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THEORY OF THE VIBRATIONS OF THE SODIUM CHLORIDE LATTICE

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INTRODUCTION

The interest in the frequency spectrum of the thermal vibrations in a crystal arose chiefly in connexion with the problem of the specific heat of crystals at low temperatures. Debye's theory of the specific heat, however, has been so successful that the actual determination of the frequency spectrum according to Born and v. Kármán (1912) has been pushed into the background. But recent investigations, especially those of Blackman (1935, 1937 *a, b,* 1938), have shown that appreciable deviations from Debye's theory should occur according to the correct atomistic treatment. These deviations appear to be most pronounced near the absolute zero of temperature. It, therefore, seemed desirable to calculate the exact frequency spectrum of a crystal.

The first attempt to calculate the frequency spectrum of a crystal was made by Born and v. Kármán in their original paper. They assumed only quasi-elastic forces between neighbouring particles. Later calculations have been made for ionic lattices, for which we have a fair knowledge of the real forces which determine the equilibrium positions and the vibrations about them. The chief difficulty in that calculation has always been the long range of the Coulomb force which makes a direct summation over all lattice points impossible.

Born and Thompson (1934), using a method developed by Ewald (1921), suggested a way of transforming these sums into more rapidly convergent expressions, and Thompson (1935) has given the final formulae for the coupling coefficients due to the Coulomb force in the equation of motion, but in his paper a slight mistake occurred in the definition of the coefficients, and so far no numerical results of these calculations have been published. Broch (1937) has given formulae for the case of a one-dimensional lattice making use of Epstein's Zeta functions. Lyddane and Herzfeld (1938) have used an extension of Madelung's method (1918) and they have given some numerical results, but their formulae are rather complicated, so that one cannot expect to compute the whole frequency spectrum by this method. Moreover, the problem of the thermal oscillations of an ionic lattice is not a purely electrostatic problem, and this point has not been made sufficiently clear by Lyddane and Herzfeld. Their treatment of the case of the residual rays is open to objection, and the question whether the potential, from which the coupling coefficients are obtained, satisfies the Laplace equation or Poisson's equation is not clear.

In this paper I have used Ewald's method mentioned above, in a new form given by him in a recent paper (1938). By this method one obtains comparatively simple and quickly convergent expressions for the coupling coefficients in the equation of motion which allow a numerical calculation to an arbitrary degree of accuracy. Because of the good convergence it has not been too laborious to compute numerical values for 48 different modes of vibration.

In § 2 the derivation of these expressions is given by treating the problem as an electrostatic problem, neglecting the retardation; but the proper way of solving the problem is to find a solution of Maxwell's equation for the electromagnetic field in the crystal. This will be done in § 3. From this field the force exerted on a particle and the coupling coefficients can be obtained (§ 4). It will be seen that in this proper treatment the case of infinitely long waves plays a special role and must be considered separately. In all the other cases this treatment leads to the same result as the electrostatic derivation. If one defines a potential function from which the coupling coefficients are obtained as second derivatives, this potential satisfies in general Laplace's equation; but in the special case of infinitely long waves it satisfies Poisson's equation with constant density.

In § 5 the coupling coefficients for the NaCl lattice are given, and in § 6 the contribution due to the repulsive forces is calculated.

In § 7 the equations for the coupling coefficients are checked by deriving from them formulae for the elastic constants.

The numerical values of the coefficients are given in § 8. In § 9 the corresponding frequencies are calculated and illustrated by figures, and finally (§ 10) the resulting distribution of the frequencies is discussed and the distribution curve is plotted.

1. THE EQUATION OF MOTION

I shall use the notation of Born's *Atomtheorie des festen Zustandes* (1923); cf. also Born and Goeppert-Mayer (1933).

The lattice vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ determine the cell of volume v_a. The positions of the s particles in the cell are represented by the basis vectors $\mathbf{r}_\kappa$ ($\kappa = 1, \ldots s$). The equilibrium position of a particle (κ, l) is determined by the vector

$$\mathring{\mathbf{r}}_\kappa^l = \mathbf{a}^l + \mathring{\mathbf{r}}_\kappa, \quad \mathbf{a}^l = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3. \tag{1.0}$$

l stands for the three arbitrary integers l_1, l_2, l_3. The distance vector between two lattice points is given by

$$\mathring{\mathbf{r}}_{\kappa\kappa'}^{ll'} = \mathring{\mathbf{r}}_\kappa^l - \mathring{\mathbf{r}}_{\kappa'}^{l'} = \mathbf{a}^l - \mathbf{a}^{l'} + \mathring{\mathbf{r}}_\kappa - \mathring{\mathbf{r}}_{\kappa'} = \mathbf{a}^{l-l'} + \mathring{\mathbf{r}}_\kappa - \mathring{\mathbf{r}}_{\kappa'}. \tag{1.1}$$

Considering small independent displacements $\mathbf{u}_k^l = (u_{kx}^l, u_{ky}^l, u_{kz}^l)$ of each particle from its equilibrium position, the vector between the displaced particles is

$$\mathbf{r}_{\kappa\kappa'}^{ll'} = \mathring{\mathbf{r}}_{\kappa\kappa'}^{l-l'} + \mathbf{u}_\kappa^l - \mathbf{u}_{\kappa'}^{l'}. \tag{1.2}$$

Assuming only *central forces*, the total potential energy of the lattice is

$$\Phi = \tfrac{1}{2}\sum_{\kappa\kappa'}\sum_{ll'}{}'\,\phi_{\kappa\kappa'}(|\,r_{\kappa\kappa'}^{ll'}\,|). \tag{1.3}$$

(The dash indicates that the terms $l = l'$, $\kappa = \kappa'$ are omitted.) Neglecting surface effects the energy density

$$\frac{1}{Nv_a}\Phi \quad (N = \text{number of cells}) \tag{1.4}$$

remains finite, and the expansion of the energy in the neighbourhood of the equilibrium position when developed in powers of the displacements $\mathbf{u}_\kappa^l$ gives

$$\Phi = \Phi_0 + \Phi_1 + \Phi_2 + \dots. \tag{1.5}$$

In equilibrium the first-order terms vanish.

