179, 8.

Penny, 1947. Proc. Camb. Phil. Soc. 44, 423.

Sarginson, 1942. Proc. Roy. Soc. A 180, 305.

Waller, 1925. Diss. (Uppsala).

Weigle, 1941. Helv. Phys. Acta. 14, 595.

Weigle, 1942. Helv. Phys. Acta. 15, 162.

PART II.

ON THE FINE STRUCTURE IN THE INFRA-RED SPECTRUM OF IONIC CRYSTALS.

8. INTRODUCTION.

In a paper on the quantum theory of pyroelectricity (Born, 1945) Professor Born has pointed out that observations of certain phenomena are at variance with the results predicted by lattice dynamics, as worked out in his book, "Atomtheorie des festen Zustandes" (Born, 1923). As an example, he discusses the theory of pyroelectricity. According to theory, the pyroelectric moment should obey a T^4- law for low temperatures, while the careful experiments of Ackermann (1915) show that a T^2- law would give much better agreement with observation. Coupled with this are the many new and accurate observations of electrical, optical and X-ray phenomena produced by the Raman school of Indian physicists, which have led them to deny the validity of the whole theory of lattice dynamics. They propose an alternative theory, which will be mentioned later.

The reason for discrepancy between experiment and theory is that Professor Born's book was written before the discovery of quantum mechanics. It is based on the Bohr modification of optics and classical mechanics and therefore does not obtain all the more refined details. Although quantum mechanics have been in existence for nearly 25 years, it is only recently that the investigation of the optical properties of a crystal has been taken up from the modern point of view. The method is described in the paper on pyroelectricity (Born, 1945) and leads to the required T^2-law for the temperature dependence of the pyroelectric moment. The principle of the method is that the wave function for a system such as a crystal can be written in the form (Born and Oppenheimer, 1927)

(8.1) $$\psi(x,X) = \chi(X)\,\varphi(x,X)$$

where X represents the co-ordinates of the nuclei, and x those of the electrons. Now any physical property (e.g. the electric moment) of the crystal will be represented by an operator, which is a function of both the nuclear co-ordinates X and the electronic co-ordinates x ~~(e.g. the electric moment)~~ and which acts on the wave function (8.1). The properties of the system are given by the matrix elements of the operators, which can be formed in two steps. The first step consists in building the electronic matrix elements with respect to the function $\varphi(x,X)$, which is a solution of the wave equation when the nuclei are considered fixed in the positions X. The second step consists in forming the matrix elements between the different vibrational states. In general the system can be considered to be in the electronic ground state. The corresponding wave function can only be calculated by solving the electronic problem explicitly, and hence the electronic matrix elements are assumed to be definite but unknown functions of the nuclear co-ordinates. They can be expanded with respect to small displacements from the equilibrium position of the particles and then the vibrational matrix elements can be formed. Not only has the quantum mechanical approach been successful in its application to pyroelectricity, but it has also been used in giving a satisfactory explanation of the Raman effect in crystals, e.g. rocksalt (Born and Bradburn, 1947) and diamond (Smith, 1948). The purpose of the present investigation is to see how far this quantum mechanical approach can go in explaining the fine structure which has been observed in the infra-red absorption bands of ionic crystals.

A cubic crystal of the NaCl type should possess according to the lattice theory (Born, 1923) only one frequency which would respond to infra-red light, the corresponding vibration being caused by the motion of the positive ions, against the negative ones.

One would therefore expect a single maximum in absorption and in reflection. Pauli (1925) attempted to account for the absorption by suggesting that the main vibration should be damped, as on account of the anharmonic character of the potential function, the main vibration becomes coupled to combinations of the other normal vibrations. In 1930, however, Czerny (1930) initiated a series of experiments, with the aim of determining the refractive index and the extinction co-efficient of rock-salt between 30 μ and 100 μ, a spectral region containing the eigen frequency of NaCl. Czerny took great pains to purify his spectrum from all traces of wavelengths shorter than those under consideration, by means of suitable filters, and preliminary reflection of the incident light from residual ray plates. He measured the transmitting and reflecting power of rock salt, and later extended his experiments to sylvine in collaboration with Barnes (Barnes and Czerny, 1931). The reflecting power of the crystals showed a very broad maximum whose centre of gravity did not coincide with the lattice vibration. In order to determine the eigen frequency, measurements were first made with crystalline plates and finally by evaporating rock salt and sylvine in a vacuum to form layers a few μ thick on thin transparent films of nitro-cellulose. The surprising result of these observations was the discovery of two subsidiary maxima in absorption and reflection for rock salt and sylvine. Czerny found that he could represent the reflective power very well by using a Drude formula for the main vibration and the principal subsidiary one. While the observed values of the extinction co-efficient agreed quite well with those calculated from the Drude formula between 30 μ and 46 μ, below 30 μ they were approximately one thousand times smaller then those calculated. On the long wavelength side Cartwright and Czerny (1933-34) found that the extinction co-efficient retained much higher values than expected from the Drude formula. Similar results have been found for all the alkali halides. Following the publication of these results, Born and Blackman (1933) using classical mechanics investigated the effect of third order terms in the potential energy in the case of a linear chain. Blackman (1933-36) extended this treatment to the three-dimensional lattice of the $NaCl$ type. These investigations gave a possible qualitative interpretation of the subsidiary maxima.

Quite extraordinary results were obtained in experiments on absorption and reflection of MgO by Barnes, Brattain and Seitz (1935). Using both thin plates and evaporated films they observed a great number of narrow weak absorption bands from 6 μ onwards, superimposed on a main absorption maximum at 15.4 μ. On the other hand, Fock (1934) found only three absorption maxima. Barnes, Brattain and Seitz developed a quantum mechanical theory for the absorption of a three-dimensional lattice of the $NaCl$ type in which third order terms are considered in the potential energy. By making the assumption that the maxima of the density of the normal vibrations coincide with the boundary of the frequency surfaces in reciprocal space, they obtained an extremely complicated secondary structure. The validity of this assumption is very doubtful. Another attempt to explain the complicated secondary structure has been made by Raman (1947), by using a few lattice frequencies and several orders of their combination frequencies.

However, another determination of the absorption of MgO has just been made by Willmott, (to be published in "Nature"). No trace whatsoever was found of the complicated secondary structure, and Willmott concludes that the anomalous results obtained by Barnes, Brattain and Seitz were due to considerable scattering of the short wave-length radiation from their source.

Another paper on infra-red absorption has been published recently by Pomeranchuk (1943), in which it is claimed that the energy of interaction of a crystal, with a centre of symmetry in an electric field, must vanish, unless there is attributed to each ion a polarisability which is a function of the position of all the atoms in the lattice. A detailed theory is not given, but Pomeranchuk deduces that the width of the infra-red absorption, lines should be proportional to the square of the temperature and not to the temperature itself, as had been shown by Pauli (1925) for the case of a linear chain with a cubic interaction potential function.

A general account of dispersion in the far infra-red is to be found in "Reports on Progress in Physics," by Kellner in 1941 and "Ergebnisse der exakten Naturwissenschaften," by Matossi (1938).

In the following pages the theory of normal dispersion in crystals is developed on the assumption that the electric moment, as has been explained already, is a function of the nuclear co-ordinates. This leads to a first order line spectrum with a continuous secondary structure superposed on it.

By making suitable assumptions about the form of the distribution of the second order combination frequencies, it is shown that the continuous secondary structure behaves qualitatively as if the crystal had a few additional absorption lines. Detailed calculations are given for the case of sodium chloride.

9. THE THEORY OF DISPERSION IN SOLIDS.

The classical theory of the optical properties of solids is based upon Maxwell's equations for an uncharged polarisable medium

$$\operatorname{div}(\underline{\mathcal{E}} + 4\pi \underline{\mathcal{M}}) = 0 \qquad \operatorname{div} \underline{\mathcal{H}} = 0$$

$$\operatorname{curl} \underline{\mathcal{E}} = -\frac{1}{c}\frac{\partial \mathcal{H}}{\partial t} \qquad \operatorname{curl} \underline{\mathcal{H}} = \frac{1}{c}\frac{\partial \mathcal{E}}{\partial t} + \frac{4\pi}{c}\frac{\partial \mathcal{M}}{\partial t} + \frac{4\pi \mathcal{J}}{c} \tag{9.1}$$

where $\underline{\mathcal{M}}$ is the electric moment per unit volume and $\mathcal{J}$ is the current per unit area. The magnetic moment per unit volume has been neglected and in all the applications to be considered here, it can be assumed that $\mathcal{M}$ and $\mathcal{J}$ are related to $\underline{\mathcal{E}}$, the electric field intensity by the equations

$$\underline{\mathcal{E}} = \underline{E}\, e^{-i\omega t} + \underline{E}^{*} e^{i\omega t} \qquad \underline{\mathcal{M}} = \underline{M}' e^{-i\omega t} + \underline{M}'^{*} e^{i\omega t} \qquad \mathcal{J} = \underline{J} e^{-i\omega t} + \underline{J}^{*} e^{i\omega t}$$

$$M'_{\alpha} = \sum_{\beta} P_{\alpha\beta} E_{\beta} \qquad J_{\alpha} = \sum_{\beta} \sigma_{\alpha\beta} E_{\beta} \tag{9.2}$$

where $P_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are the polarisability and the conductivity tensors of the medium. Maxwell's equations in a material medium are phenomenalogical in so far as these tensors are phenomenalogical descriptions of the medium.

Among the many attempts that have been made to base the equations on more or less definite atomic models and to deduce the dielectric tensor from atomic properties, Ewald's (1912, 1916) theory is the most precise. Originally he set out to show that an orthorhombic lattice arrangement of isotropic atoms can account for optical anisotropy in crystals. In his treatment, the isotropic atoms are represented by isotropic harmonic oscillators, which he placed on a simple rhombic lattice of infinite extent. He showed that if all the oscillators vibrate with the same frequency and with phases corresponding to the passage of a plane wave, the resultant electromagnetic field has the same phase at the lattice points as the oscillators themselves. For a given wave-length and direction of propagation, it is possible to choose a frequency such that the electro-magnetic field just suffices to maintain the assumed vibrations of the oscillators. A self-sustaining oscillation of this kind, corresponds to the passage of an optical wave.

The oscillaters in the Ewald theory correspond to the electronic oscillations within the atoms themselves. If the atoms are charged, i.e. the lattice is ionic, the ions will move as a whole under the influence of the electro-magnetic field. But, as it is well-known, the lattice particles are so closely coupled, that they do not oscillate independently of one another. It is not possible, therefore, to treat the ions as individual oscillators and apply the Ewald theory directly. Born,(1923), has extended the Ewald theory, by assuming, much as in the original case, that all the ions vibrate with the same frequency, and with phases corresponding to the passage of a plane wave. Since the electro-magnetic field, together with the other applied forces must just suffice to cause the assumed vibration, Born is able to obtain on the one hand, equations of optics, in agreement with the Maxwell theory, and on the other hand, equations to determine the dielectric tensor from the lattice forces. In this treatment, the motion of the lattice particles has to be dealt with by classical mechanics. However, in a paper by Dr. Huang, to be published soon, the quantum mechanical treatment of the lattice motion is given, and the result agrees exactly with the classical theory.

Such detailed considerations will not be employed here. Instead, the method of introducing the theory of normal dispersion (Sections 9 - 12), will follow closely the manuscript of a book, to be published in the near future, by M. Born and K. Huang. The formulae developed by them for a general atomic system are modified for the particular case of crystal lattices, and when necessary, put in a form more suited to the present purpose. The crystal will be treated as if it were a molecule in which an electric moment is produced by an applied field. The field will be treated according to classical electrodynamics ~~mechanics~~, but quantum mechanics applied to the crystal itself. This semi-classical approach has the disadvantage that the classical theory of radiation does not account for spontaneous emission, and hence leads to the result that the radiation damping, being solely due to induced effects, depends on the incident intensity. On the other hand, the semi-classical method has the decided advantage over the Dirac theory of radiation that, in obtaining the polarisability, the order of perturbation theory required, is halved. In the effects to be discussed, first order perturbation theory will be used, but to obtain the equivalent results, using the Dirac theory, second order perturbations would be needed, with a corresponding increase in the complexity of the calculations.

Let H_M denote the Hamiltonian of the system, and suppose it is acted upon by an electric field of the form

$$\underline{\mathcal{E}} = \underline{E}\, e^{-i\omega t} + \underline{E}^{*}\, e^{i\omega t}$$

(9.3)

On account of the action of the external electric field the energy of the system becomes changed by $H' = -\underline{M}.\underline{\mathcal{E}}$ where $\underline{M}$ is the operator electric moment of the unperturbed system. This gives for the total Hamiltonian

(9.4) $$H = H_M - \underline{M}.\underline{\mathcal{E}}$$

The interaction term H' is now treated in the well-known manner as a perturbation in the time-dependent Schrödinger equation, which causes transitions from one state to another. If the field is zero, the system is unperturbed, and cannot change its state. If, on the other hand, the field is finite, scattering and induced emission or absorption of the light will take place.

Let the stationary states of the unperturbed system be ψ_r, E_r [*] where

(9.5) $$H_M \psi_r = E_r \psi_r$$

and try to obtain a solution of

(9.6) $$(H_M + H')f = -\frac{\hbar}{i}\frac{\partial f}{\partial t}$$

which reduces to a given state ψ_0 at a time $t=0$. If f is expanded in the usual way,

(9.7) $$f = \sum_r a_r \psi_r e^{-i/\hbar E_r t}$$

and substituted in the Schrödinger equation (9.6), there arise equations for the coefficients a_r of the form

(9.8) $$-\frac{\hbar}{i}\dot{a}_r = \sum_k H'_{rk} a_k e^{-i/\hbar (E_k - E_r)t}$$

(9.9) $$H'_{rk} = \int \psi_r^* H' \psi_k \, d\tau$$

The expansion co-efficients are, of course, dependent on time, and $|a_r|^2$ is interpreted as the probability of finding the system in the state $|a_r|^2$ at the time t.

The initial conditions are that at $t=0$, $a_0 = 1$ and all the other $a_r = 0$. For small times, approximate solutions of (9.8) can be obtained by inserting the initial values of the co-efficients a_k in the right-hand side of the equation. If this is done,

---

[*] The amplitude of the electric field is denoted by E, but this should not lead to confusion.

and it is noted, using (9.3) that

(9.10) $$H'_{rk} = -\underline{M}_{rk}.\left(\underline{E}\,e^{-i\omega t} + \underline{E}^{*}e^{i\omega t}\right)$$

The equations for the co-efficients a_r become

(9.11) $$-\frac{\hbar}{i}\,\dot{a}_r = -\underline{M}_{r0}\cdot\left\{\underline{E}\,e^{-i/\hbar(E_0-E_r+\hbar\omega)t} + \underline{E}^{*}e^{-i/\hbar(E_0-E_r-\hbar\omega)t}\right\}$$

The integral of this equation, that vanishes at $t=0$, is

(9.12) $$a_r = \underline{M}_{r0}.\left\{\underline{E}\,\frac{1-e^{-\frac{i}{\hbar}(E_0-E_r+\hbar\omega)t}}{E_0-E_r+\hbar\omega} + \underline{E}^{*}\,\frac{1-e^{-i/\hbar(E_0-E_r-\hbar\omega)t}}{E_0-E_r-\hbar\omega}\right\}$$

Unless one of the relations

(9.13) $$E_0-E_r\pm\hbar\omega=0$$

is nearly satisfied, a_r oscillates very rapidly about the value zero. Thus it may be said that the system remains in the state ψ_0, and behaves as if it were undergoing forced oscillations, far from resonance. On the other hand, when either one of the relations in (9.13) is satisfied, the system resonates and changes its state. In the case of resonance, $|a_r|^2$ is the probability that, at the time t, the system is found in the state ψ_r. Since $\hbar\omega$ is positive, the case in which $E_0-E_r=\hbar\omega$ must correspond to induced emission, while the case in which $E_r-E_0=\hbar\omega$ to absorption.