The second-order terms

$$\Phi_2 = -\tfrac{1}{2}\sum_{\kappa\kappa'}\sum_{ll'}\sum_{xy}(\phi_{\kappa\kappa'}^{l-l'})_{xy}\,u_{\kappa x}^l\,u_{\kappa'y}^{l'}, \tag{1.6}$$

where

$$(\phi_{\kappa\kappa'}^l)_{xy} = \left[\frac{\partial^2}{\partial x\,\partial y}\phi_{\kappa\kappa'}(r)\right]_{r=r_{\kappa\kappa}^l},$$

with the definition

$$(\phi_{\kappa\kappa'}^0)_{xy} = -\sum_{k'}\sum_l{}'\,(\phi_{\kappa\kappa'}^l)_{xy},$$

lead to the equation of motion

$$m_\kappa \ddot{u}_{\kappa x}^l - \sum_{\kappa'}\sum_{l'}\sum_y(\phi_{\kappa\kappa'}^{l-l'})_{xy}\,u_{\kappa'y}^{l'} = 0, \tag{1.7}$$

where a dot denotes differentiation with regard to time and m_κ is the mass of the particle of type κ.

Considering one of the independent normal modes of vibration with frequency ω, wave-length λ and wave vector $\mathbf{k}$, $k = |\,\mathbf{k}\,| = 1/\lambda$ the displacements of the particles are then

$$\mathbf{u}_\kappa^l = \mathbf{U}_\kappa\,e^{-i\omega t}\,e^{2\pi i(\mathbf{k},\,\hat{\mathbf{r}}_\kappa^l)} \tag{1.8}$$

(the index 0 will be omitted in the following equations) and the equation of motion becomes

$$\omega^2 m_\kappa U_{\kappa x} + \sum_{\kappa'}\sum_y \begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} U_{\kappa'y} = 0, \tag{1.9}$$

where

$$\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} = \sum_l (\phi_{\kappa'\kappa}^l)_{xy}\,e^{2\pi i(\mathbf{k},\,\mathbf{r}_{\kappa'\kappa}^l)}. \tag{1.10}$$

From the definition (1.6) there follows

$$\sum_{\kappa'}\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}_{k=0} = 0. \tag{1.11}$$

The corresponding contributions of different forces to these bracket symbols (coefficients of the equation of motion) are additive. For example,

$$\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} = {}^C\!\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} + {}^R\!\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}, \tag{1.12}$$

where C may denote the Coulomb forces and R the repulsive forces.

The choice of the wave vectors $\mathbf{k}$ is restricted by the boundary condition of the "cyclic lattice" (Born 1923, p. 588). It postulates that the displacement be periodic in a volume having the same shape as the elementary cell and containing $n^3 = N$ cells. To formulate this, introduce the base vectors $\mathbf{b}_j$ of the reciprocal lattice

$$(\mathbf{a}_i, \mathbf{b}_j) = \delta_{ij}, \quad \mathbf{b}_1 = \frac{1}{v_a}[\mathbf{a}_2 \times \mathbf{a}_3], \quad \mathbf{b}_2 = ..., \tag{1.13}$$

and the radius vector $\mathbf{b}_h$ of this lattice,

$$\mathbf{b}_h = h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3 \quad (h_j \text{ arbitrary integers}). \tag{1.14}$$

Then the condition of cyclic behaviour leads to

$$\mathbf{k} = \frac{1}{n}\mathbf{b}_h = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3, \tag{1.15}$$

where $\quad k_1 = h_1/n, \quad k_2 = h_2/n, \quad k_3 = h_3/n \quad (h_1, h_2, h_3 = 0, 1, ..., n-1). \tag{1.16}$

2. The coupling coefficients of the electrostatic interaction

Consider now especially the case of electrostatic forces. Here the series (1.10) are not absolutely convergent and have to be transformed into other series which correspond to the physical conditions (neutral cell) and are quickly convergent.

Following Ewald (1921, 1938) I consider a lattice sum of the form

$$\bar{F}^k(\mathbf{r}) = \sum_l \bar{f}(\mathbf{r} - \mathbf{a}^l)\, e^{2\pi i(\mathbf{k}, \mathbf{a}^l)}, \tag{2.0}$$

which can be written $\quad \bar{F}^k(\mathbf{r}) = e^{2\pi i(\mathbf{k}, \mathbf{r})} \sum_l \bar{f}(\mathbf{r} - \mathbf{a}^l)\, e^{2\pi i(\mathbf{k}, \mathbf{a}^l - \mathbf{r})} \tag{2.1}$

and be considered as a periodic function which is modulated by a wave

$$\exp\{2\pi i(\mathbf{k}, \mathbf{r})\}.$$

The sum can then be represented by a Fourier series

$$\sum_l \bar{f}(\mathbf{r} - \mathbf{a}^l)\, e^{2\pi i(\mathbf{k}, \mathbf{a}^l - \mathbf{r})} = \sum_h \bar{F}_h^k e^{2\pi i(\mathbf{b}_h, \mathbf{r})}, \tag{2.2}$$

with the Fourier coefficients

$$\bar{F}_h^k = \frac{1}{v_a}\int \bar{f}(\mathbf{r})\, e^{-2\pi i(\mathbf{b}_h + \mathbf{k}, \mathbf{r})}\, dv = \frac{1}{v_a}\bar{\varphi}(\mathbf{b}_h + \mathbf{k}), \tag{2.3}$$

where the integration extends over the whole of space and

$$\bar{\varphi}(\mathbf{b}) = \int \bar{f}(\mathbf{r})\, e^{-2\pi i(\mathbf{b}, \mathbf{r})}\, dv, \quad dv = dx_1 dx_2 dx_3, \tag{2.4}$$

is the Fourier transform of $\bar{f}(\mathbf{r})$.

I apply the transformation (2.2) to the function

$$\bar{f}(\mathbf{r}) = \frac{2}{\sqrt{\pi}} e^{-\epsilon^2 r^2}, \quad \int_0^\infty \bar{f}(\mathbf{r})\, d\epsilon = \frac{1}{|r|}. \tag{2.5}$$

It is then only necessary to determine $\overline{\varphi}(\mathbf{b})$ from (2·4) and to insert it into (2·2) and find Ewald's well-known formula of the Theta function transformation (cf. Born 1923, p. 765)

$$\overline{F}^k(\mathbf{r}) = \frac{2}{\sqrt{\pi}} \sum_l e^{-\epsilon^2(\mathbf{r}-\mathbf{a}^l)^2 + 2\pi i(\mathbf{k}, \mathbf{a}^l)} = \frac{2\pi}{v_a} \sum_h \frac{1}{\epsilon^3} e^{-\frac{\pi^2}{\epsilon^2}(\mathbf{b}_h+\mathbf{k})^2 + 2\pi i(\mathbf{b}_h+\mathbf{k}, \mathbf{r})}. \tag{2·6}$$

Applying this to the Coulomb potential

$$\varphi_{\kappa'\kappa}(|r|) = e_{\kappa'} e_\kappa f(\mathbf{r}), \quad f(\mathbf{r}) = \frac{1}{|r|}, \tag{2·7}$$

where e_κ is the charge of the κth type of particle at the lattice points $\mathbf{r}_\kappa^l$, we obtain for (1·10), since $|-\mathbf{r}_{\kappa'\kappa}-\mathbf{a}^l| = |\mathbf{r}_{\kappa'\kappa}^l|$,

$$\left.\begin{aligned}
{}^C\!\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} &= e_{\kappa'} e_\kappa \lim_{\mathbf{r}\to-\mathbf{r}_{\kappa'\kappa}} \sum_l \frac{\partial^2}{\partial x \partial y} f(\mathbf{r}-\mathbf{a}^l)\, e^{2\pi i(\mathbf{k}, \mathbf{r}_{\kappa'\kappa}^l)}, \quad \kappa \neq \kappa', \\
{}^C\!\begin{bmatrix} \kappa & \kappa \\ x & y \end{bmatrix} &= e_\kappa^2 \lim_{\mathbf{r}\to 0}\left[\sum_l \frac{\partial^2}{\partial x \partial y} f(\mathbf{r}-\mathbf{a}^l)\, e^{2\pi i(\mathbf{k}, \mathbf{a}^l)} - \frac{\partial^2}{\partial x \partial y} f(\mathbf{r})\right].^*
\end{aligned}\right\} \tag{2·8}$$

As a quickly convergent representation of the sums in (2·8) can be found, it is permissible to exchange differentiation and summation and to define a function

$$F^k(\mathbf{r}) = \sum_l f(\mathbf{r}-\mathbf{a}^l)\, e^{2\pi i(\mathbf{k}, \mathbf{a}^l)}, \tag{2·9}$$

so that

$$\frac{\partial^2}{\partial x \partial y} F^k(\mathbf{r}) = \sum_l \frac{\partial^2}{\partial x \partial y} f(\mathbf{r}-\mathbf{a}^l)\, e^{2\pi i(\mathbf{k}, \mathbf{a}^l)} = F_{xy}^k(\mathbf{r}), \tag{2·10}$$

and since

$$-\mathbf{r}_{\kappa'\kappa} = \mathbf{r}_{\kappa\kappa'}$$

(cf. (1·0), (1·1)) one can write for the coupling coefficients (2·8)

$$\left.\begin{aligned}
{}^C\!\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} &= e_{\kappa'} e_\kappa \sum_l \left[\frac{\partial^2}{\partial x \partial y} f(\mathbf{r}-\mathbf{a}^l)\right]_{\mathbf{r}=\mathbf{r}_{\kappa\kappa'}} e^{2\pi i(\mathbf{k}, \mathbf{a}^l-\mathbf{r}_{\kappa\kappa'})} \\
&= e_\kappa e_{\kappa'} e^{-2\pi i(\mathbf{k}, \mathbf{r}_{\kappa\kappa'})} F_{xy}^k(\mathbf{r}_{\kappa\kappa'}), \quad \kappa \neq \kappa',\dagger \\
{}^C\!\begin{bmatrix} \kappa & \kappa \\ x & y \end{bmatrix} &= e_\kappa^2 \lim_{\mathbf{r}\to 0}\left[F_{xy}^k(\mathbf{r}) - f_{xy}(\mathbf{r})\right], \quad f_{xy} = \frac{\partial^2 f}{\partial x \partial y}.
\end{aligned}\right\} \tag{2·11}$$

* It must be remembered that the term $(\varphi_{\kappa\kappa}^0)_{xy}$ is defined by (1·6) and is not equal to

$$e_\kappa^2 \left[\frac{\partial^2}{\partial x \partial y} f(\mathbf{r})\right]_{\mathbf{r}=0},$$

which is infinite. $(\varphi_{\kappa\kappa}^0)_{xy}$ represents the force exerted on the particle (κ, l) if it is displaced by a small amount, all other particles being kept at their equilibrium positions. It can easily be shown that for Coulomb forces and cubic symmetry this term vanishes.

$\dagger$ Thompson (1935) has not defined the coefficients ${}^C\!\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}$ correctly. He leaves out the exponential function $\exp\{-2\pi i(\mathbf{k}, \mathbf{r}_{\kappa\kappa'})\}$.

Now it is at once seen that the lattice sum $\overline{F}^k$ (2·1), (2·6) is connected by (2·5) with the lattice sum F^k (2·9) from which the coefficients are derived, namely,

$$\int_0^\infty \overline{F}^k(\mathbf{r})\, d\epsilon = F^k(\mathbf{r}). \qquad (2\cdot12)$$

Thus immediate use can be made of (2·6) for the transformation of the coupling coefficients. It should be noted that the sum in the first representation of $\overline{F}^k$ in (2·6) converges rapidly for large values of ϵ but not for small values, and the opposite holds for the second representation. Therefore, following Ewald, I divide the integration (2·12) into two parts $\int_0^\infty = \int_0^E + \int_E^\infty$, taking as integrand in the first integral the second and in the second integral the first expression (2·6).

The integration yields

$$F^k(\mathbf{r}) = \frac{1}{\pi v_a} \sum_h \frac{1}{(\mathbf{b}_h + \mathbf{k})^2} e^{-\frac{\pi^2}{E^2}(\mathbf{b}_h + \mathbf{k})^2 + 2\pi i(\mathbf{b}_h + \mathbf{k}, \mathbf{r})} + \sum_l \frac{1 - G(E\,|\,\mathbf{r} - \mathbf{a}^l\,|)}{|\,\mathbf{r} - \mathbf{a}^l\,|} e^{2\pi i(\mathbf{k}, \mathbf{a}^l)}, \qquad (2\cdot13)$$

where G is Gauss's function

$$G(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\xi^2} d\xi, \quad G(\infty) = 1. \qquad (2\cdot14)$$

This expression (2·13) is very quickly convergent, as the arbitrary parameter E can be chosen in such a way that the two series $\underset{h}{\Sigma}$ and $\underset{l}{\Sigma}$ converge rapidly, so justifying the interchange of differentiation and summation in (2·10).