In order to calculate the scattering of light by the semi-classical method, when the frequency is not too near resonance, it is usual to take the mean value of the induced electric moment, with respect to the wave functions given above (Placzek, 1934). Here, the mean value of the perturbation energy H' is evaluated, and the electric moment is obtained by comparing this energy with the energy that would be produced by a classical moment of the form

$$\underline{\mathcal{M}} = \underline{M}'e^{-i\omega t} + \underline{M}'^{*} e^{i\omega t} \tag{9.14}$$

and the polarisability tensor is introduced in the form

$$M'_{\alpha} = \sum_{\beta} P_{\alpha\beta} E_{\beta} \tag{9.15}$$

The energy produced by this moment, interacting with the applied field is

$$-\ \underline{\mathcal{M}}.\underline{\mathcal{E}} = -\left\{\sum_{\alpha} M'_{\alpha} E_{\alpha} e^{-2i\omega t} + M'^{*}_{\alpha} E^{*}_{\alpha} e^{2i\omega t} + M'_{\alpha} E^{*}_{\alpha} + M'^{*}_{\alpha} E_{\alpha}\right\}$$

$$= -\left\{\sum_{\alpha\beta} P_{\alpha\beta} E_{\alpha} E_{\beta} e^{-2i\omega t} + P^{*}_{\alpha\beta} E^{*}_{\alpha} E^{*}_{\beta} e^{2i\omega t} + P_{\alpha\beta} E^{*}_{\alpha} E_{\beta} + P^{*}_{\alpha\beta} E_{\alpha} E^{*}_{\beta}\right\} \tag{9.16}$$

The mean value of the interaction energy H' say $\mathcal{H}'$, is

$$\mathcal{H}' = -\int f^{*}\underline{M}.\underline{\mathcal{E}}\, f\, d\tau \tag{9.17}$$

Substituting the expansion of f from (9.7) this becomes

$$\mathcal{H}' = -\underline{M}_{00}.\underline{\mathcal{E}} - \sum_{r}{}' \left\{a_r \underline{M}_{0r}.\underline{\mathcal{E}}\, e^{i\omega_{0r}t} + a^{*}_{r} \underline{M}_{r0}.\underline{\mathcal{E}}\, e^{-i\omega_{0r}t}\right\} \tag{9.18}$$

The first term of this equation represents the energy due to the permanent moment of the system, and will not be considered further. Substituting the value of a_r from (9.12), the value of the next term is

$$-\sum_r{}' \left\{ \frac{\underline{M}_{r0}.\underline{E}\{\underline{M}_{0r}.\underline{E}e^{-2i\omega t} + \underline{M}_{0r}.\underline{E}^*\}}{\hbar(\omega_{0r}+\omega)} + \frac{\underline{M}_{r0}.\underline{E}\{\underline{M}_{0r}.\underline{E}^* e^{2i\omega t} + \underline{M}_{0r}.\underline{E}\}}{\hbar(\omega_{0r}-\omega)} \right\}$$

(9.19)

where $\hbar\omega_{0r} = E_0 - E_r$

The value of $\mathcal{H}'$ is obtained by adding the conjugate complex expression to (9.19). The result has the same form as (9.16). By comparing co-efficients of $e^{-2i\omega t}$, the polarisability is seen to be given by

$$(9.20)\quad \left(P_{\alpha\beta}^{\omega}\right)_{00} = \frac{n_0}{\hbar}\sum_r \left\{ \frac{(M_\beta)_{0r}(M_\alpha)_{r0}}{\omega_{r0}-\omega} + \frac{(M_\alpha)_{0r}(M_\beta)_{r0}}{\omega_{r0}+\omega} \right\}$$

where n_0 is the number of systems per unit volume. This is the usual dispersion formula, e.g. Placzek, (1934).

The thermal average of this quantity gives the polarisability which has to be used in constructing the mean electric moment of Maxwell's theory ($\underline{\mathcal{M}} = \frac{1}{4\pi}(\underline{D} - \underline{\mathcal{E}})$).

10. PLACZEK'S APPROXIMATION.

If the wave functions of the system can be taken as the product of the electronic wave function $\varphi(x,X)$ for fixed nuclei and the nuclear wave function $\chi(X)$ as in (8.1), the expression for the polarisability can be simplified by a method due to Placzek (1934). In this case, the energy levels are represented by sums of electronic energies E_n and much smaller vibrational energies ε_v

(10.1) $$E_r = E_n + \varepsilon_v$$

Thus the frequencies also split additively

(10.2) $$\omega_{rs} \rightarrow \omega_{nv}, \quad \omega_{n'v'} = \omega_{nn'} + \omega_{vv'}$$

where $\omega_{vv'}$ is small compared with $\omega_{nn'}$. Therefore one can approximately neglect $\omega_{vv'}$ in the denominators of (9.20) except for the diagonal elements $\omega_{nn} = 0$, provided always that the incident frequency ω is not too close to any one of the transition frequencies ω_{on} of the electronic levels.

If only properties of the electronic ground state are considered, in (9.20)

(10.3) $$o \rightarrow ov$$

where o now means the state of lowest electronic energy. For the intermediate state

(10.4) $$r \rightarrow n, v$$

The intermediate matrix elements of M_α are written in the form

(10.5) $M_\alpha(X)_n = M_\alpha(X)_{0n} = \int \varphi_0^*(x,X)\, M_\alpha(x,X)\, \varphi_n(x,X)\, dx$

then

(10.6) $$M_\alpha(X)_n^* = M_\alpha(X)_{n0}$$

Now the term $r \to 0,v$ is split off from the summation in (9.20), then omitting the index 0 in $\left(P_{\alpha\beta}^{(\omega)}\right)_{0v,0v}$, the approximate expression for the polarisability is

$$\left(P_{\alpha\beta}\right)_{vv} = \frac{n_0}{\hbar} \sum_{v'} \left(\frac{(M_\beta)_{0v,0v'} (M_\alpha)_{0v',0v}}{\omega_{v'v} - \omega} + \frac{(M_\alpha)_{0v,0v'} (M_\beta)_{0v',0v}}{\omega_{v'v} + \omega} \right)$$
$$+ \frac{n_0}{\hbar} \sum_{n} \left(\frac{\sum_{v'} (M_\beta)_{0v,nv'} (M_\alpha)_{nv',0v}}{\omega_{n0} - \omega} + \frac{\sum_{v'} (M_\alpha)_{0v,nv'} (M_\beta)_{nv',0v}}{\omega_{n0} + \omega} \right)$$

(10.7)

In the first sum, the matrix elements occurring have the form

(10.8) $$(M_\beta)_{0v,0v'} = \left(M_\beta(X)_{00} \right)_{vv'} = M_\beta(X)_{vv'}$$

They are the vibrational elements of the electronic ground state, and the indices $0, 0$ can be omitted. Since the second sum has resonant maxima at the electronic levels, it will not be considered further. Now the infra-red part of the polarisability is explicitly represented by

(10.9) $$P_{\alpha\beta}{}^{(\omega,X)}{}_{vv} = \frac{n_0}{\hbar} \sum_{v'} \left(\frac{M_\beta(X)_{vv'} M_\alpha(X)_{v'v}}{\omega_{v'v} - \omega} + \frac{M_\alpha(X)_{vv'} M_\beta(X)_{v'v}}{\omega_{v'v} + \omega} \right)$$

where the $M_\alpha(X)$ are regarded as known functions of the nuclear co-ordinates. The refractive properties depend on the thermal average, written thus $\langle P_{\alpha\beta}(\omega, X)_{vv}\rangle$ or explicitly, it is given by

$$\langle P_{\alpha\beta}(\omega, X)_{vv}\rangle = \frac{n_0}{\hbar}\sum_{v'}\left(\frac{\langle M_\beta(X)_{vv'} M^*_\alpha(X)_{vv'}\rangle}{\omega_{v'v}-\omega} + \frac{\langle M_\alpha(X)_{vv'} M^*_\beta(X)_{vv'}\rangle}{\omega_{v'v}+\omega}\right)$$

(10.10)

$$= \frac{2n_0}{\hbar}\sum_{v'}\frac{1}{\omega^2_{v'v}-\omega^2}\left\{\omega_{v'v} R\langle M_\alpha(X)_{vv'} M^*_\beta(X)_{vv'}\rangle + i\omega R^{i}\langle M_\alpha(X)_{vv'} M^*_\beta(X)_{vv'}\rangle\right\}$$

11. THE EXPANSION OF THE ELECTRIC MOMENT.

The formulae of the preceding section show that the polarisability can be expressed in terms of the function $\underline{M}(X)$, or, more correctly, as a function of the vibrational matrix elements $M_\alpha(X)_{vv'}$. It is now necessary to expand the electric moment into a power series of the oscillation amplitudes $u_\alpha\binom{l}{k}$. Similarly, as in the case of the potential energy, the expansion is written

(11.1) $$M_\alpha(X) = M_\alpha^0 + M_\alpha^1 + M_\alpha^2$$

where the upper indices ($0, 1, 2$) denote the order in the nuclear co-ordinates. The last two terms of this equation are given by

(11.2) $$M_\alpha^1 = \sum_\beta \sum_{lk} M_{\alpha,\beta}\binom{l}{k} u_\beta\binom{l}{k}$$

(11.3) $$M_\alpha^2 = \frac{1}{2} \sum_{\beta\gamma} \sum_{ll'kk'} M_{\alpha,\beta\gamma}\binom{l\,l'}{k\,k'} u_\beta\binom{l}{k} u_\gamma\binom{l'}{k'}$$

The co-efficients M_α^0, $M_{\alpha,\beta}\binom{l}{k}$, $M_{\alpha,\beta\gamma}\binom{l\,l'}{k\,k'}$ are the values of $M_\alpha(X)$ and of its derivatives with respect to $X_\beta\binom{l}{k}$, taken for equilibrium. These co-efficients satisfy a number of identities. The first of these are consequences of the periodicity of the lattice. Any quantity which describes an equilibrium property, and depends on only one single particle, $\binom{l}{k}$, must be the same for all cells, and hence independent of l. Thus, $M_{\alpha,}\binom{k}{\beta}$ may be written for $M_{\alpha,\beta}\binom{l}{k}$. In the same way, any equilibrium quantity depending on two points $\binom{l}{k}$, and $\binom{l'}{k'}$ is invariant if l and l' are subject to the same cell displacements and hence, depends only on the difference $l-l'$ ($l_1-l_1', l_2-l_2', l_3-l_3'$) so one can write

$$(11.4) \quad M_{\alpha,\beta\gamma}\binom{ll'}{kk'} = M_{\alpha,\beta\gamma}\binom{l-l'}{kk'}$$

A second set of identities is obtained from the consideration that any translation of the crystal as a whole, does not change its electric moment. Hence, if all the $\underline{u}\binom{l}{k}$ are taken equal, (independent of l and k) M_α^1 , M_α^2 must vanish. Therefore

$$(11.5) \quad \sum_{k} M_{\alpha,\beta}(k) = 0 \qquad \sum_{lkk'} M_{\alpha,\beta\gamma}\binom{l}{kk'} = 0$$

A simpler relation can be found between the coefficients $M_{\alpha,\beta\gamma}\binom{l-l'}{kk'}$ by the following consideration, which applies the condition of the invariance of the electric moment against displacement, to a displacement of the lattice when the particles are not necessarily at their equilibrium positions. The differential of M_α^2 is given by

$$(11.6) \quad dM_\alpha^2 = \sum_{lk\beta} \frac{\partial M_\alpha^2}{\partial u_\beta\binom{l}{k}}\, du_\beta\binom{l}{k}$$

Thus, the condition of invariance is

$$(11.7) \quad \sum_{lk} \frac{\partial M_\alpha^2}{\partial u_\beta\binom{l}{k}} = \sum_{lk}\sum_{l'k'\gamma} M_{\alpha,\beta\gamma}\binom{l-l'}{kk'}\, u_\gamma\binom{l'}{k'} = 0$$

For this to be independent of the displacements $u_\gamma\binom{l'}{k'}$

$$\sum_{lk} M_\alpha\binom{l}{kN} = 0$$

(11.8)

Further relations follow from infinitesimal rotations, but these will not be required.

Now, normal co-ordinates are introduced by

(11.9) $u_\alpha\binom{l}{k} = \frac{1}{\sqrt{m_k}} \sum_{Q\gamma} e_\alpha(k|{}^{Q}_{\gamma})\, e^{i(l,Q)}\, q\binom{Q}{\gamma}$

Then one can write

(11.10) $M'_\alpha = \sum_{Q\gamma} M_\alpha\binom{Q}{\gamma}\, q\binom{Q}{\gamma}$

Here $M_\alpha\binom{Q}{\gamma}$ is given by

$$M_\alpha\binom{Q}{\gamma} = \sum_{\beta l k} \frac{1}{\sqrt{m_k}} M_{\alpha,\beta}{}^{(k)}\, e_\beta(k|{}^{Q}_{\gamma})\, e^{i(l,Q)}$$

(11.11)

there the factor $\sum_{l} e^{i(l,Q)}$ splits off. It is N times a δ - function vanishing except for $\underline{Q} = 0$. Hence

$$M'_\alpha = \sum_{\gamma} M_\alpha(\gamma)\, q\binom{0}{\gamma} \qquad M_\alpha(\gamma) = N \sum_{\beta k} \frac{1}{\sqrt{m_k}} M_{\alpha,\beta}(k)$$

(11.12)

The first order polarisability is therefore due only to vibrations of wave numbers zero or infinite wave-lengths, where each of the simple lattices, corres:-ponding to the points of the base moves like a rigid system.

The matrix elements $q\binom{Q}{j}_{vv'}$ vanish except for transitions belonging to the frequencies $\pm\,\omega\binom{Q}{j}$. Therefore the first order effect is a line spectrum of not more than $3S-3$ lines (omitting the three acoustic branches), each line corresponding to a normal mode of the system of S interpenetrating rigid simple lattices. In the same way it follows from (11.3) and (11.9) that

$$(11.13)\quad M_\alpha^2 = \frac{1}{2}\sum_{\substack{Q\,Q'\\ j\,j'}}\;\sum_{\substack{lk\beta\\ l'k'\gamma}} \frac{1}{\sqrt{m_k m_{k'}}}\, M_{\alpha,\beta\gamma}\binom{l-l'}{kk'}\, e_\beta\left(k\middle|\begin{smallmatrix}Q\\ j\end{smallmatrix}\right) e_\gamma\left(k'\middle|\begin{smallmatrix}Q'\\ j'\end{smallmatrix}\right) e^{i[(l,Q)+(l',Q')]}\, q\binom{Q}{j}\, q\binom{Q'}{j'}$$

If $l-l'$ is replaced by l, the factor $\sum\limits_{l'} e^{i(l,Q+Q')}$ splits off; again it is N times a δ-function of ($Q+Q'$). Hence, in the sum (11.13) only the terms, $Q'=-Q$ appear. Using this fact, one can write

$$(11.14)\quad M_\alpha^2 = \sum_{Q\,j\,j'} M_\alpha\binom{Q}{jj'}\, q\binom{Q}{j}\, q^*\binom{Q}{j'}$$

where

$$(11.15)\quad M_\alpha\binom{Q}{jj'} = \frac{N}{2}\sum_{lkk'}\;\sum_{\beta\gamma} \frac{1}{\sqrt{m_k m_{k'}}}\, M_{\alpha,\beta\gamma}\binom{l}{kk'}\, e^{i(l,Q)}\, e_\beta\left(k\middle|\begin{smallmatrix}Q\\ j\end{smallmatrix}\right) e^*_\gamma\left(k'\middle|\begin{smallmatrix}Q\\ j'\end{smallmatrix}\right)$$

Before proceeding further, it is instructive to consider a special case, where the expression for $\underline{M}$ is simplified in virtue of its physical meaning. At first, it is supposed, that exchange of electrons, between the atoms, can be neglected, so that all the electrons in the system can be assigned to their own nuclei. For simplicity, only the case of a molecule is discussed. Let Z_k be the atomic number of the nucleus k , $X_\alpha(k)$, its co-ordinates; $x_\beta(k,s)$ the co-ordinates of the electrons in the cloud surrounding this nucleus, $s=1,2,\cdots Z'_k$ where Z'_k is the number of these electrons. Hence

$$(11.16) \qquad Z_k - Z'_k = z_k$$

the electro-valency of the particle k (ion or atom) then

$$(11.17) \qquad M_\alpha = e\sum_k \left\{ Z_k X_\alpha(k) - \sum_{s=1}^{Z'_k} x_\beta(k,s) \right\}$$

and

$$(11.18) \qquad 0 = \sum_k \left(Z_k - Z'_k \right) = \sum_k z_k$$

since the total system is neutral. Now is considered the extreme case of atoms, which are only loosely bound together, in such a way, that the electron cloud surrounding the nucleus is unaffected by the motion of the other nuclei, (the approximation of rigid ions). Then the total electronic wave function φ will contain the co-ordinates of the nuclei and electrons only in the combinations

$$(11.19) \qquad x'_\alpha(k,s) = x_\alpha(k,s) - X_\alpha(k)$$

If these relative co-ordinates are taken as the variables, determining the position of the electrons, and substituted into (11.17) one gets

$$M_\alpha = \sum_k \left\{ Z_k X_\alpha(k) - \sum_{s=1}^{Z'} \left[x'_\alpha(k,s) + X_\alpha(k) \right] \right\}$$

$$= e\sum_k \left\{ z_k X_\alpha(k) - \sum_{s=1}^{Z'} x'_\alpha(k,s) \right\} \tag{11.20}$$

The intermediate matrix element of this quantity $M_\alpha(X) = \int \varphi_0^*(x,X) M_\alpha \varphi_0(x,X) dx$ becomes by the substitution (11.19)

$$M_\alpha(X) = \int \varphi_0^*(x') M_\alpha \varphi_0(x') dx' \tag{11.21}$$

where $\varphi_0(x')$ is independent of the X. Using the expression (11.20), one obtains

$$M_\alpha(X) = e\sum_k z_k X_\alpha(k) + \mu^0_\alpha \tag{11.22}$$

where μ^0_α is the electronic contribution to the moment, and independent of the X. In this extreme case, one has therefore

$$M^0_\alpha = e\sum_k z_k X^0_\alpha(k) + \mu^0_\alpha$$

$$M^1_{\alpha,\beta}(k) = e z_k \delta_{\alpha\beta}$$

$$M^2_\alpha = M^3_\alpha = \cdots 0 \tag{11.23}$$

For neutral atoms, ($z_k = 0$), the electric moment is therefore a constant, and for ions, it behaves as if the total charge $e z_k = e(Z_k - Z'_k)$ were concentrated in the nucleus. In general, if the ions are polarisable, and exchange of electrons and free electrons are taken into account, one has

$$M^1_\alpha = e\sum_k Z_k u_\alpha(k) + \mu^1_\alpha$$

$$M^2_\alpha = \qquad\qquad \mu^2_\alpha$$

(11.24)

where $\underline{\mu}^1$, $\underline{\mu}^2$ will be small.

The constant term $\underline{M}^0$, drops out when the vibrational matrix elements are formed, and therefore plays no part in the optical phenomena (unless the rotational levels of a system are included).

12. THERMAL AVERAGES OF PHYSICAL QUANTITIES.

In the last section, the electric moment was expanded in a power series of the displacements of the nuclei from the equilibrium positions, and then normal co-ordinates were introduced. In order to obtain the Maxwell polarisability of the system, these expansions have to be put into (10.10) for the polarisability, and the thermal average taken. Thus, it is necessary to consider thermal averages of the form $A_{vv'}B_{vv'} = N_{vv'}$ where the two functions $A(X)$, $B(X)$, are functions of the nuclear configuration for any transition $v \rightarrow v'$. It is now supposed that $A(X)$ is expanded into a power series.

$$A(X) = A(X^0+u) = A^0 + A^1 + A^2 \tag{12.1}$$

where the upper index indicates the order in u or in the normal co-ordinates, q. At first q will be taken as real. The vibration matrix elements have similar expansions.

$$A_{vv'} = A^0_{vv'} + A^1_{vv'} + A^2_{vv'} \tag{12.2}$$

If $B_{vv'}$ is also expanded, one has for $N_{vv'}$

$$N_{vv'} = N^0_{vv'} + N^1_{vv'} + N^2_{vv'} \tag{12.3}$$

where

$$N^0_{vv'} = A^0_{vv'} B^0_{vv'}$$

$$N^1_{vv'} = A^0_{vv'} B^1_{vv'} + A^1_{vv'} B^0_{vv'}$$

$$N^2_{vv'} = A^0_{vv'} B^2_{vv'} + A^2_{vv'} B^0_{vv'} + A^1_{vv'} B^1_{vv'}. \tag{12.4}$$

Now, every $N^r_{vv'}$ with an odd r, vanishes, for it is a sum of products $A^{r_1}_{vv'} B^{r_2}_{vv'}$ with $r_1 + r_2 = r$ odd; hence, either r_1 is even, and r_2 odd, or vice versa. The corresponding products of the q, have no elements belonging to the same transition, $v \to v'$ (see below).

The $N^r_{vv'}$ for even r are the following

$$N^0_{vv'} = A^0 B^0 \delta_{vv'}$$

$$N^2_{vv'} = (A^0 B^2_{vv'} + A^2_{vv'} B^0) \delta_{vv'} + A^1_{vv'} B^1_{vv'}$$

$$N^4_{vv'} = (A^0 B^4_{vv'} + A^4_{vv'} B^0) \delta_{vv'} + A^2_{vv'} B^2_{vv'} + A^1_{vv'} B^3_{vv'} + A^3_{vv'} B^1_{vv'} \tag{12.5}$$

Now, it is easily seen that $A^0_{vv'}$ only exists for $v = v'$, that is, zero frequency. $A^1_{vv'}$ is zero, unless one oscillator (J), jumps by one, i.e. $v_J \to v_{J\pm1}$ and thus it is associated with the frequencies $\pm\omega_J$. In the same way $A^2_{vv'}$ is associated with the fre:-quencies $\pm\omega_J \pm \omega_{J'}$. Thus it follows that the terms of $N_{vv'}$ may be ordered according to the frequencies to which they belong. The diagonal terms belong to the frequency zero; the term $A^1_{vv'} B^1_{vv'}$ belongs to the frequency $\pm\omega_J$, and $A^1_{vv'} B^3_{vv'}$ to the same frequency, as it is the only jump that is common to the matrix elements of $q_J q^2_{J'}$ and q_J; finally, $A^2_{vv'} B^2_{vv'}$ belongs to the frequencies $\pm\omega_J \pm \omega_{J'}$. Hence one can write, up to the fourth order

(12.6) $$N_{vv'} = N^{0}_{vv'}\,\delta_{vv'} + N^{I}_{vv'} + N^{II}_{vv'}$$

where

$$N^{0}_{vv} = A^{0}_{vv}B^{0}_{vv} + (A^{0}_{vv}B^{2}_{vv} + B^{0}_{vv}A^{2}_{vv}) + A^{0}_{vv}B^{4}_{vv} + B^{0}_{vv}A^{4}_{vv} + A^{2}_{vv}B^{2}_{vv}\,\delta_{JJ'} \qquad \omega_{vv'}=0$$

$$N^{I}_{vv'} = A^{1}_{vv'}B^{1}_{vv'} + (A^{1}_{vv'}B^{3}_{vv'} + B^{1}_{vv'}A^{3}_{vv'}) \qquad \omega_{vv'} = \pm\omega_J$$

$$N^{II}_{vv'} = A^{2}_{vv'}\,B^{2}_{vv'} \qquad \omega_{vv'} = \pm\omega_J \pm \omega_{J'}$$

(12.7)

Now assume the normal co-ordinate expansion

$$A^{1} = \sum_{J} A(J)\,q_J$$

$$A^{2} = \sum_{JJ'} A(JJ')\,q_J\,q_{J'}$$

(12.8)

where all the co-efficients are supposed to be symmetrical in the arguments $J\,J' \ldots\ldots$ and, similarly, for B. All matrix elements can be collected together into groups, which belong to a given type of frequency combination. Here these groups will be restricted to $0,\ \pm\omega_J,\ \pm\omega_J \pm \omega_{J'}$; to each of these belong many transitions $v \to v'$, and it is necessary to calculate the thermal average of these. The matrix elements are given below in Table V..

TABLE V.

	0	$-\omega_J$	ω_J	$-2\omega_J$	$2\omega_J$	$-\omega_J-\omega_{J'}$	$\omega_J+\omega_{J'}$	$-\omega_J+\omega_{J'}$
q_J		$c_J\sqrt{v_J+1}$	$c_J\sqrt{v_J}$					
$q_J q_{J'}$						$c_J c_{J'}\sqrt{(v_J+1)(v_{J'}+1)}$	$c_J c_{J'}\sqrt{v_J v_{J'}}$	$c_J c_{J'}\sqrt{(v_J+1)v_{J'}}$
q_J^2	$c_J^2(2v_J+1)$			$c_J^2\sqrt{(v_J+2)(v_J+1)}$	$c_J^2\sqrt{v_J(v_J-1)}$			

$$c_J = \sqrt{\frac{\hbar}{2\omega_J}}$$

Each matrix element can be multiplied by a factor of modulus one, which can be arbitrarily chosen for one of the transitions $v \to v'$, $v' \to v$, but is conjugate imaginary for the other. Hence, products such as $[f(q)]_{vv'}\,[f(q)]_{v'v}$ are real, and are obtained by squaring the quantities given in Table V.

All physical properties depend on thermal averages of the matrix elements of functions of oscillator amplitudes. If these are expanded in power series, (as above), these matrix elements can be reduced to those given in Table V. Hence, all such averages can be expressed in terms of the averages of the powers of the quantum number of a single oscillator. It is therefore sufficient in the present case to give the averages of v and v^2 . Using the abbreviations

$$Z = \frac{1}{1-e^{-\beta}} \qquad \beta = \frac{\hbar\omega}{kT} \tag{12.9}$$

these become

$$\langle v\rangle = \frac{\sum_{v=0}^{\infty} v e^{-\beta v}}{\sum_{v=0}^{\infty} e^{-\beta v}} = -\frac{1}{Z}\frac{dZ}{d\beta} = -\frac{d\log Z}{d\beta} = \frac{1}{e^{\beta}-1}$$

(12.10)

$$\langle v^2\rangle = \frac{\sum_{v=0}^{\infty} v^2 e^{-\beta v}}{\sum_{v=0}^{\infty} e^{-\beta v}} = \frac{1}{Z}\frac{d^2Z}{d\beta^2} = \frac{d^2\log Z}{d\beta^2} + \left(\frac{d\log Z}{d\beta}\right)^2 = \frac{e^{\beta}+1}{(e^{\beta}-1)^2}$$

(12.11)

The following abbreviations will also be used

(12.12) $$b_{(J)} = \frac{c_J^2}{1-e^{-\beta_J}} = \frac{\hbar/2\omega_J}{1-e^{-\hbar\omega_J/kT}}$$

Elementary calculations lead to the following Table.

TABLE VI.

	ω_J	$-\omega_J$	$2\omega_J$	$-2\omega_J$	$\omega_J+\omega_{J'}$	$-\omega_J-\omega_{J'}$	$\omega_J-\omega_{J'}$	$\omega_{J'}-\omega_J$
$\langle (q_J)_{vv'}(q_J)_{v'v}\rangle$	$b_J e^{-\beta_J}$	b_J						
$\langle (q_J^2)_{vv'}(q_J^2)_{v'v}\rangle$			$2b_J^2 e^{-2\beta_J}$	$2b_J^2$				
$\langle (q_J q_{J'})_{vv'}(q_J q_{J'})_{v'v}\rangle$					$b_J b_{J'} e^{-\beta_J-\beta_{J'}}$	$b_J b_{J'}$	$b_J b_{J'} e^{-\beta_J}$	$b_J b_{J'} e^{-\beta_{J'}}$

So far, only real oscillators have been considered. However, products of matrix elements of complex co-ordinates can always be reduced to those of the real and imaginary parts of the complex co-ordinates. Let

(12.13) $q_\tau = \overset{r}{q}_\tau + i\,\overset{i}{q}_\tau$, then

$$(q_\tau)_{vv'}(q_{\tau'})_{v'v} = (\overset{r}{q}_\tau)_{vv'}(\overset{r}{q}_{\tau'})_{v'v} + i^2(\overset{i}{q}_\tau)_{vv'}(\overset{i}{q}_{\tau'})_{v'v} + i(\overset{i}{q}_\tau)_{vv'}(\overset{r}{q}_\tau)_{v'v}$$

(12.14) $$+\,i(\overset{r}{q}_\tau)_{vv'}(\overset{i}{q}_{\tau'})_{v'v}$$

The last two products are zero as they always contain different oscillators. The first two exist, if $q_{\tau'} = q_\tau$ or q^*_τ . In the first case, the first two terms are equal, but of opposite sign, but in the latter case, they have the same sign. So the only possible product is

(12.15) $$(q_\tau)_{vv'}(q^*_\tau)_{v'v} = 2(\overset{r}{q}_\tau)_{vv'}(\overset{r}{q}_\tau)_{v'v}$$

In the same way,

(12.16) $$(q_\tau q^*_{\tau'})_{vv'}(q^*_\tau q_{\tau'})_{v'v} = 4(\overset{r}{q}_\tau \overset{r}{q}_{\tau'})_{vv'}(\overset{r}{q}_\tau \overset{r}{q}_{\tau'})_{v'v}$$

(12.17) $$(q_\tau q^*_\tau)_{vv'}(q_\tau q^*_\tau)_{v'v} = 2(\overset{r}{q}{}^2_\tau)_{vv'}(\overset{r}{q}{}^2_\tau)_{v'v}$$

All other products vanish.

From the results of this section, it is clear that

(12.18) $$(M_\alpha)_{vv'}(M_\beta)^*_{vv'} = M^0_{\alpha\beta} + M^{I}_{\alpha\beta} + M^{II}_{\alpha\beta}$$

where

(12.19) $M^0_{\alpha\beta} = \left\{ M^0_\alpha M^{0*}_\beta + M^0_\alpha (M^2_\beta)^*_{vv'} + (M^2_\alpha)_{vv'} M^{0*}_\beta + \cdots \right\} \delta_{vv'}$

(1220) $M^{I}_{\alpha\beta} = (M^1_\alpha)_{vv'} (M^1_\beta)^*_{vv'} + \left\{ (M^1_\alpha)_{vv'} (M^3_\beta)^*_{vv'} + (M^3_\alpha)_{vv'} (M^1_\beta)^*_{vv'} \right\}$

(12.21) $M^{II}_{\alpha\beta} = (M^2_\alpha)_{vv'} (M^2_\beta)^*_{vv'}$

$M^0_{\alpha\beta}$ will not be discussed further, for the reasons given at the end of the last section.

If the second term in equation (12.20) for $M^I_{\alpha\beta}$ is dropped (because it is of a lower order then the first one), one has for $M^I_{\alpha\beta}$.