Finally the differentiation (2·11) gives

$$^C\!\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} = e_\kappa e_{\kappa'} \left\{ -\frac{4\pi}{v_a} \sum_h \frac{(b_{hx} + k_x)(b_{hy} + k_y)}{(\mathbf{b}_h + \mathbf{k})^2} e^{-\frac{\pi^2}{E^2}(\mathbf{b}_h + \mathbf{k})^2 - 2\pi i(\mathbf{b}_h, \mathbf{r}_{\kappa'\kappa})} \right.$$

$$\left. + E^2 \sum_l \left[\psi'(E\,|\,r_{\kappa\kappa'}^l\,|) \frac{\delta_{xy}}{|\,r_{\kappa\kappa'}^l\,|} + \left[E\psi''(E\,|\,r_{\kappa\kappa'}^l\,|) - \frac{\psi'(E\,|\,r_{\kappa\kappa'}^l\,|)}{|\,r_{\kappa\kappa'}^l\,|} \right] \frac{x_{\kappa\kappa'}^l y_{\kappa\kappa'}^l}{|\,r_{\kappa\kappa'}^l\,|^2} \right] e^{2\pi i(\mathbf{k}, \mathbf{r}_{\kappa'\kappa})} \right\},$$

$$^C\!\begin{bmatrix} \kappa & \kappa \\ x & y \end{bmatrix} = e_\kappa^2 \left\{ -\frac{4\pi}{v_a} \sum_h \frac{(b_{hx} + k_x)(b_{hy} + k_y)}{(\mathbf{b}_h + \mathbf{k})^2} e^{-\frac{\pi^2}{E^2}(\mathbf{b}_h + \mathbf{k})^2} + \frac{4}{3\sqrt{\pi}} E^3 \delta_{xy} \right.$$

$$\left. + E^2 \sum_l \left[\psi'(E\,|\,a^l\,|) \frac{\delta_{xy}}{|\,a^l\,|} + \left[E\psi''(E\,|\,a^l\,|) - \frac{\psi'(E\,|\,a^l\,|)}{|\,a^l\,|} \right] \frac{a_x^l a_y^l}{|\,a^l\,|^2} \right] e^{2\pi i(\mathbf{k}, \mathbf{a}^l)} \right\},$$

$$\frac{1 - G(x)}{x} = \psi(x), \quad \psi'(x) = \frac{\partial \psi}{\partial x}, \quad \psi''(x) = \frac{\partial^2 \psi}{\partial x^2}.$$

$$(2\cdot15)$$

For $\mathbf{k} = 0$ the zero term in F^k (2·13) gives rise to a divergence so that the electrostatic derivation breaks down. The reason is that the problem of describing the electromagnetic interaction in the crystal is not a purely electrostatic problem. One has to bear in mind that because of the vibrations of the ions there will in general be an electromagnetic field in the crystal. The proper way, therefore, of determining the

coupling coefficients $^c\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}$ must be to start from Maxwell's equations and to find the proper solution of our problem. In the electromagnetic treatment, then, the divergence encountered in the function F^k for $\mathbf{k} = 0$ will disappear.

3. THE ELECTROMAGNETIC FIELD OF THE CRYSTAL

Born (1923) has calculated the electromagnetic field of the crystal as originated by a superposition of spherical waves arising from the vibrating point charges. (This corresponds to the introduction of the "optical" instead of the electrostatic potentials (cf. Ewald 1921).) I shall give here the derivation as far as is necessary for our purposes. From the electromagnetic field the forces acting on any particle and therefore the coupling coefficients will be obtained.

The result will be that the coefficients derived in this way will again be expressible as the second derivatives of a potential function to which one can apply the same transformation as used in the preceding section. It will be found that for all wave vectors $\mathbf{k} \neq 0$ the two potential functions are identical, so that the results of the preceding section can be used without modification. In the case of infinitely long waves ($\mathbf{k} = 0$) which leads to the frequency of the residual rays, the electromagnetic derivation will show that a modification of the potential function (2·13) is necessary. This can be applied immediately by comparing the potential function obtained by the electromagnetic derivation, with the representation (2·13) of the electrostatic values with $E = \infty$. This modification will remove the divergent term in the potential function (2·13).

It may be surprising at first sight that the case of infinite waves has to be treated separately and cannot be obtained as a limiting case of long waves. The reason for this can easily be seen (cf. Born and Goeppert-Mayer 1933, p. 732). Starting from a finite crystal with $n^3 = N$ cells and a finite wave-length λ, one has to deal with a double limit: $N \to \infty$ and $\lambda \to \infty$. Now for finite wave-lengths and a finite crystal one has in general

$$r_0 \leqslant \lambda \ll nr_0 \quad (r_0 \text{ lattice constant}).$$

Here one must proceed clearly first to the limit $N \to \infty$. For infinite wave-lengths, on the other hand, one must first put $\lambda \to \infty$ and then proceed to the limit $N \to \infty$. There is, of course, an intermediate region where λ is of the order of the linear dimensions of the crystal. But this region is negligibly small in the scale of the numbers $k_1 = h_1/n$, $k_2 = h_2/n$, $k_3 = h_3/n$ (cf. (1·15), (1·16)), which are the components of the wave vector $\mathbf{k}$ in the reciprocal lattice. For, if λ is of the order $l = nr_0$ then $k = 1/\lambda$ is of the order $k \sim 1/nr_0 \sim b/n$, hence k_1, k_2, k_3 are of the order $1/n \sim 10^{-8}$ for $l = 1$ cm. If the accuracy of the determination of k_1, k_2, k_3 is even as high as 10^{-6}, the region of the waves of "macroscopic dimensions" is not detectable and can be replaced by the point $k_1 = k_2 = k_3 = 0$. There is an apparent discontinuity at $\mathbf{k} = 0$, and it is therefore no

contradiction that this point satisfies another equation than the rest of the spectrum. For a detailed discussion of this discontinuity the knowledge of the electromagnetic field will be needed.

The electromagnetic field can be represented (Born 1923, p. 761) by the field of vibrating dipoles plus an electrostatic field, the latter of which does not give rise to a force in lattices of cubical symmetry and for small displacements.