(12.22) $M^I_{\alpha\beta} = \sum_j M_\alpha(j) M_\beta(j)^* \left(q\binom{0}{j}\right)_{vv'} \left(q\binom{0}{j}\right)^*_{vv'}$

The thermal averages, ordered according to the fre: -quencies, are

$$\left\langle M^I_{\alpha\beta}\ {-\omega}\binom{0}{j} \right\rangle = 2\, b\binom{0}{j}\, m_{\alpha\beta}(j)$$

$$m_{\alpha\beta}(j) = M_\alpha(j)\, M^*_\beta(j)$$

$$\left\langle M^I_{\alpha\beta}\ \omega\binom{0}{j} \right\rangle = 2\, b\binom{0}{j}\, e^{-\beta\binom{0}{j}}\, m_{\alpha\beta}(j)$$

(12.23)

In the same way, the second order terms in the moment give

(12.24) $M^{II}_{\alpha\beta} = \sum_{Qjj'} M_\alpha\binom{Q}{j\,j'} M^*_\beta\binom{Q}{j\,j'} \left[q\binom{Q}{j} q^*\binom{Q}{j'} \right]_{vv'} \left[q\binom{Q}{j} q^*\binom{Q}{j'} \right]^*_{vv'}$

with the thermal averages

$$\left\langle M^{II}_{\alpha\beta}\, 2\omega\binom{q}{j}\right\rangle = 2\, b^2\binom{q}{j}\, e^{-2\beta\binom{q}{j}}\, m_{\alpha\beta}\binom{q\,q}{j\,j}$$

$$m_{\alpha\beta}\binom{q\,q}{j\,j} = M_\alpha\binom{q}{j} M^*_\beta\binom{q}{j}$$

$$\left\langle M^{II}_{\alpha\beta}\, -2\omega\binom{q}{j}\right\rangle = 2\, b^2\binom{q}{j}\quad m_{\alpha\beta}\binom{q\,q}{j\,j}$$

(12.25)

$$\left\langle M^{II}_{\alpha\beta}\ \omega\binom{q}{j}+\omega\binom{q'}{j'}\right\rangle = 2\, b\binom{q}{j}\, b\binom{q'}{j'}\, e^{-\beta\binom{q}{j}-\beta\binom{q'}{j'}}\, m_{\alpha\beta}\binom{q\,q'}{j\,j'}$$

$$\left\langle M^{II}_{\alpha\beta}\ -\omega\binom{q}{j}-\omega\binom{q'}{j'}\right\rangle = 2\, b\binom{q}{j}\, b\binom{q'}{j'}\qquad m_{\alpha\beta}\binom{q\,q'}{j\,j'}$$

$$m_{\alpha\beta}\binom{q\,q'}{j\,j'} = M_\alpha\binom{q}{j} M^*_\beta\binom{q'}{j'}$$

$$\left\langle M^{II}_{\alpha\beta}\ \omega\binom{q}{j}-\omega\binom{q'}{j'}\right\rangle = 2\, b\binom{q}{j}\, b\binom{q'}{j'}\, e^{-\beta\binom{q}{j}}\, m_{\alpha\beta}\binom{q\,q'}{j\,j'}$$

$$\left\langle M^{II}_{\alpha\beta}\ -\omega\binom{q}{j}+\omega\binom{q'}{j'}\right\rangle = 2\, b\binom{q}{j}\, b\binom{q'}{j'}\, e^{-\beta\binom{q'}{j'}}\, m_{\alpha\beta}\binom{q\,q'}{j\,j'}$$

(12.26)

In these formulae, the summation over q has again been extended to all the points in reciprocal space.

If one considers the special case of a system with independent rigid atoms, where the electric moment μ_α in (11.24) vanishes, then only the first order thermal average, given by (12.23) exists. In the general case, where the system is not necessarily a crystal, the value of $M_\alpha(j)$ is given by

$$M_\alpha(j) = e\sum_k \frac{z_k}{\sqrt{m_k}}\, e_\alpha(k|j) \tag{12.27}$$

This is real, and hence also the polarisability, (10.10). It follows that

$$\left\langle P_{\alpha\beta}(\omega X)_{vv}\right\rangle = \frac{2n_0}{\hbar}\sum_j \frac{\omega_j b_j}{\omega_j^2-\omega^2}\, m_{\alpha\beta}(j)\,(1-e^{-\beta_j}) \tag{12.28}$$

but, according to (12.12),

$$b_j\,(1-e^{-\beta_j}) = c_j^2 = \frac{\hbar}{2\omega_j} \tag{12.29}$$

Hence,

$$(12.30)\ \langle P_{\alpha\beta}(\omega,X)_{vv}\rangle = \sum_{j} \frac{M_{\alpha}(j)\,M^{*}_{\beta}(j)}{\omega_j^2-\omega^2}$$

This is the classical dispersion formula for ions considered as vibrating mass points, and it would appear that so far, no one has worked out the generalisations which are contained in the preceding general theory.

The remarkable feature of this formula (12.30) is that the dependence on temperature has completely disappeared. This is due to the factor $(1-e^{-\beta j})$ in (12.28) where the term $-e^{-\beta j}$ obviously has its origin in the anti-Stoke's terms $(+\omega_j)$ of the scattering. They produce the "negative dispersion" (Ladenburg, 1921); ordinary and negative dispersion together are thus independent of temperature.

The formula (12.30) will be the main term in the infra-red refraction in ionic crystals, where the resultant charges, $e z_k$, do not vanish. But the general theory developed here adds to these ionic terms, others with the combination frequencies $\pm 2\omega_J, \pm\omega_J \pm \omega_{J'}$, and these will be the dominant ones in non-ionic crystals, where (12.30) vanishes.

In the general case $\langle (P_{\alpha\beta}(\omega X))_{vv}\rangle$ can be written

$$(12.31)\ \langle (P_{\alpha\beta}(\omega,X))_{vv}\rangle = \langle (P^{1}_{\alpha\beta}(\omega,X))_{vv}\rangle + \langle (P^{2}_{\alpha\beta}(\omega,X))_{vv}\rangle$$

where the first term corresponds to the single jump $\pm\omega(j)$ and the second to the double jumps $\pm\omega(j)\pm\omega(j')$.

They are second and fourth order with respect to the expansion (11.1). Their explicit expressions are obtained by substituting (12.23), (12.25), (12.26), in (10.10). After some reduction, one obtains

$$(12.32)\quad \left\langle \left(P^1_{\alpha\beta}\omega\right)_{vv}\right\rangle = \frac{2n_0}{\hbar}\sum_{v'}\frac{1}{\omega^2_{vv'}-\omega^2}\left\{-\omega_{vv'}R\left\langle M^I_{\alpha\beta}\,\omega_{vv'}\right\rangle + i\omega Ri\left\langle M^I_{\alpha\beta}\,\omega_{vv'}\right\rangle\right\}$$

$$(12.33)\quad = \frac{4n_0}{\hbar}\sum_{j}\frac{1}{\omega\binom{0}{j}^2-\omega^2}\left\{\tfrac{1}{2}R\,m_{\alpha\beta}(j) + i\omega\, b\binom{0}{j}\left(1+e^{-\beta\binom{0}{j}}\right)Ri\,m_{\alpha\beta}(j)\right\}$$

and similarly

$$\left\langle\left(P^2_{\alpha\beta}(\omega)\right)_{vv}\right\rangle = \frac{4n_0}{\hbar}\sum_{Qjj'}\frac{b\binom{Q\cdot}{j}\,b\binom{Q\cdot 1}{j'}}{\left[\omega\binom{Q\cdot}{j}+\omega\binom{Q\cdot 1}{j'}\right]^2-\omega^2}\left\{\left[\omega\binom{Q\cdot}{j}+\omega\binom{Q\cdot 1}{j'}\right]\left[1-e^{-\beta\binom{Q\cdot}{j}-\beta\binom{Q\cdot 1}{j'}}\right]R\,m_{\alpha\beta}\binom{Q\cdot -1}{j\,j'}\right.$$
$$\left. + i\omega\left[1+e^{-\beta\binom{Q\cdot}{j}-\beta\binom{Q\cdot 1}{j'}}\right]Ri\,m_{\alpha\beta}\binom{Q\cdot -1}{j\,j'}\right\}$$
$$+\frac{4n_0}{\hbar}\sum_{Qjj'}{}'\frac{b\binom{Q\cdot}{j}\,b\binom{Q\cdot 1}{j'}}{\left[\omega\binom{Q\cdot}{j}-\omega\binom{Q\cdot 1}{j'}\right]^2-\omega^2}\left\{\left[\omega\binom{Q\cdot}{j}-\omega\binom{Q\cdot 1}{j'}\right]\left[e^{-\beta\binom{Q\cdot 1}{j'}}-e^{-\beta\binom{Q\cdot}{j}}\right]R\,m_{\alpha\beta}\binom{Q\cdot -1}{j\,j'}\right.$$
$$\left. + i\omega\left[e^{-\beta\binom{Q\cdot 1}{j'}}+e^{-\beta\binom{Q\cdot}{j}}\right]Ri\,m_{\alpha\beta}\binom{Q\cdot -1}{j\,j'}\right\}$$

(12.34)

The accent on the summation sign of the difference term in (12.33) indicates that the term $\binom{Q}{j} = \binom{Q}{j'}$ has to be omitted, while in the summation term, $\binom{Q}{j} = \binom{Q}{j'}$ is included. As $m_{\alpha\beta} = M_\alpha M^*_\beta$ one has $m^*_{\alpha\beta} = m_{\beta\alpha}$. Hence, the average polarisability ten:-sor is Hermitean. The optical meaning of this is that the two elementary elliptic waves, into which the field can be decomposed, are propagated with different velocities (elliptical birefraction, optical activity). The formulae, of course, only hold for ω sufficiently different from the resonance frequencies $\pm\omega_J$, $\pm\omega_J \pm \omega_{J'}$. If the immediate neighbourhood of these is to be included, one has to introduce damping. Born and Huang have done this, perhaps rather arbitrarily by replacing ω_J by $\omega_J + i\Gamma_J$, $\omega_J + \omega_{J'}$ by $\omega_J + \omega_{J'} + i\Gamma^{+}_{JJ'}$ and $\omega_J - \omega_{J'}$ by $\omega_J - \omega_{J'} + i\Gamma^{-}_{JJ'}$. The damping constants can be, in principle, calculated from lattice dynamics, but this is a very complicated theory. The Γ are taken as given small constants (small compared with the frequencies themselves). One has then to replace in (12.33) $\frac{1}{\omega\binom{q}{j}^2 - \omega^2}$ by

$$(12.35)\quad \frac{1}{\left[\omega\binom{q}{j} + i\Gamma\binom{q}{j}\right]^2 - \omega^2} = \frac{1}{\omega\binom{q}{j}^2 - \omega^2 + 2i\,\omega\binom{q}{j}\Gamma\binom{q}{j}}$$

$$= \frac{\omega\binom{q}{j}^2 - \omega^2 - 2i\,\omega\binom{q}{j}\Gamma\binom{q}{j}}{\left[\omega\binom{q}{j} - \omega^2\right]^2 + 4\,\omega\binom{q}{j}^2\Gamma\binom{q}{j}^2}$$

if $\Gamma\binom{q}{j}^2$ is neglected, this again can approximately be replaced by

$$(12.36)\quad \frac{1}{2\omega\binom{q}{j}}\,\frac{1}{\omega\binom{q}{j} - \omega + i\Gamma\binom{q}{j}} = \frac{1}{2\omega\binom{q}{j}}\,\frac{\omega\binom{q}{j} - \omega - i\Gamma\binom{q}{j}}{\left(\omega\binom{q}{j} - \omega\right)^2 + \Gamma\binom{q}{j}^2}$$

and correspondingly in (12.34). Hence there appear new imaginary terms, which make the diagonal terms of the polarisability complex. They indicate absorption of the light wave. With neglect of elliptical birefraction and optical activity the complex polarisability now becomes

$$(12.37)\quad \left\langle \left(P'_{\alpha\beta}\omega\right)_{vv}\right\rangle = \frac{2n_0}{\hbar}\sum_{j} \frac{\omega\binom{q}{j}^2 - \omega^2 - 2i\,\omega\binom{q}{j}\Gamma\binom{q}{j}}{\left[\omega\binom{q}{j}^2 - \omega^2\right]^2 + 4\,\omega\binom{q}{j}^2\Gamma\binom{q}{j}^2}\,R\,m_{\alpha\beta}(\dot{j})$$

which, in the region of resonance reduces to

$$\text{(12.38)}\quad \left\langle \left(P^{1}_{\alpha\beta}\,\omega\right)_{vv} \right\rangle = \frac{n_0}{\hbar}\sum_{j}\frac{1}{\omega\binom{Q}{j}}\left\{\frac{\omega\binom{Q}{j}-\omega+i\Gamma\binom{Q}{j}}{\left(\omega\binom{Q}{j}-\omega\right)^2+\Gamma\binom{Q}{j}^2}\right\}R\,m_{\alpha\beta}(j)$$

and

$$\text{(12.39)}\quad \left\langle \left(P^{2}_{\alpha\beta}\,\omega\right)_{vv} \right\rangle = \frac{2n_0}{\hbar}\sideset{}{'}\sum_{Qjj'}\frac{\overset{\pm}{\omega}\binom{Q}{jj'}-\omega+i\overset{\pm}{\Gamma}\binom{Q}{jj'}}{\left(\overset{\pm}{\omega}\binom{Q}{jj'}-\omega\right)^2+\overset{\pm}{\Gamma}\binom{Q}{jj'}^2}\,b\binom{Q}{j}\,b\binom{Q}{j'}R\,m_{\alpha\beta}\binom{Q}{jj'}\left\{\begin{matrix}1-e^{-\beta\binom{Q}{j}-\beta\binom{Q}{j'}}\\ e^{-\beta\binom{Q}{j'}}-e^{-\beta\binom{Q}{j}}\end{matrix}\right\}$$

$$\overset{\pm}{\omega}\binom{Q}{jj'} = \omega\binom{Q}{j}\pm\omega\binom{Q}{j'}$$

The dash over the summation sign denotes that the term $j = j'$ is to be included when the plus sign is taken, and excluded when the negative sign is taken. The summation over Q will be replaced by an integration.

13. THE SECOND ORDER POLARISABILITY TENSOR.

From the preceding sections, it follows that the second order polarisability tensor is given by

$$P^{2}_{\alpha\beta} = \frac{2n_0}{\hbar}\sum_{jj'}{}' \int \frac{\overset{\pm}{\omega}\binom{Q}{jj'}-\omega+i\overset{\pm}{\Gamma}\binom{Q}{jj'}}{\left(\overset{\pm}{\omega}\binom{Q}{jj'}-\omega\right)^2+\overset{\pm}{\Gamma}\binom{Q}{jj'}^2}\, b\binom{Q}{j}\, b\binom{Q}{j'}\, R\, m_{\alpha\beta}\binom{Q}{jj'} \left\{\begin{matrix} 1-e^{-\beta\binom{Q}{j}-\beta\binom{Q}{j'}} \\ e^{-\beta\binom{Q}{j'}}-e^{-\beta\binom{Q}{j}} \end{matrix}\right\} d\underline{Q}$$

(13.1)

The factors $m_{\alpha\beta}\binom{Q}{jj'}$ can be simplified by means of symmetry considerations. This, however, would be extremely involved if it had to be done for all points, $\underline{Q}$ of the reciprocal space. The integral (13.1) will actually depend very little on the whole distribution of

$$b\binom{Q}{j}\, b\binom{Q}{j'}\, R\, m_{\alpha\beta}\binom{Q}{jj'} \left\{\begin{matrix} 1-e^{-\beta\binom{Q}{j}-\beta\binom{Q}{j'}} \\ e^{-\beta\binom{Q}{j'}}-e^{-\beta\binom{Q}{j}} \end{matrix}\right\}$$

(13.2)

in $\underline{Q}$ – space, but mainly on those parts where the frequencies have a maximum density. Even the general problem of finding these regions of space would be very involved. Here the approximation is made that the point $\underline{Q}/2\pi = \left[\frac{1}{2},\frac{1}{2},\frac{1}{2}\right]$ in reciprocal space at which the functions $\overset{\pm}{\omega}\binom{Q}{jj'}$ are constant corresponds to a maximum in the frequency density. Thus it is assumed that no great error occurs in taking the factor (13.2) out of the integral and taking its value at $\underline{Q}/2\pi = \left[\frac{1}{2},\frac{1}{2},\frac{1}{2}\right]$ Thus (13.1) becomes

$$P^{2}_{\alpha\beta} = \frac{2n_0}{\hbar} \sum_{jj'}' b_j b_{j'} R\, m_{\alpha\beta}(jj') \begin{Bmatrix} 1-e^{-\beta j-\beta j'} \\ e^{-\beta j'}-e^{-\beta j} \end{Bmatrix} \int \frac{\overset{\pm}{\omega}\binom{Q}{jj'}-\omega+i\overset{\pm}{\Gamma}\binom{Q}{jj'}}{\left(\overset{\pm}{\omega}\binom{Q}{jj'}-\omega\right)^2+\overset{\pm}{\Gamma}\binom{Q}{jj'}^2}\, d\underline{Q}$$

(13.3)

where j is written for $\binom{Q}{j}$ when $\frac{Q}{2\pi} = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$
Similar approximations have been made by Born and Bradburn (1947) and Smith (1948) in discussing the Raman effect.

One further simplification has yet to be made. Up to this point, a damping constant $\overset{\pm}{\Gamma}\binom{Q}{jj'}$ has been associated with each combination frequency $\overset{\pm}{\omega}\binom{Q}{jj'}$ but now, all the damping constants will be taken as equal to a single constant, Γ. As will be seen, the final expression for the polarisability will not contain Γ. The physical meaning of this is that the absorption depends not on the shape of the individual lines, but on the density of their distribution on the frequency scale.

Now integration over $\underline{Q}$ may be replaced by integrals over the corresponding combination frequencies. With the definition

$$(13.4) \quad \overset{\pm}{Z}_{jj'}(\overset{\pm}{\omega}_{jj'}) = \int_{\overset{\pm}{\omega}_{jj'} < \overset{\pm}{\omega}\binom{Q}{jj'} < \overset{\pm}{\omega}_{jj'} + d\overset{\pm}{\omega}_{jj'}} d\underline{Q}$$

and the substitution

$$(13.5) \quad \overset{\pm}{f}_{\substack{jj' \\ \alpha\beta}} = \frac{2n_0}{\hbar} b_j b_{j'} R\, m_{\alpha\beta}(jj') \begin{Bmatrix} 1-e^{-\beta j-\beta j'} \\ e^{-\beta j'}-e^{-\beta j} \end{Bmatrix}$$

(13.3) becomes

$$(13.6)\quad P^2_{\alpha\beta} = \sum_{jj'}{}' \underset{\alpha\beta}{\overset{\pm}{f}}{}_{jj'} \int \frac{\overset{\pm}{\omega}_{jj'} - \omega + i\Gamma}{(\overset{\pm}{\omega}_{jj'} - \omega)^2 + \Gamma^2} \overset{\pm}{Z}_{jj'}(\overset{\pm}{\omega}_{jj'})\, d\overset{\pm}{\omega}_{jj'}$$

The real and imaginary parts of the polarisability $\overset{r}{P}{}^2_{\alpha\beta}$, $\overset{i}{P}{}^2_{\alpha\beta}$ are now discussed in turn. From the last equation, one obtains from the imaginary part

$$(13.7)\quad \overset{i}{P}{}^2_{\alpha\beta} = +\sum_{jj'}{}' \underset{\alpha\beta}{\overset{\pm}{f}}{}_{jj'} \int \frac{\Gamma}{(\overset{\pm}{\omega}_{jj'} - \omega)^2 + \Gamma^2} \overset{\pm}{Z}_{jj'}(\overset{\pm}{\omega}_{jj'})\, d\overset{\pm}{\omega}_{jj'}$$

If the first factor in the integrand of (13.7) is taken as a delta function, $\overset{i}{P}{}^2_{\alpha\beta}$ simplifies to

$$(13.8)\quad \overset{i}{P}{}^2_{\alpha\beta} = +\pi \sum_{jj'} \underset{\alpha\beta}{\overset{\pm}{f}}{}_{jj'} \overset{\pm}{Z}_{jj'}(\omega)$$

In the same way, one has for the real part of the polarisability

$$(13.9)\quad \overset{r}{P}{}^2_{\alpha\beta} = \sum_{jj'}{}' \underset{\alpha\beta}{\overset{\pm}{f}}{}_{jj'} \int \frac{\overset{\pm}{\omega}_{jj'} - \omega}{(\overset{\pm}{\omega}_{jj'} - \omega)^2 + \Gamma^2} \overset{\pm}{Z}_{jj'}(\overset{\pm}{\omega}_{jj'})\, d\overset{\pm}{\omega}_{jj'}$$

It is impossible to evaluate this integral without knowing the function, $\overset{\pm}{Z}_{jj'}$.

Now it has been assumed that the frequency density function $\overset{\pm}{Z}_{jj'}(\overset{\pm}{\omega}_{jj'})$, has a principal maximum corresponding to the frequencies in the neighbourhood of the point $\frac{q}{2\pi} = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$. Hence, in order to make further progress, the assumption is made that $\overset{\pm}{Z}_{jj'}(\overset{\pm}{\omega}_{jj'})$ can be represented by

$$(13.10) \quad \frac{A_{jj'}\, b_{jj'}}{(\overset{\circ}{\omega}_{jj'}-\omega_{jj'})^2 + b^2_{jj'}} .$$

This function has a maximum of height $\frac{A_{jj'}}{b_{jj'}}$ and width $2b_{jj'}$ at $\omega_{jj'}=\overset{\circ}{\omega}_{jj'}$. Now if $\overset{\pm}{Z}_{jj'}(\overset{\pm}{\omega}_{jj'})$ is replaced by (13.10), the imaginary part of the polarisability becomes,

$$(13.11) \quad \overset{i}{P}{}^2_{\alpha\beta} = +\pi \sum_{jj'}{}' \overset{\pm}{f}_{\underset{\alpha\beta}{jj'}} \frac{A^{\pm}_{jj'}\ b^{\pm}_{jj'}}{(\overset{\pm}{\omega}_{(\overset{0}{jj'})}-\omega)^2 + b^{\pm 2}_{jj'}}$$

and the real part

$$(13.12) \quad \overset{r}{P}{}^2_{\alpha\beta} = \sum_{jj'}{}' \overset{\pm}{f}_{\underset{\alpha\beta}{jj'}} \int_{-\infty}^{\infty} \frac{\overset{\pm}{\omega}_{jj'}-\omega}{(\overset{\pm}{\omega}_{jj'}-\omega)^2+\Gamma^2} \times \frac{A^{\pm}_{jj'}\, b^{\pm}_{jj'}}{(\overset{\pm}{\omega}_{(\overset{0}{jj'})}-\overset{\pm}{\omega}_{jj'})^2+b^{\pm 2}_{jj'}}\, d\overset{\pm}{\omega}_{jj'}$$

where it has been assumed that no great error occurs, in extending the limits of the integration to infinity

By the theorem of residues, it is easy to show, (Appendix 1), that

$$(13.13) \quad \int_{-\infty}^{\infty} \frac{x\,dx}{(x^2+a^2)(x-c^2+b^2)} = \frac{\pi c}{b}\ \frac{(a-b)^2+c^2}{(c^2+b^2-a^2)^2+4a^2c^2}$$

The two integrals become identical, if one puts

$$(13.14) \quad x = \overset{\pm}{\omega}_{jj'}-\omega, \quad a=\Gamma, \quad c = \overset{\pm}{\omega}_{(\overset{0}{jj'})}-\omega \qquad b = b^{\pm}_{jj'}$$

This gives

$$(13.15)\quad \overset{r}{P}{}^{2}_{\alpha\beta} = \pi \sum_{jj'}{}' \frac{f^{\pm}_{\alpha\beta\, jj'} A^{\pm}_{jj'} \left(\overset{\pm}{\omega}\binom{0}{jj'} - \omega\right)\left[\left(\overset{\pm}{\omega}\binom{0}{jj'} - \omega\right)^2 + \left(b^{\pm}_{jj'} - \Gamma\right)^2\right]}{\left[\left(\overset{\pm}{\omega}\binom{0}{jj'} - \omega\right)^2 + b^{\pm\,2}_{jj'} - \Gamma^2\right]^2 + 4\Gamma^2\left(\overset{\pm}{\omega}\binom{0}{jj'} - \omega\right)^2}$$

Now Γ will always be small compared with $b^{\pm}_{jj'}$, so that terms containing Γ can be neglected in 13.15.

So,

$$(13.16)\quad \overset{r}{P}{}^{2}_{\alpha\beta} = \pi \sum_{jj'}{}' f^{\pm}_{\alpha\beta\, jj'} A^{\pm}_{jj'} \frac{\overset{\pm}{\omega}\binom{0}{jj'} - \omega}{\left(\overset{\pm}{\omega}\binom{0}{jj'} - \omega\right)^2 + b^{\pm\,2}_{jj'}}$$

On combining (13.11) and (13.16) one obtains for the complex polarisability.

$$(13.17)\quad P^{2}_{\alpha\beta} = \pi \sum_{jj'}{}' \frac{f^{\pm}_{\alpha\beta\, jj'} A^{\pm}_{jj'}}{\overset{\pm}{\omega}\binom{0}{jj'} - \omega \pm i b^{\pm}_{jj'}}$$

From these equations, one sees that in the approximation that has been used, the second order polarisability is equivalent to a number of simple absorption lines. The total number of these additional lines is, of course $(3s)^2 - 3s$, but symmetry considerations may reduce this number, that is, the factor $f^{\pm}_{\alpha\beta\, jj'}$ may be zero. Thus one sees that dispersion in crystals of the $NaCl$ type is due to a first order absorption line on to which are super-posed a few second order absorption "lines." This result is in agreement with the observed spectrum, but differs from that predicted by Raman's theory. From the theory worked out in the preceding sections, it follows that the secondary absorption "lines" are really continuous bands of absorption, while in Raman's theory, the absorption is assumed to be due to nine eigen-frequencies and their combination frequencies, up to the third order. Raman claims to have identified thirty lines in the case of MgO, but he uses the anomalous results of Barnes, Brattain and Seitz (1935). It is to be stressed that Willmott finds only three secondary absorption lines on the short wave length side of the first order line, (as is the case in $NaCl$), and one on the long wave-length side.

It is, of course, not possible to measure the refractive index directly in the absorption region. In practice, measurements are made of the reflection and transmission co-efficients. From these, the refractive index and the extinction co-efficient can be obtained. The two latter are, of course, related to the real and imaginary parts of the polarisability. Before applying the theory specifically to $NaCl$, a brief account of these relations is given.

For the case of an isotropic body, (or a cubic crystal), it follows from Maxwell's equations, that if n is the refractive index for a plane wave pass:-ing through a medium of dielectric constant K .

(13.18) $$n^2 = 1 + 4\pi P = K$$

In the case of absorption, these quantities become complex, If n is replaced by $n - ik$, where k is the extinction co-efficient, then

$$(n-ik)^2 = 1+4\pi \overset{r}{P} + i4\pi \overset{i}{P}$$

i.e.
$$n^2-k^2 = 1+4\pi \overset{r}{P}$$

$$nk = -2\pi \overset{i}{P}$$

13.19)

The reflection co-efficient R is related to n and k by

(13.20)
$$R = \frac{(1-n)^2+k^2}{(1+n)^2+k^2}$$

The transmission co-efficient D, (Kellner, 1929, and Czerny, 1930), is given by

(13.21)
$$D = \frac{R+\frac{1}{R} - 2\cos 2\psi}{Re^{-2k\theta}+\frac{1}{R}e^{2k\theta}-2\cos 2(n\theta+\psi)}$$

where

(13.22)
$$\tan\psi = \frac{2k}{n^2+k^2-1}$$

$$\theta = \frac{\omega d}{30}$$

and d is the thickness of the plate measured in μ and the frequency of the incident light is given by $\frac{\omega}{2\pi} \times 10^{13}\ \mathrm{sec}^{-1}$

14. THE POLARISABILITY OF SODIUM CHLORIDE.

The vibration spectrum of the NaCl lattice has been calculated by Kellermann (1940), for a set of values sufficiently complete to get a good idea of all the branches. His assumptions are Coulomb forces acting between all the ions, and repulsive force between next neighbours; the two constants appearing from the latter can be calculated by using the exper:-imental values of the lattice constant and the compressibility. Hence, his results are independent of arbitrary assumptions and they are checked by the calculation of the specific heat (Kellermann, 1941).

In the case of NaCl, there are two different particles in each cell, $s=2$. Now, if one introduces a rectangular co-ordinate system with axes parallel to the edges of a cubic cell, the rhombohedral cell vectors and the basis of the NaCl lattice, are given by

$$\underline{a}_1 = (0, a, a) \qquad \underline{a}_2 = (a, 0 a) \qquad \underline{a}_3 = (a, a, 0)$$

(14.1) $$\underline{r}_1 = (0\ 0\ 0) \qquad r_2 = r_{21} = (a, a, a) \quad v_a = 2a^3$$

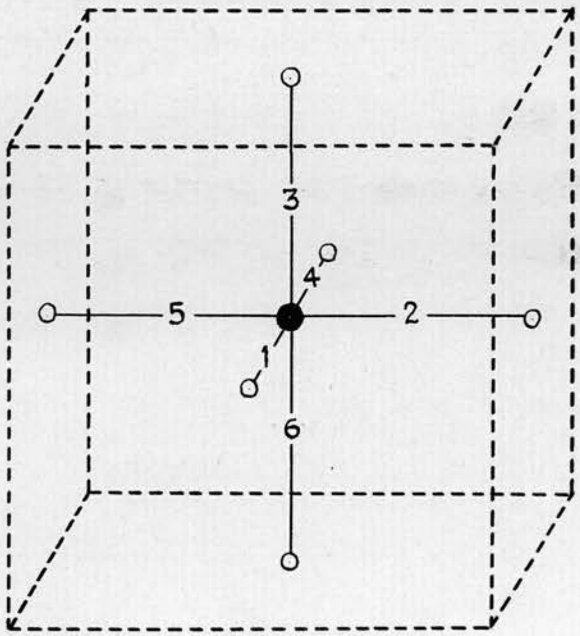
where a is the distance between nearest neighbours or $\frac{1}{2}$ the lattice constant, and v_a the volume of the rhombohedral cell. The positions of the particles are therefore given by

$$\underline{r}^{l}_{kk} = \underline{a}^{l} \qquad = l_1\underline{a}_1 + l_2\underline{a}_2 + l_3\underline{a}_3 = (\overline{l_2+l_3}\,a, \overline{l_3+l_1}\,a, \overline{l_1+l_2}\,a) = (l_x, l_y, l_z)$$

(14.2) $$\underline{r}^{l}_{21} = \underline{a}^{l} + \underline{r}_{21} = (\overline{l_2+l_3+1}\,a, \overline{l_3+l_1+1}\,a, \overline{l_1+l_2+1}\,a) = (m_x, m_y, m_z)$$

FIGURE IV.

First Neighbours of a Point in the Unit Cell of the Sodium Chloride Lattice.



where $l_x + l_y + l_z$ is an even integer and $m_x + m_y + m_z$ is an odd integer times a. Each particle has six first neighbours, which are of a different kind. If those of the particle at the origin $\underline{r}_1^l = 0$, are labelled ($\mu = 1, 2 \cdots\cdots 6$), Fig. IV., the co-ordinates and cell vectors are given by table VII.

TABLE VII.

μ	1	2	3	4	5	6
m_x	a	0	0	$-a$	0	0
m_y	0	a	0	0	$-a$	0
m_z	0	0	a	0	0	$-a$
l_1	-1	0	0	0	-1	-1
l_2	0	-1	0	-1	0	-1
l_3	0	0	-1	-1	-1	0

As stated before, the constants in the expansion of the electric moment, $M_{\alpha,\beta\gamma}^{\binom{l}{kk'}}$, can be simplified by symmetry considerations. The constants will be taken as zero, except those which refer to nearest neighbours. They behave like covariant tensors with respect to the suffixes $\alpha, \beta\gamma$. It follows that, in the case of a symmetry transformation (c.f. Section 2).