The moment of such a dipole is

$$e_\kappa \mathbf{u}_\kappa^l, \quad \text{where} \quad \mathbf{u}_\kappa^l = \mathbf{U}_\kappa e^{-i\omega t} e^{2\pi i(\mathbf{k},\, \mathbf{r}_\kappa^l)}.$$

The field can be described by the Hertz vector

$$\mathbf{Z} = \mathbf{S}\, e^{-i\omega t} e^{2\pi i(\mathbf{k},\, \mathbf{r})}, \tag{3.0}$$

which is the sum of Hertz's solutions for the various vibrating dipoles. The vector $\mathbf{S}$ is a function of space. It has been determined by Born (1923); he finds

$$\mathbf{S} = \sum_\kappa \mathbf{p}_\kappa S(\mathbf{r} - \mathbf{r}_\kappa), \quad \mathbf{p}_\kappa = e_\kappa \mathbf{U}_\kappa, \tag{3.1}$$

where S is the Fourier series

$$S = \frac{1}{\pi v_a} \sum_h \frac{e^{2\pi i(\mathbf{b}_h,\, \mathbf{r})}}{(\mathbf{b}_h + \mathbf{k})^2 - k_0^2}, \tag{3.2}$$

$$k_0 = \frac{1}{\lambda_0} = \frac{\omega_0}{2\pi c}.$$

λ_0 is the wave-length in vacuum corresponding to the frequency ω_0.

Now separate the zero term of the series (3.2) which represents the mean value of the electromagnetic field

$$\left. \begin{aligned} S &= \bar{S} + \tilde{S}, \\ \bar{S} &= \frac{1}{\pi v_a} \frac{1}{k^2 - k_0^2} = \frac{1}{\pi v_a} \frac{n^2/k^2}{n^2 - 1}, \\ \tilde{S} &= \frac{1}{\pi v_a} \sum_h{}' \frac{e^{2\pi i(\mathbf{b}_h,\, \mathbf{r})}}{(\mathbf{b}_h + \mathbf{k})^2 - k_0^2}, \end{aligned} \right\} \tag{3.3}$$

where the refractive index $n = k/k_0 = \lambda_0/\lambda$ has been introduced.

The Hertz vector corresponding to the mean electromagnetic field is, according to (3.1), (3.0), given by

$$\bar{\mathbf{Z}} = \frac{1}{\pi} \mathbf{P} \frac{n^2/k^2}{n^2 - 1}, \tag{3.4}$$

where

$$\left. \begin{aligned} \mathbf{P} &= \mathbf{P}_0 e^{-i\omega t} e^{2\pi i(\mathbf{k},\, \mathbf{r})}, \\ \mathbf{P}_0 &= \frac{1}{v_a} \sum_\kappa \mathbf{p}_\kappa. \end{aligned} \right\} \tag{3.5}$$

$\mathbf{P}$ may be interpreted as the moment per unit volume.

From the Hertz vector (3·4) the mean electromagnetic field vectors are obtained:

$$\overline{\mathbf{E}} = \operatorname{grad}\operatorname{div}\overline{\mathbf{Z}} - \frac{1}{c^2}\frac{\partial^2\overline{\mathbf{Z}}}{\partial t^2} = 4\pi\frac{1}{n^2-1}\{\mathbf{P}-n^2\mathbf{s}(\mathbf{P},\mathbf{s})\},$$

$$\overline{\mathbf{H}} = \frac{1}{c}\operatorname{curl}\frac{\partial\overline{\mathbf{Z}}}{\partial t} = 4\pi\frac{n}{n^2-1}[\mathbf{s}\times\mathbf{P}], \tag{3·6}$$

$$\mathbf{k} = |\mathbf{k}|\,\mathbf{s}.$$

Here $\mathbf{s}$ is a unit vector in the direction of propagation of the wave.

These are the same formulae as those which one obtains as a solution of Maxwell's equations for a plane wave by putting $\mathbf{B} = \mathbf{H}$ and splitting up $\mathbf{D}$ into $\mathbf{E}+4\pi\mathbf{P}$ as has been pointed out by Born and Goeppert-Mayer (1933, p. 776).

In order to discuss the formulae (3·6) one has to consider the magnitude of

$$n = k/k_0 = \lambda_0/\lambda$$

which will make it possible to distinguish between the two different cases $k = 0$ and $k \neq 0$.

The frequency of the fastest vibrations occurring in crystals is of the order 10^{13} sec.$^{-1}$, and the corresponding smallest wave-length $\lambda_0 = 1/k_0 \sim 10^{-3}$ cm. This is very large compared with the lattice distance ($\sim 10^{-8}$ cm.). For the thermal vibrations of the crystal one can consider the wave-length λ as very small compared with the length λ_0 of the light wave of the same frequency *in vacuo* and can therefore put $n = \infty$. The only exception is $k = 0$; in this case n vanishes since $1/k_0 \neq 0$ (cf. (3·2): $\omega_0 \neq 0$).

Therefore, in the case $k = 0$ (3·6) becomes

$$\overline{\mathbf{E}} = -4\pi\mathbf{P}, \quad \overline{\mathbf{H}} = 0; \quad k = 0,\ k_0 \text{ not neglected,} \tag{3·7}$$

and in the case $k \neq 0$

$$\overline{\mathbf{E}} = -4\pi\mathbf{s}(\mathbf{P},\mathbf{s}), \quad \overline{\mathbf{H}} = 0; \quad k \neq 0,\ k_0 \text{ neglected.} \tag{3·8}$$

The value (3·0) for the Hertz vector developed here can be used for the solution of the dynamical problem of the proper vibrations of the crystal only under the condition that the system can be considered as closed, i.e. that there is no emission of radiation. It will be seen, however, that this is the case for all values of k except $k = 0$. In these cases ($k \neq 0$) the total moment of the crystal must vanish, since all the dipoles in the crystal vibrate with a difference of phase which is not invariant against a translation of the lattice vector. That can be seen at once (cf. Born and Goeppert-Mayer 1933, p. 643) from the expression for the total moment itself

$$\sum_l \sum_\kappa \mathbf{p}_\kappa^l = \sum_l \sum_\kappa e_\kappa \mathbf{u}_\kappa^l = e^{-i\omega t}\sum_\kappa e_\kappa \mathbf{U}_\kappa e^{2\pi i(\mathbf{k},\,\mathbf{r}_\kappa)}\sum_l e^{2\pi i(\mathbf{k},\,\mathbf{a}^l)}. \tag{3·9}$$

This sum is zero for all values of $\mathbf{k}$ except $\mathbf{k} = 0$.