(14.3) $$M_{A,BC}^{\binom{L}{KK'}} = \sum_{\alpha,\beta\gamma} T_{A\alpha}, T_{B\beta}, T_{C\gamma} \, M_{\alpha,\beta\gamma}^{\binom{l}{kk'}}$$

where

$$x_A\binom{L}{K} = \sum_{\alpha} T_{A\alpha} \, x_\alpha\binom{l}{k}$$

(14.4)

The symmetry operators of a cubic lattice, are represented in matrix notation, by

$$T_t = \underset{(321)(654)}{\begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}} \quad T_m = \underset{(36)}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}} \quad T_d = \underset{(12)\,(45)}{\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}} \tag{14.5}$$

where the change in the indices h, is given by the substitution groups under each matrix. The meaning of a bracket is that a co-efficient $M^{h}_{\alpha,\beta\gamma}$ with a certain number in a cycle, is to be derived from the co-efficient with the number following it in the cycle, in the manner described by (14.4). The effect of these operators can be described by the scheme,

$$T_t = (T_{13}\,T_{21}\,T_{32}),\ T_m = (T_{11}\,T_{22}\,-T_{33}),\ T_d = (T_{12}\,T_{21}\,T_{33}) \tag{14.6}$$

where

$$\pm T_{\alpha\beta} M^{h}_{\beta,\cdot\cdot} = \pm M^{h'}_{\alpha,\cdot\cdot} \tag{14.7}$$

Now, it is easily seen that $M^{1}_{\alpha,\beta\gamma}$ is invariant under the transformations T_m and $T_t T_d$ where

$$T_m = (T_{11}\,T_{22}\,-T_{33}) \qquad T_t T_d = (T_{11}\,T_{23}\,T_{32}) \tag{14.8}$$

From this, it follows firstly, that all those $M^1_{\alpha,\beta\gamma}$ which can be got by interchanging all suffixes 2 and 3 must be equal, and secondly, that all those terms containing an odd number of suffixes 3 (and by the first rule, the same holds for the suffixes 2) must vanish. The non-vanishing constants are

$$M^1_{1,11} = a \qquad\qquad M^1_{1,33} = b$$

$$M^1_{2,12} = M^1_{3,13} = c \qquad M^1_{2,21} = M^1_{3,31} = d \tag{14.9}$$

$M^2_{\alpha,\beta\gamma}$ and $M^3_{\alpha,\beta\gamma}$ can be obtained by cyclic interchange from $M^1_{\alpha,\beta\gamma}$. By application of the transformation Tm, it follows for the non-vanishing co-efficients that $M^3_{\alpha,\beta\gamma} = -M^6_{\alpha,\beta\gamma}$ and so, by cyclic interchange, that $M^2_{\alpha,\beta\gamma} = -M^5_{\alpha,\beta\gamma}$ and $M^1_{\alpha,\beta\gamma} = -M^4_{\alpha,\beta\gamma}$ or from the fact that $NaCl$ has a centre of symmetry, $T = (-T_{11}, -T_{22}, -T_{33})$ it is seen that

$$M^{h\,(kk')}_{\alpha,\beta\gamma} = -M^{-h\,(kk')}_{\alpha,\beta\gamma} \tag{14.10}$$

where the particles that have been denoted by $h = 4, 5, 6$ are now taken to be $h = -1, -2, -3$ respectively.

By definition

$$M^{h\,(kk')}_{\alpha,\beta\gamma} = M^{-h\,(k'k)}_{\alpha,\gamma\beta} \tag{14.11}$$

If $l = 0$, and $k \neq k'$, the particles concerned are not next neighbours, and so

(14.12) $M_{\alpha,\beta\gamma}\binom{0}{kk'} = 0$

If $l = 0$ and $k = k'$, from (11.8) it follows that

$$M_{\alpha,\beta\gamma}\binom{0}{kk} = -\sum_{hk'}{}' M_{\alpha,\beta\gamma}\binom{h}{kk'} = 0$$

(14.13)

This completes the simplification of the expansion coefficients. However, what is required are the co-efficients for the expansion in normal co-ordinates at $\frac{Q}{2\pi} = [\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}]$. Inserting this value of Q in (11.15) and using (14.10) and (14.11) gives

$$M_\alpha(jj') = \frac{N}{2}\sum_{\beta\gamma}\sum_{lkk'}\frac{1}{\sqrt{m_k m_{k'}}}M_{\alpha,\beta\gamma}\binom{l}{kk'}e^{i\pi(l_1+l_2+l_3)}\,e_\beta(k|j)\,e^*_\gamma(k'|j')$$

$$= \frac{N}{2}\sum_{\beta\gamma}\sum_{h}^{123}\frac{1}{\sqrt{m_1 m_2}}\Big\{\Big[-M_{\alpha,\beta\gamma}^{h}(12) + M_{\alpha,\beta\gamma}^{-h}(12)\Big]e_\beta(1|j)\,e^*_\gamma(2|j')$$

$$+\Big[M_{\alpha,\beta\gamma}^{h}(21) - M_{\alpha,\beta\gamma}^{-h}(21)\Big]e_\beta(2|j)\,e^*_\gamma(1|j')\Big\}$$

$$= N\sum_{\beta\gamma}\sum_{h}^{123}\frac{1}{\sqrt{m_1 m_2}}\Big\{M_{\alpha,\beta\gamma}^{h}(21)\,e_\beta(2|j)\,e^*_\gamma(1|j') - M_{\alpha,\beta\gamma}^{h}(12)\,e_\beta(1|j)\,e^*_\gamma(2|j')\Big\}$$

$$= \frac{-N}{\sqrt{m_1 m_2}}\sum_{\beta\gamma}\sum_{h}^{123}\Big\{M_{\alpha,\beta\gamma}^{h}(12)\,e_\beta(1|j)\,e^*_\gamma(2|j') + M_{\alpha,\beta\gamma}^{h}(21)\,e_\beta(2|j)\,e^*_\gamma(1|j')\Big\}$$

(14.14)

Let $$\sum_{h}^{123} M_{\alpha,\beta\gamma}^{h}(12) = M_{\alpha,\beta\gamma}$$

(14.15)

2

then

(14.16) $$M_\alpha(jj') = \frac{-N}{\sqrt{m_1 m_2}} \sum_{\beta\gamma} M_{\alpha,\beta\gamma} \left\{ e_\beta(1|j)\, e^*_\gamma(2|j') + e^*_\beta(1|j')\, e_\gamma(2|j) \right\}$$

It is well-known that only those elements of the polarisability tensor $P_{\alpha\beta}$ for $NaCl$ exist for which $\alpha = \beta$ and that these elements are all equal. For this reason, it is only necessary to consider $P_{\alpha\alpha}$ and in particular $|M_1(jj')|^2$. It is easy to show that the constants $M_{\alpha,\beta\gamma}$ have the values

$$\begin{aligned} M_{1,11} &= a \\ M_{1,22} = M_{1,33} &= b \\ M_{1,31} = M_{1,21} &= c \\ M_{1,12} = M_{1,13} &= d \\ M_{1,23} = M_{1,32} &= 0 \end{aligned}$$

(14.17)

In order to evaluate $e_\alpha(k|j)$ the equations of motion must be established at the point $\frac{Q}{2\pi} = \left[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right]$. It can be shown by simple symmetry considerations (Kellermann, 1940), that the six equations (2.13) split into two sets of three. The first equation of either set is of the form

(14.18) $$(A - m_k\omega^2)\, e_1(k|j) + B\left[e_2(k|j) + e_3(k|j)\right] = 0$$

with two others, obtained by cyclic interchange of the suffix α, of $e_\alpha(k|j)$. The two sets are distinguished by $k = 1$ or 2. The values of j are chosen to correspond with Kellermann's notation. With the help of the orthogonality relations (2.22) the solutions of these equations are easily obtained (Born and Bradburn, 1947), and are shown by Table VIII.

TABLE VIII.

$\binom{k}{\alpha}$ \ j	1	2	3	4	5	6
$\binom{1}{1}$	$\frac{1}{\sqrt{3}}$	0	$\sum_\alpha e_\alpha(1\|3)=0$ $\sum_\alpha e_\alpha^2(1\|3)=1$	$\sum_\alpha e_\alpha(1\|4)=0$ $\sum_\alpha e_\alpha^2(1\|4)=1$	0	0
$\binom{1}{2}$	$\frac{1}{\sqrt{3}}$	0			0	0
$\binom{1}{3}$	$\frac{1}{\sqrt{3}}$	0			0	0
$\binom{2}{1}$	0	$\frac{1}{\sqrt{3}}$	0	0	$\sum_\alpha e_\alpha(2\|5)=0$ $\sum_\alpha e_\alpha^2(2\|5)=1$	$\sum_\alpha e_\alpha(2\|6)=0$ $\sum_\alpha e_\alpha^2(2\|6)=1$
$\binom{2}{2}$	0	$\frac{1}{\sqrt{3}}$	0	0		
$\binom{2}{3}$	0	$\frac{1}{\sqrt{3}}$	0	0		

Now one can obtain $M_1(jj')$ by substituting the values of $M_{\alpha,\beta\gamma}$ from (14.17) and $e_\alpha(k|j)$ into equation (14.16). Inspection of Table VIII. shows that the six values of j can be split into the two groups $(j=1,3,4)$ and $(j=2,5,6)$ and only those values of $M_1(jj')$ exist for which j and j' are taken from different groups. Simple calculations show that the non-vanishing co-efficients are given by

$$M_1(1,2) = \frac{-N}{3\sqrt{m_1 m_2}} \left\{ a + 2(b+c+d) \right\}$$

$$M_1(1,5) = \frac{-N}{\sqrt{3 m_1 m_2}} \left\{ a - b - d + 2c \right\} e_1^*(215)$$

$$M_1(1,6) = \frac{-N}{\sqrt{3 m_1 m_2}} \left\{ a - b - d + 2c \right\} e_1^*(216)$$

$$M_1(3,5) = \frac{-N}{\sqrt{m_1 m_2}} \left\{ a - b - c - d \right\} e_1(113) e_1^*(215)$$

$$M_1(3,6) = \frac{-N}{\sqrt{m_1 m_2}} \left\{ a - b - c - d \right\} e_1(113) e_1^*(216)$$

$$M_1(4,5) = \frac{-N}{\sqrt{m_1 m_2}} \left\{ a - b - c - d \right\} e_1(114) e_1^*(215)$$

$$M_1(4,6) = \frac{-N}{\sqrt{m_1 m_2}} \left\{ a - b - c - d \right\} e_1(114) e_1^*(216)$$

$$M_1(3,2) = \frac{-N}{\sqrt{3 m_1 m_2}} \left\{ a - b - c + 2d \right\} e_1(113)$$

$$M_1(4,2) = \frac{-N}{\sqrt{3 m_1 m_2}} \left\{ a - b - c + 2d \right\} e_1(114)$$

(14.19)

with the relation $M_1(jj') = M_1(j'j)^*$ **from (14.16).**

From these, it is easy to find $m_{11}(jj') = |M_1(jj')|^2$ **They are given by**

$$m_{11}(1,2) = \frac{N^2}{9 m_1 m_2} \left\{ a + 2(b+c+d) \right\}^2$$

$$m_{11}(1,j') = \frac{2N^2}{9 m_1 m_2} \left\{ a - b - d + 2c \right\}^2 \qquad j' = 5, 6$$

$$m_{11}(j2) = \frac{2N^2}{9 m_1 m_2} \left\{ a - b - c + 2d \right\}^2 \qquad j = 3, 4$$

$$m_{11}(j,j') = \frac{4N^2}{9 m_1 m_2} \left\{ a - b - c - d \right\}^2 \qquad \begin{cases} j = 3, 4 \\ j' = 5, 6 \end{cases}$$

(14.20)

$$m_{11}(j,j') = m_{11}(j'j)$$

As regards the constants occuring in the first order polarisability $P'_{\alpha\beta}$, it is easy to show that the only non-vanishing co-efficients in the expansion (11.2) of the first order moment are

$$M_{1,1}^{(1)} = M_{2,2}^{(1)} = M_{3,3}^{(1)} = M_s \tag{14.21}$$

and with the help of (11.5)

$$M_{1,1}^{(2)} = M_{2,2}^{(2)} = M_{3,3}^{(2)} = -M_s \tag{14.22}$$

From (11.12) it follows that the co-efficients in the expansion in terms of normal co-ordinates, $M_\alpha(\gamma)$ are given by

$$M_\alpha(\gamma) = N M_s\left(\frac{1}{\sqrt{m_1}} - \frac{1}{\sqrt{m_2}}\right) \qquad (\alpha = 1, 2, 3) \tag{14.23}$$

and so

$$m_{\alpha,\alpha}(\gamma) = N^2 M_s^2 \left(\frac{1}{\sqrt{m_1}} - \frac{1}{\sqrt{m_2}}\right)^2 \qquad (\alpha = 1, 2, 3) \tag{14.24}$$

This completes the simplification of the expansion co-efficients in the moment by means of symmetry considerations.

15. NUMERICAL CALCULATIONS.

It is well known that $NaCl$ possesses one first order absorption line. From (12.37) the corresponding polarisability is written

$$(15.1) \qquad P'(\omega) = A_0 \frac{\omega_0^2 - \omega^2 + 2i\omega_0 b_0}{(\omega_0^2 - \omega^2)^2 + 4\omega_0^2 b_0^2}$$

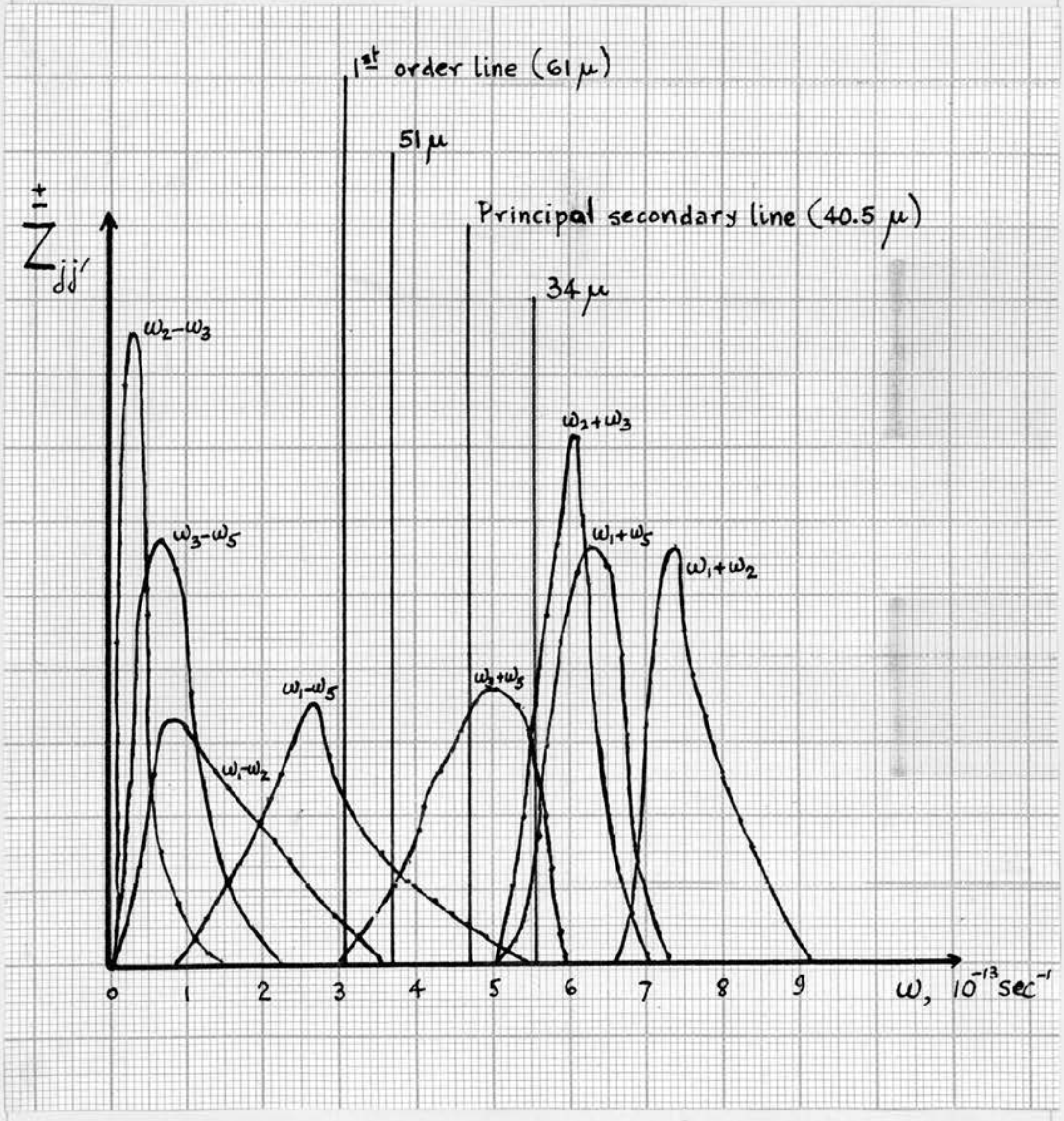
where the two constants A_0 and b_0 will be adjusted to give the best possible fit with experiment for the range of frequencies which will be considered. ω_0 is taken from the observations of Barnes and Czerny (1931) as $3\cdot 1 \times 10^{13}\,sec^{-1}$.