I shall now show that our solution for the Hertz vector corresponds to this fact. The optical properties of crystals have been carefully investigated by Ewald (cf. Born

1923, p. 774). Consider a crystal which is bounded on one side by a plane perpendicular to the vector $\mathbf{b}_3$, so that

$$\left.\begin{aligned} (\mathbf{r}, \mathbf{b}_3) &> 0, \quad \text{inside the crystal,} \\ (\mathbf{r}, \mathbf{b}_3) &< 0, \quad \text{outside the crystal.} \end{aligned}\right\} \tag{3.10}$$

The Hertz vector for such a "half-crystal" has been found by Ewald. It is

$$\left.\begin{aligned} \mathbf{Z}^{(\mathrm{in})} &= \mathbf{Z}^{(0)} + \mathbf{Z}^{(1)}, \\ \mathbf{Z}^{(\mathrm{out})} &= \mathbf{Z}^{(2)}, \end{aligned}\right\} \tag{3.11}$$

where $\mathbf{Z}^{(\mathrm{in})}$ and $\mathbf{Z}^{(\mathrm{out})}$ are the Hertz vectors inside and outside the crystal. Here the vectors $\mathbf{Z}^{(j)}$ ($j = 0, 1, 2$) are determined with the help of equations (3.0), (3.1) by the functions $S^{(j)}$ given by

$$\left.\begin{aligned} S^{(0)} &= \frac{1}{\pi v_a} \sum_h \frac{e^{2\pi i (\mathbf{b}_h, \mathbf{r})}}{(\mathbf{b}_h + \mathbf{k})^2 - k_0^2}, \\ S^{(1)} &= \frac{2i}{v_a} \sum_{\substack{l_1, l_2 \\ -\infty}}^{+\infty} \frac{e^{2\pi i [l_1 (\mathbf{r}, \mathbf{b}_1) + l_2 (\mathbf{r}, \mathbf{b}_2) + \eta_1 (\mathbf{r}, \mathbf{b}_3)]}}{b_3^2 (\eta_1 - \eta_2)(1 - e^{-2\pi i \eta_1})}, \\ S^{(2)} &= \frac{2i}{v_a} \sum_{\substack{l_1, l_2 \\ -\infty}}^{+\infty} \frac{e^{2\pi i [l_1 (\mathbf{r}, \mathbf{b}_1) + l_2 (\mathbf{r}, \mathbf{b}_2) + \eta_2 (\mathbf{r}, \mathbf{b}_3)]}}{b_3^2 (\eta_1 - \eta_2)(1 - e^{-2\pi i \eta_2})}. \end{aligned}\right\} \tag{3.12}$$

$S^{(0)}$ is identical with the expression (3.2) for the infinite lattice.

The constants η_1, η_2 in (3.12) are the two solutions of the equation

$$(l_1 \mathbf{b}_1 + l_2 \mathbf{b}_2 + \eta \mathbf{b}_3 + \mathbf{k})^2 = k_0^2. \tag{3.13}$$

These are given by

$$\left.\begin{aligned} \eta_1, \eta_2 &= \frac{1}{b_3^2} [-(\mathbf{b}_3, \mathbf{q}) \pm \sqrt{\{(\mathbf{b}_3, \mathbf{q})^2 + b_3^2 (k_0^2 - q^2)\}}], \\ \mathbf{q} &= l_1 \mathbf{b}_1 + l_2 \mathbf{b}_2 + \mathbf{k}. \end{aligned}\right\} \tag{3.14}$$

I consider first the case when either l_1 or l_2 or both are different from zero. Writing $\mathbf{k}$ as

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3,$$

where $-\frac{1}{2} \leqslant k_i \leqslant \frac{1}{2}$ (cf. § 5), we see that $\mathbf{q}$ cannot be parallel to $\mathbf{b}_3$, so that

$$(\mathbf{b}_3, \mathbf{q})^2 < q^2 b_3^2.$$

Since $k_0 \ll |\mathbf{b}_j|$ it follows that k_0 in (3.14) may be neglected, so that the square root is imaginary and $\eta_{1,2}$ are conjugate complex. In this case for η_1 the solution with positive imaginary part must be used, and for η_2 the solution with negative imaginary part. If such a complex solution is inserted in (3.12) it follows with (3.10) that $S^{(1)}$ and $S^{(2)}$ decrease exponentially with the distance from the surface. They represent only small surface effects and may be neglected.

Turning to the zero terms of the series $S^{(1)}$ and $S^{(2)}$ (i.e. $l_1 = l_2 = 0$) it is found that the solution $(3 \cdot 14)$ reduces to

$$\eta_{1,2} = \frac{1}{b_3^2} [-(\mathbf{b}_3, \mathbf{k}) \pm \sqrt{\{(\mathbf{b}_3, \mathbf{k})^2 + b_3^2(k_0^2 - k^2)\}}], \quad \text{for} \quad l_1 = l_2 = 0. \quad (3 \cdot 15)$$

If $k \neq 0$, so that $k_0 \ll k$, k_0 may be neglected again and the solutions $\eta_{1,2}$ are again conjugate complex, if $\mathbf{k}$ is not parallel to $\mathbf{b}_3$. In this case exponentially decreasing expressions are again obtained. The only exception is when $\mathbf{k}$ is parallel to $\mathbf{b}_3$. Here I get from $(3 \cdot 15)$

$$\eta_{1,2} = \frac{-k \pm k_0}{b_3}; \quad \text{for} \quad (\mathbf{b}_3, \mathbf{k}) = |\mathbf{b}_3| |\mathbf{k}| \quad (3 \cdot 16)$$

and

$$\eta_{1,2} \mathbf{b}_3 = -\mathbf{k} \pm \mathbf{k}_0. \quad (3 \cdot 17)$$

Inserting these values in $(3 \cdot 12)$ one obtains with $(3 \cdot 0)$, $(3 \cdot 1)$ the Hertz vectors $\mathbf{Z}^{(1)}$, $\mathbf{Z}^{(2)}$ corresponding to the zero terms of $S^{(1)}$, $S^{(2)}$.

$$\begin{aligned}
\mathbf{Z}^{(1)} &= \frac{i}{v_a} e^{-i\omega t} \frac{e^{2\pi i(\mathbf{r}, \mathbf{k}_0)}}{b_3 k_0(1 - e^{2\pi i(k-k_0)/b_3})} \sum_\kappa \mathbf{p}_\kappa e^{2\pi i(\mathbf{r}_\kappa, \mathbf{k}-\mathbf{k}_0)}, \\
\mathbf{Z}^{(2)} &= \frac{i}{v_a} e^{-i\omega t} \frac{e^{-2\pi i(\mathbf{r}, \mathbf{k}_0)}}{b_3 k_0(1 - e^{2\pi i(k+k_0)/b_3})} \sum_\kappa \mathbf{p}_\kappa e^{2\pi i(\mathbf{r}_\kappa, \mathbf{k}+\mathbf{k}_0)}.
\end{aligned} \right\} \quad (3 \cdot 18)$$

Since $k_0 \ll k$, $k_0 \ll b_3$ and $(\mathbf{r}_\kappa, \mathbf{b}_j) \sim 1$ it follows that $(\mathbf{r}_\kappa, \mathbf{k}_0) \ll 1$. To the first order in k_0 the result is

$$\begin{aligned}
\mathbf{Z}^{(1)} &= \frac{i}{v_a} \frac{e^{-i\omega t} e^{2\pi i(\mathbf{r}, \mathbf{k}_0)}}{b_3 k_0} \frac{\sum_\kappa \mathbf{p}_\kappa}{1 - e^{2\pi i k/b_3}}, \\
\mathbf{Z}^{(2)} &= \frac{i}{v_a} \frac{e^{-i\omega t} e^{-2\pi i(\mathbf{r}, \mathbf{k}_0)}}{b_3 k_0} \frac{\sum_\kappa \mathbf{p}_\kappa}{1 - e^{2\pi i k/b_3}}.
\end{aligned} \right\} \quad (3 \cdot 19)$$

In this case there is indeed an outgoing radiation field. But the effect of this field is negligible. This may be seen either by calculating the force from $\mathbf{Z}^{(1)}$ or by calculating the energy flow of the outgoing radiation from $\mathbf{Z}^{(2)}$ and comparing it with the energy of the oscillator. If this is calculated by means of $(3 \cdot 6)$ only values of the magnitude k_0/b_3 are obtained which can be neglected.

The field of the crystal for $\mathbf{k} \neq 0$ is, therefore, completely determined by $S^{(0)}$ $(3 \cdot 12)$ or $(3 \cdot 2)$, which gives the right solution for our problem for $\mathbf{k} \neq 0$.

Now only the case $\mathbf{k} = 0$ remains to be considered. For the zero term of the Hertz vectors $\mathbf{Z}^{(1)}$, $\mathbf{Z}^{(2)}$ one obtains once more the expression $(3 \cdot 18)$ and need only put $k = 0$. But in this case k_0/b_3 in the exponential function of the denominator cannot be neglected. Expanding this exponential we find, instead of $(3 \cdot 19)$,

$$\begin{aligned}
\mathbf{Z}^{(1)} &= \frac{1}{2\pi v_a} \frac{e^{-i\omega t} e^{2\pi i(\mathbf{r}, \mathbf{k}_0)}}{k_0^2} \sum_\kappa \mathbf{p}_\kappa, \\
\mathbf{Z}^{(2)} &= -\frac{1}{2\pi v_a} \frac{e^{-i\omega t} e^{-2\pi i(\mathbf{r}, \mathbf{k}_0)}}{k_0^2} \sum_\kappa \mathbf{p}_\kappa.
\end{aligned} \right\} \quad (3 \cdot 20)$$

$\mathbf{Z}^{(2)}$ represents again an outgoing wave, but the amplitude contains $1/k_0^2$ and therefore it cannot be neglected.

Therefore the crystal cannot be considered as being in a stationary state for $\mathbf{k} = 0$; in order to render it stationary radiation has to be sent to and absorbed by the crystal. Indeed, residual rays can only be observed by absorption or reflexion measurements, as the loss of energy of the incident beam. Now it is well known that the boundary conditions for electromagnetic waves are such that the incident wave is continued in the interior by the diffracted wave, but this is identical with the mean wave of the dipoles. This latter has, therefore, to be considered as produced by the incident wave, i.e. as a given external wave which acts on the particles of the lattice. The interaction forces of the vibration proper of the lattice are therefore described only by the periodic terms of the field strength. *For this reason one has to cancel the constant term in the expression* (3·2), (3·1), (3·0) *of the Hertz vector.*

In this way is found the nature of the apparent discontinuity in the spectrum at $\mathbf{k} = 0$ which has been introduced at the beginning of this paragraph.

4. THE COUPLING COEFFICIENTS OF THE ELECTRODYNAMIC INTERACTION

It is now possible to write down the Hertz vector for all states of vibrations of the crystal (3·0), (3·1), (3·2). Since $\mathbf{k}_0$ is small compared to the vectors of the reciprocal lattice, $\mathbf{k}_0$ may be neglected in (3·2) except for the zero term $\mathbf{b}_h = (0, 0, 0)$. As long as $\mathbf{k} \neq 0$, $\mathbf{k}_0$ may be neglected also in the zero term, as has just been shown. For $\mathbf{k} = 0$, on the other hand, the zero term must be omitted. Therefore one finds for S:

$$S = \frac{1}{\pi v_a} \sum_h{}' \frac{e^{2\pi i(\mathbf{b}_h, \mathbf{r})}}{(\mathbf{b}_h + \mathbf{k})^2}, \tag{4·0}$$

where the dash indicates that for $\mathbf{k} = 0$ the zero term $\mathbf{b}_h = 0$ must be omitted.†

Having now determined the Hertz vector one arrives in the same way as in § 1 at the equation of motion by writing down the expression for the force which is determined by the Hertz vector

$$\mathbf{Z}_\kappa^{l*} = \mathbf{Z} - \mathbf{z}_\kappa^l, \tag{4·1}$$

where $\mathbf{z}_\kappa^l$ is the Hertz vector of the dipole (κ, l) itself which has to be subtracted. From (4·1) one obtains by means of (3·6) the electromagnetic field which is given by (cf. (3·0), (3·1), (3·2))

$$E_{\kappa x}^l = \text{grad}_x \, \text{div} \, \mathbf{Z}_\kappa^{l*} - \frac{1}{c^2} \ddot{Z}_{\kappa x}^{l*}$$

$$= e^{-i\omega t} e^{2\pi i(\mathbf{k}, \mathbf{r}_\kappa^l)} \left\{ \sum_y p_{\kappa y} \frac{\partial^2}{\partial x \, \partial y} \overline{\psi}^k(\mathbf{r} - \mathbf{r}_\kappa^l) + \sum_{\substack{\kappa' \\ \kappa' \neq \kappa}} \sum_y p_{\kappa' y} \frac{\partial^2}{\partial x \, \partial y} \psi^k(\mathbf{r} - \mathbf{r}_{\kappa'}^l) \, e^{2\pi i(\mathbf{k}, \mathbf{r}_{\kappa'} - \mathbf{r}_\kappa)} \right\}, \tag{4·2}$$