In Section 13, it has been shown that the second order polarisability consists of a sum of terms corresponding to the possible combinations of j and j' for both summation and difference frequencies. In the last section, it was shown that on account of symmetry considerations, only those terms will occur in the summation for which j has one of the values ($1, 3, 4$) and j', ($2, 5, 6$) or vice versa. The constants $A^{\pm}_{jj'}$, $b^{\pm}_{jj'}$ and $\overset{\pm}{\omega}\left(\overset{0}{jj'}\right)$ have to be determined so that the function (13.10) gives a best fit for the frequency density function $\overset{\pm}{Z}_{jj'}$.

The latter functions have been calculated by Dr. Smith from Kellermann's results. The result of the calculation appear in graphical form in the paper of Born and Bradburn, (1947), on the Raman effect. There, the mean has been taken between the $j = 3$ and $j = 4$ branches, and between the $j = 5$ and $j = 6$ branches

FIGURE V.

Frequency Density Functions Allowed by the Selection Rules.



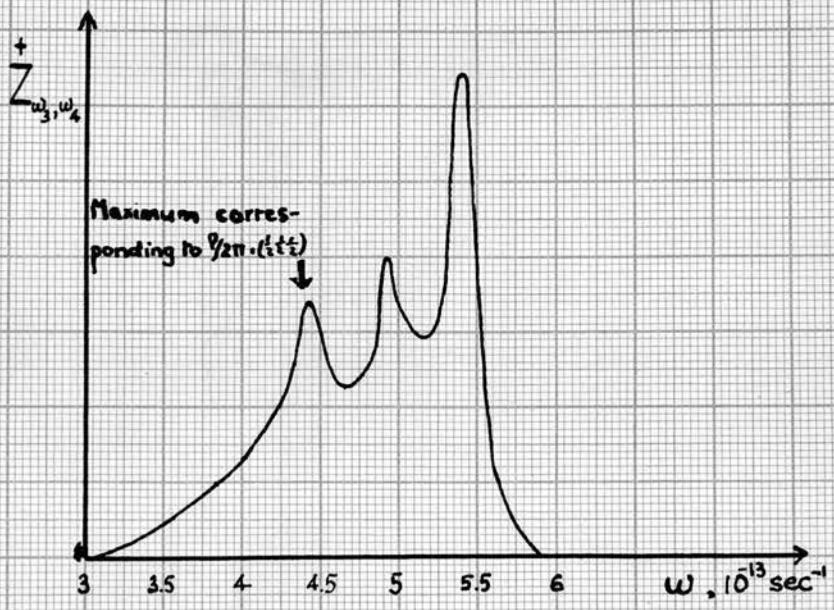
corresponding to the fact that $\omega\binom{q}{3} = \omega\binom{q}{4}$, and $\omega\binom{q}{5} = \omega\binom{q}{6}$ at the point $\frac{q}{2\pi} = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$.

Omitting the branches $j = 4$ and $j = 6$ one has only the four combinations $(j\,j') = (1,2); (1,5); (2,3); (3\,5$. The corresponding density curves are plotted in Fig. V.

Barnes and Czerny (1931) have shown that the frequency corresponding to a maximum of absorption of a light ray in its passage through a thin film, is near the resonance frequency of an absorption line. From the theory given here, it follows that the maxima in absorption should correspond to the maxima of the frequency density functions in Fig. V. The results of observation (Barnes, and Czerny, 1931, Czerny, 1930, Mentzel, 1934) show that secondary absorption maxima occur at wave-lengths of $51\,\mu$, $40.5\,\mu$, $34\,\mu$. The one at $40.5\,\mu$ with a corresponding maximum in reflection at $38\,\mu$ is the most prominent. These wave lengths have been marked in Fig. V. It is seen that ohly one of the maxima of the allowed frequency density functions corresponds with the given wave-lengths. This is the maximum of the frequency density of $\omega_3+\omega_5$, the sum combination of the transverse vibrations $j = (3)$ $j' = (5)$, corresponding to the principal secondary absorption maximum. Since no absorption has been observed corresponding to combinations which include the frequencies of the longitudinal vibrations, the constants a, b, c, d of equation (14.20) are given the following values.,

FIGURE VI.

Frequency Density Function for the Branch $\omega_3+\omega_5$
by Interpolation of Kellermann's Results.



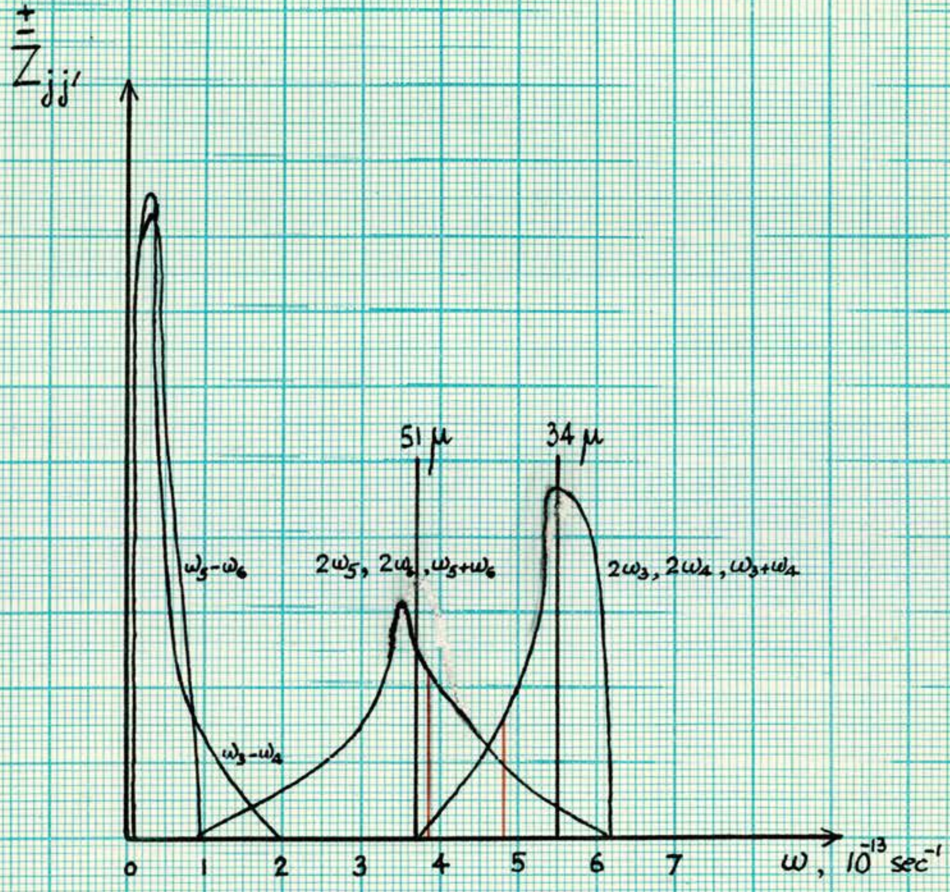
$$(15.2) \qquad a = 2a_0, \quad b = a_0, \quad c = d = -a_0$$

where a_0 is still arbitrary. According to (14.20) this assumption causes $m_{\alpha\beta}^{(jj')}$ and hence $f_{\alpha\beta}^{(jj')}$ to vanish, if j or $j' = 1, 2$ (i.e. corresponding to longitudinal vibrations).

In order to account for the existence of the two subsidiary maxima at 51μ and 34μ, it is necessary to extend kellermann's work on the calculation of the frequency spectrum of sodium chloride. Besides the maximum of the density curve due to the flat section of the frequency as a function of Q near the point $Q/2\pi = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$, other maxima may occur. For, to a given small interval of frequency $\Delta\omega$, there correspond also other parts of the frequency surface which cannot be found analytically, but only by just counting out a sufficiently dense table of the frequencies. This has been done in the following way for the branch $\omega_3 + \omega_5$. Kellermann evaluated the frequencies corresponding to a network of a thousand points in the unit cell of the reciprocal lattice. The network was based on cell vectors which were one tenth of the cell vectors of the reciprocal lattice. The number of points are now to be extended to eight thousand, by basing the network on cell vectors which were one twentieth of the cell vectors of the reciprocal lattice. Thus, the additional points

FIGURE VII.

The Additional Frequency Density Functions.



The frequencies corresponding to $q/2\pi : (\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ have been marked in red.

considered are the midpoints of every two adjacent points in Q-space which were considered by Kellermann. The frequencies associated with these points have been taken as the mean of those associated with the corresponding adjacent points. This has enabled the density to be obtained by counting the number of frequencies that fall in intervals of $\Delta\omega = \cdot 1 \times 10^{13}$ instead of $\Delta\omega = \cdot 6 \times 10^{13}$ as was done by Born and Bradburn (1947). The result for the branch $\omega_3 + \omega_5$ is the curve in Fig. V1, showing the maximum at $\omega = 4 \cdot 4 \times 10^{13}$ associated with the point $Q/2\pi = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$, and two other maxima at $\omega = 4 \cdot 9 \times 10^{13}$ and $\omega = 5 \cdot 4 \times 10^{13}$. These last two maxima cannot be associated with a definite state of vibration, and therefore no selection rules can be given for them. Nevertheless, they may contribute to the optical behaviour. While the experimental results show no trace of an absorption maximum at $\omega = 4 \cdot 9 \times 10^{13}$ the main maximum at $\omega = 5 \cdot 4 \times 10^{13}$ almost coincides with the subsidiary absorption maximumobserved at $\lambda = 34\,\mu$.

The density curves for other combination frequencies should be treated in the same way. However, an examination of the frequency density curves of Born and Bradburn for the combinations $2\omega_3$ and $2\omega_5$ which have been reproduced in Fig. VII , shows that the maxima of these curves do not occur at frequencies corresponding to $Q/2\pi = [\frac{1}{2},\frac{1}{2},\frac{1}{2}]$. It is therefore assumed that these maxima are due to frequencies which come from other unknown parts of Q-space, just as is the case for the main maximum in the density curve for $\omega_3+\omega_5$. It has already been shown that for the curves for $2\omega_3$ and $2\omega_5$ no absorption is to be expected for the maxima corresponding to $Q/2\pi = [\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ and so these maxima need notbe considered further. From Fig. VII it is seen that the maxima of the density curves for $2\omega_3$ at $\omega = 5.4\times10^{13}$ and $2\omega_5$ at $\omega = 3.5\times10^{13}$ agree quite well with the frequencies of the two subsidiary maxima observed at $\lambda = 34\,\mu$ and $\lambda = 51\,\mu$ respectively. No absorption maxima have been observed for frequencies which would correspond to the combinations containing the frequencies of longitudinal modes of vibration.

If second neighbours are taken into account in the expansion of the electric moment, (still with the restriction of Q-space to the region of $Q/2\pi = [\frac{1}{2},\frac{1}{2},\frac{1}{2}]$.) one would expect, since the second neighbours of a given particle are of the same kind as the particle itself, additional terms to appear in the polarisability, corresponding to the values of both j and j'

being taken from either one of the groups (1, 3, 4) or (2, 5, 6). However, since the NaCl lattice has a centre of symmetry, it is easily verified that the additional constants appearing in the expansion of the moment in the displacements $u_\alpha\binom{l}{k}$, have values such that the additional terms $M_1(jj')$ appearing in the expansion in normal co-ordinates $q\binom{q}{j}$ for $q/2\pi = [\frac{1}{2},\frac{1}{2},\frac{1}{2}]$ vanish. Thus, the introduction of second neighbours contributes nothing further to the polarisability.

The polarisability of the principal secondary line is proportional to the factor $f(jj')\,A_{jj'}$. Besides the arbitrary constant a_0. $f(jj')$ contains the temperature dependence of the polarisability, but since no investigation has been made of the temperature dependence of the absorption, the two constants will be combined into one Ar - the intensity factor of the line. A relation exists between the two constants $f^+(jj')$ and $f^-(jj')$, corresponding to the lines, due to the sum and difference combination. However, practically no observations exist in the region of the difference line, so one cannot compare this relation with observation.

The same form for the polarisability is taken for the two remaining secondary lines. For since their origin is due to the consideration of regions of $\underline{Q}$ -space other than the neighbourhood of $\underline{Q}/2\pi = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$, there seems no reason for taking one value of $\underline{Q}$, rather than another, in evaluating the constant $f\binom{Q}{jj'}$. Therefore, in comparing the theory with observation, the polarisability of the crystal is taken in the form

$$(15.3) \quad P = 1{\cdot}328 + A_0 \frac{\omega_0^2 - \omega^2 + 2i\omega_0 b_0}{(\omega_0^2-\omega^2)^2 + 4\omega_0^2 b_0^2} + \sum_{r=1,2,3} A_r \frac{\omega_r - \omega + i b_r}{(\omega_r - \omega)^2 + b_r^2}$$

The effect of the ultra-violet terms on the polarisability has been taken from the work of Fuchs and Wolff (1928) as 1.328. The A and b are taken as arbitrary constants, but one expects, however, that the b_r $(r = 1, 2, 3)$ will be of the order of the width of the corresponding frequency distribution.

On account of the presence of the abritrary constants in (15.3), the simplest method of comparing the theory with experiment would be to start from the experimental values of the reflection and transmission co-efficients R and D. Using these, one could solve (13.20) and (13.21) for the refractive index n, and the extinction co-efficient k. These are directly related to the real and imaginary parts of the polarisability, by equation (13.19). The equation (13.21) for the transmission co-efficient D, is transcendental. However, one can solve (13.20) for n thus

$$(15.4) \quad n = \frac{1+R}{1-R} \pm \sqrt{\frac{4R}{(1-R)^2} - k^2}$$

FIGURE VIII

The Reflection Co-efficient.

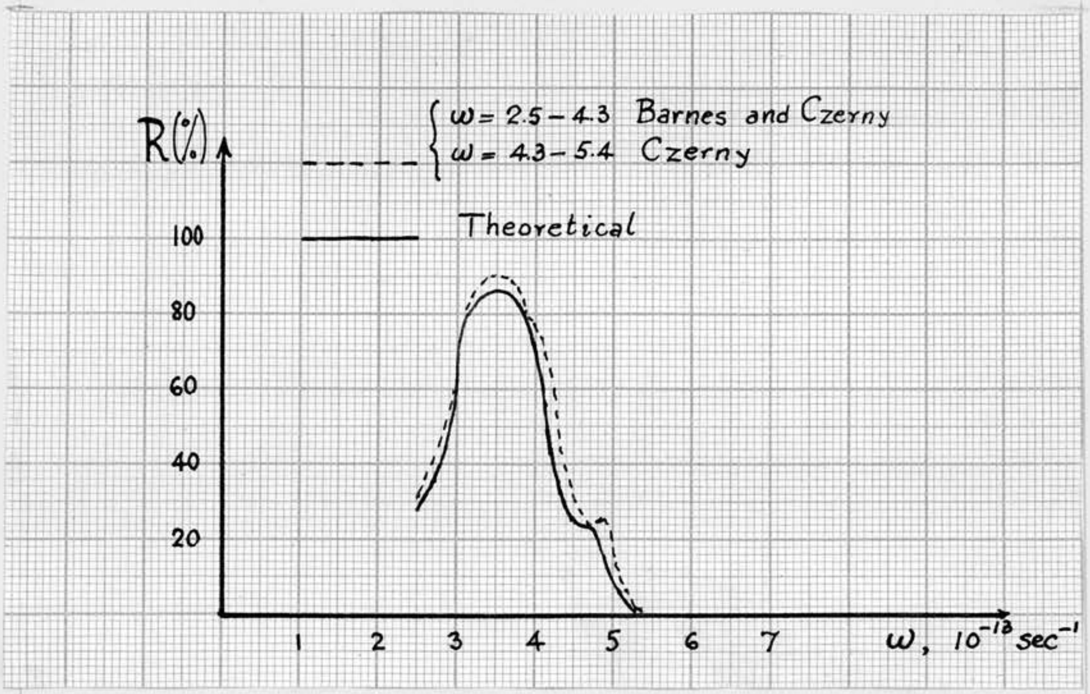
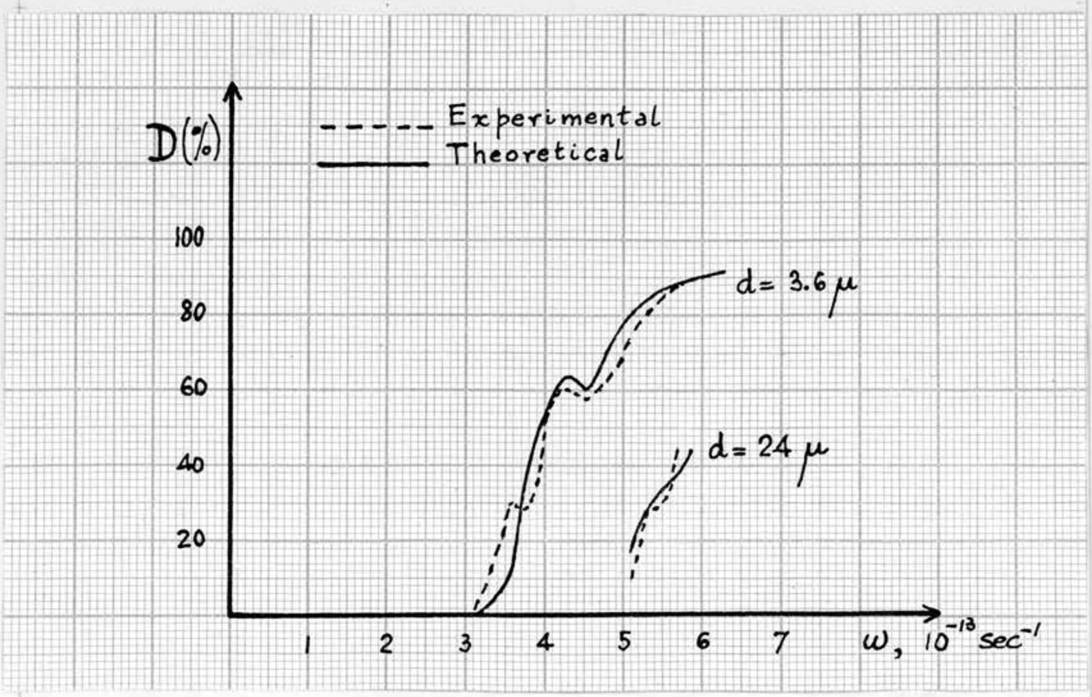


FIGURE IX

The Transmission Co-efficient.



Then the transcendental equation for D , can be solved by testing various values for k . This procedure was carried out for several sets of plates, but the resulting values of the polarisability showed a fair amount of scatter, and in the region of the first order maximum, it was impossible to find solutions. This was presumably due to the fact that the relation (15.4) between n and k is very sensitive to the value of R when R is near unity.

In view of these facts, it was decided to reverse the procedure. The constants A and b were adjusted to give a best fit for the reflection and transmission co-efficients. The results are shown in Figs. VIII and IX. The values of the co-efficients used are

$$\begin{array}{llll}
\omega_0 = 3{\cdot}1 & A_0 = 13{\cdot}75 & b_0 = {\cdot}058 & \\
\omega_1 = 4{\cdot}5 & A_1 = {\cdot}1 & b_1 = {\cdot}32 & ({\cdot}2) \\
\omega_2 = 3{\cdot}6 & A_2 = {\cdot}05 & b_2 = 1{\cdot}0 & (1{\cdot}0) \\
\omega_3 = 5{\cdot}7 & A_3 = {\cdot}04 & b_3 = {\cdot}7 & (1{\cdot}0)
\end{array}$$

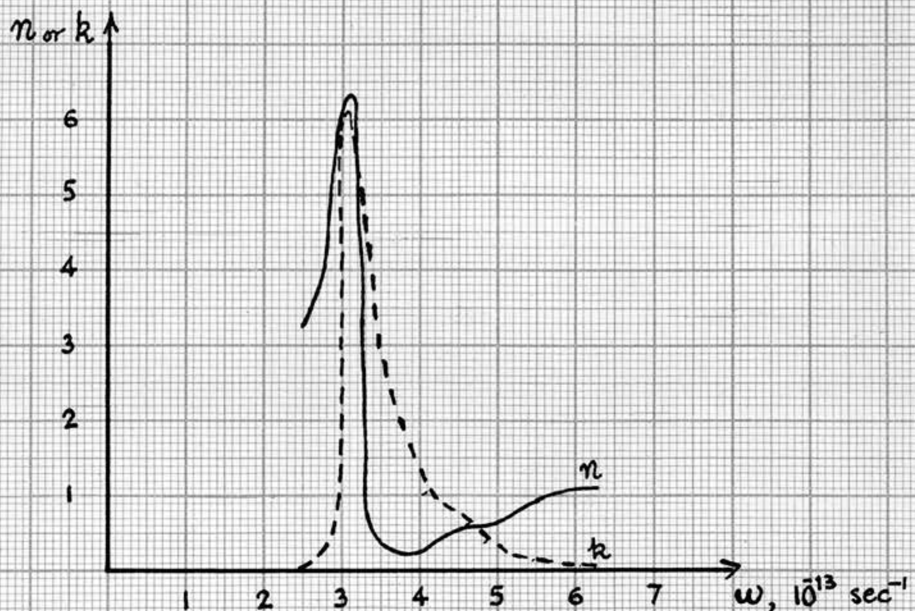
(15.5)

The unit of angular frequency is taken as $10^{13}\,sec^{-1}$ The numbers in brackets after b_1 , b_2 , b_3 , are the widths of the corresponding frequency density functions, estimated from Figs. VI. and VII.

The experimental values for R are from Czerny

FIGURE X

The Refractive Index and the Extinction Co-efficient.



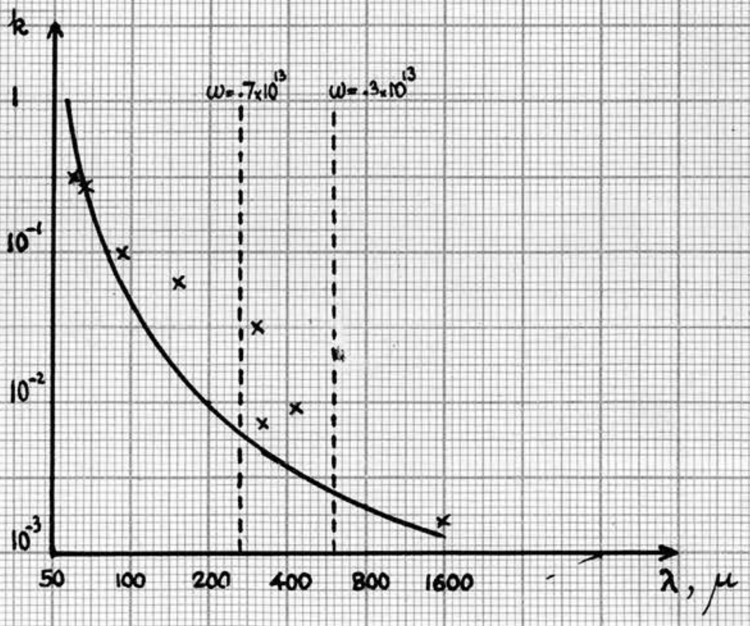
(1930) and Barnes and Czerny (1931). The values of D for $d = 3\cdot6\,\mu$ are from Barnes and Czerny (1931), and for $d = 24\,\mu$ from Mentzel, (1934). The agreement between the theoretical and experimental curves can no doubt be improved by further manipulation of the constants. The process is tedious, and in view of the number of approximations made, the additional work involved is hardly justified. From the preceding work, it is seen that as far as the positions of the secondary lines are concerned, the agreement between theory and experiment is quite good. Further, the values selected for the constants b_1, b_2, b_3, are of the correct order of magnitude. The values of the refractive index n and the extinction co-efficient k are shown in Fig. X.

So far, the difference terms have not been considered in the polarisability. They will give rise to absorption on the long wave-length side of the first order line. Corresponding to the principal secondary summation line at $40\cdot5\,\mu$, one would expect from Fig. V. a difference line $\omega = \cdot7 \times 10^{13}$. The only additional terms that could appear would be due to the combination $(j j') = (34)$ and (56). From Fig. VII it is seen they would give rise to a line at $\omega = \cdot3 \times 10^{13}$. There are only a few single measurements in this region. They are quoted in Czerny (1930). The values of the extinction co-efficient k are shown by crosses in Fig. XI. The full curves are values of k obtained from a

FIGURE XI.

The Extinction Co-efficient for Long Wave Lengths.

The experimental values are shown by crosses. The full curve is obtained by Czerny from a Drude formula with two infra-red terms.



Drude formula, for the first order line and the principal secondary line, by Czerny. It is seen that the prediction of maximum absorption at the frequencies $\omega = \cdot 7 \times 10^{13}$ and $\omega = \cdot 3 \times 10^{13}$ agrees quite well with the observations.

It can thus be said, that the secondary structure in the absorption spectrum and the maxima in reflection, can be explained by assuming that the electric moment of the crystal can be expanded in terms of the nuclear displacements. This is equivalent, as has been stated before to assuming that the ions are polarisable, and that exchange of electrons can take place between them.

In conclusion, the author wishes to express his gratitude to Professor Born for suggesting these two problems, and for his kindly supervision during the progress of the work.

SUMMARY

An account is given of Professor Born's modern quantum-mechanical theory of dispersion in crystals, in which the polarisability is given as a function of the vibrational matrix elements of the electric moment of the unperturbed crystal. The electric moment is expanded with respect to the amplitudes of vibrations, and the polarisability consists of contributions of different orders. The first order

effect is a line spectrum depending only on the vibrations of infinite wavelength, the second order effect is a continuous spectrum depending on combination frequencies of all pairs of branches of the lattice vibrations, each pair taken for the same wave-vector. Absorption is taken account of in a phenomenological way, by introducing a damping constant for each absorbing frequency. Each branch of the second order polarisability is expressed as the integral over all wave vectors of the product of factors depending on the temperature, the moment, and the shape of the individual lines.

Professor Born's general theory is simplified in order to obtain results which can be compared directly with experiment. The integral over all wave vectors is transformed into one over the spectrum of the combination frequencies by introducing a frequency density function. The frequency range of integration is divided so that each division contains one maximum of the frequency density function. The moment and temperature factors being slowly varying functions, are assumed to have a definite value for each range of integration. Each maximum of a frequency density function is represented by an analytical form and the integrations over the frequency spectrum are carried out. In the final result, the polarisability is represented by a superposition of a number of simple "Drude" lines with arbitrary intensity factors.

The theory is applied in detail to sodium chloride. The frequency density curves are obtained from Kellermann's calculation of the frequencies of vibration of the sodium chloride lattice. By extending this work, it is shown that the density curves have several maxima. Without any arbitrary assumptions the theory predicts the frequencies of all the observed secondary absorption maxima in fair agreement with experiment.

One maximum in each frequency density function is due to frequencies associated with wave vectors nearly equal to $[\pi, \pi, \pi]$. In this case, the intensity factors of the corresponding absorption maxima are given explicitly in terms of the four independent first-neighbour coupling constants. By adapting the arbitrary intensity factors for the frequency region of the sum combination branches, a good fit is obtained with the experimentally observed reflection and transmission coefficients. This is not done for the difference branches, because one cannot fit the first order effect over such a wide range of the spectrum.

The results show that lattice dynamics can account quantitatively for the fine structure observed in the absorption spectra of crystals, and that Raman's attacks against the theory are unfounded.

APPENDIX I.

The evaluation of $\int_{-\infty}^{\infty} \frac{x\,dx}{(x^2+a^2)[(x-c)^2+b^2]}$

The integrand has poles at $x = \pm ia,\ c \pm ib$.

The residues at these poles are given by

$$\frac{1}{2(c^2+b^2-a^2-2iac)} = \frac{c^2+b^2-a^2+2iac}{2(a^4+b^4+c^4+2b^2c^2+2a^2c^2-2a^2b^2)} \qquad (x = ia)$$

(1)

$$\frac{c+ib}{2ib[(c+ib)^2+a^2]} = \frac{(1+\frac{c}{ib})[a^2+c^2-b^2-2ibc]}{2(a^4+b^4+c^4+2b^2c^2+2a^2c^2-2a^2b^2)} \qquad (x = c+ib)$$

(2)

If the value of the integral is I, one has

$$I = 2\pi i(\text{sum of the residues})$$

(3)
$$= \frac{\pi c}{b} \; \frac{(a-b)^2+c^2}{(c^2+b^2-a^2)^2+4a^2c^2}$$

$$= \frac{\pi c}{b} \; \frac{1}{(a+b)^2+c^2}$$

REFERENCES (PART II.)

Ackermann, 1915. Ann. d. Physik. 46, 197.

Barnes, Brattain and Seitz, 1935. Phy. Rev. 48, 582.

Barnes and Czerny, 1931. Z. Phys. 72, 447.

Blackman, 1933. Z. Phys. 86, 421.

Blackman, 1936. Philos. Trans. 236, 103.

Born, 1923. Atomtheorie des festen Zustandes.

Born, 1945. Rev. Mod. Phys. 17, 245.

Born and Blackman, 1933. Z. Phys. 82, 551.

Born and Bradburn, 1947. Proc. Roy. Soc. 188, 161.

Born and Oppenheimer, 1927. Ann. d. Physik. 46, 197.

Cartwright and Czerny, 1933. Z. Phys. 85, 269.

Cartwright and Czerny, 1933. Z. Phys. 90, 54.

Czerny, 1930. Zs. f. Phys. 56, 215.

Ewald, 1912. Munchen Dissertation.

Ewald, 1916. Ann. d. Phys. 49, 1.

Fock, 1934. Z. Phys. 90, 44.

Fuchs and Wolff, 1928. Zs. f. Phys. 46, 506.

Kellermann, 1940. Phil. Trans. A238, 513.

Kellermann, 1941. Proc. Roy. Soc. A178, 17.

Kellner, 1929. Zs. f. Phys. 56, 215.

Kellner, 1941. Rep. Prog. Phys. 8, 200.

Ladenburg, 1921. Zeitschr. f. Phys. 7, 751.

Matossi, 1938. Ergebnisse der exakten Naturwissenschaften, 17, 108.

Mentzel, 1934. Zs. f. Phys. 88, 178.

Pauli, 1925. Verh. deuts. Phys. Ges. 6, 10.

REFERENCES (PART II) (Contd.)

Placzek, 1934. Marx Handbuch der Radiologie-Quantum mechanik der Materie und Strahlung. 2, 209.

Pomeranchuk, 1943. Journ. Phys. 6, 262.

Raman, 1947. Nature, 161, 165.

Smith, 1948. Phil. Trans. A241, 105.