† While following closely and in formal identity the derivation of Born and Goeppert-Mayer (1933, p. 776) it must be emphasized that the dash in Born's function S means complete omission of the zero term, irrespective of the value of $\mathbf{k}$.

where
$$\psi^k(\mathbf{r}) = S(\mathbf{r})\, e^{2\pi i(\mathbf{k},\mathbf{r})} = \frac{1}{\pi v_a}\sum_h{}' \frac{e^{2\pi i(\mathbf{b}_h+\mathbf{k},\mathbf{r})}}{(\mathbf{b}_h+\mathbf{k})^2},$$
$$\overline{\psi}^k(\mathbf{r}) = \psi^k(\mathbf{r}) - \frac{1}{|r|}. \tag{4.3}$$

The terms due to grad div $\mathbf{Z}_\kappa^{l*}$ contain factors $(b_h+k)_x(b_h+k)_y$, whereas the term due to $-\frac{1}{c^2}\ddot{\mathbf{Z}}_\kappa^{l*}$ has the factor $\frac{\omega^2}{c^2} = 4\pi^2 k_0^2$ and can therefore be neglected. The magnetic field vector, too, can be neglected as it gives only a second order contribution to the force.

From (4.2) one obtains easily the force exerted on the particle (κ, l) and the equation of motion
$$\omega^2 m_\kappa U_{\kappa x} + \sum_{\kappa'}\sum_y \begin{bmatrix}\kappa & \kappa' \\ x & y\end{bmatrix} U_{\kappa' y} = 0, \tag{4.4}$$

with
$$\begin{aligned}
{}^C\!\begin{bmatrix}\kappa & \kappa' \\ x & y\end{bmatrix} &= e_\kappa e_{\kappa'}\left[\frac{\partial^2}{\partial x\,\partial y}\psi^k(\mathbf{r})\right]_{\mathbf{r}=\mathbf{r}_{\kappa\kappa'}} e^{-2\pi i(\mathbf{k},\,\mathbf{r}_{\kappa\kappa'})}, \\
{}^C\!\begin{bmatrix}\kappa & \kappa \\ x & y\end{bmatrix} &= e_\kappa^2\left[\frac{\partial^2}{\partial x\,\partial y}\overline{\psi}^k(\mathbf{r})\right]_{\mathbf{r}=0}.
\end{aligned} \tag{4.5}$$

Comparing these electrodynamic expressions with the corresponding electrostatic ones (2.11) it follows that they are identical, if the function $F^k(\mathbf{r})$ is replaced by $\psi^k(\mathbf{r})$. In order to compare these two functions I take the parameter E in (2.13) equal to ∞. Then F^k is given by
$$F^k(\mathbf{r}) = \frac{1}{\pi v_a}\sum_h \frac{e^{2\pi i(\mathbf{b}_h+\mathbf{k},\mathbf{r})}}{(\mathbf{b}_h+\mathbf{k})^2}. \tag{4.6}$$

This is identical with the expression (4.3) for $\psi^k(\mathbf{r})$, with the exception of the case $\mathbf{k}=0$. In this case the divergent zero term in F^k is omitted in ψ^k. One finds
$$\begin{aligned}
\psi^k(\mathbf{r}) &= F^k(\mathbf{r}); & \mathbf{k} &\neq 0, \\
\psi^0(\mathbf{r}) &= \lim_{k\to 0}\left[F^k(\mathbf{r}) - \frac{1}{\pi v_a}\frac{e^{2\pi i(\mathbf{k},\mathbf{r})}}{k^2}\right]; & \mathbf{k} &= 0.
\end{aligned} \tag{4.7}$$

Thus for $\mathbf{k}\neq 0$ the electrostatic derivation is justified which is only natural since the retardation represented by k_0 can be neglected. F^k (2.9) is defined as a sum of potentials of point charges. Therefore it satisfies Laplace's equation
$$\Delta F^k = \Delta \psi^k = 0; \quad \mathbf{k}\neq 0. \tag{4.8}$$

With (4.5) the following relation follows:
$$\,^C\!\begin{bmatrix}\kappa & \kappa' \\ x & x\end{bmatrix} + \,^C\!\begin{bmatrix}\kappa & \kappa' \\ y & y\end{bmatrix} + \,^C\!\begin{bmatrix}\kappa & \kappa' \\ z & z\end{bmatrix} = \sum_x \,^C\!\begin{bmatrix}\kappa & \kappa' \\ x & x\end{bmatrix} = 0. \tag{4.9}$$

For $\mathbf{k} = 0$ (cf. Born 1923, p. 728), on the other hand, direct differentiation gives

$$\Delta\psi^0 = \lim_{k\to 0}\Delta\left[F^k - \frac{1}{\pi v_a}\frac{e^{2\pi i(\mathbf{k},\,\mathbf{r})}}{k^2}\right] = \lim_{k\to 0}\left[\Delta F^k + \frac{4\pi}{v_a}\,e^{2\pi i(\mathbf{k},\,\mathbf{r})}\right] \tag{4.10}$$

$$= \frac{4\pi}{v_a};\quad \mathbf{k} = 0$$

and

$$\sum_x{}^C\begin{bmatrix}\kappa & \kappa' \\ x & x\end{bmatrix}_{\mathbf{k}=0} = 4\pi\frac{e_\kappa e_{\kappa'}}{v_a}. \tag{4.11}$$

This holds also for $\kappa' = \kappa$ if one substitutes $\overline{\psi}^0$ for ψ^0 in (4.10). The potential ψ^0 satisfies, therefore, Poisson's equation, which may be interpreted as the existence of a uniform charge distribution of amount -1 per unit cell.

In the case of cubical symmetry it follows that

$$\begin{aligned}{}^C\begin{bmatrix}\kappa & \kappa' \\ x & x\end{bmatrix}_{\mathbf{k}=0} &= \frac{4\pi}{3}\frac{e_\kappa e_{\kappa'}}{v_a}, & {}^C\begin{bmatrix}\kappa & \kappa \\ x & x\end{bmatrix}_{\mathbf{k}=0} &= \frac{4\pi}{3}\frac{e_\kappa^2}{v_a}; \\ {}^C\begin{bmatrix}\kappa & \kappa' \\ x & y\end{bmatrix}_{\mathbf{k}=0} &= {}^C\begin{bmatrix}\kappa & \kappa \\ x & y\end{bmatrix}_{\mathbf{k}=0} = \text{cycl} = 0.\end{aligned} \tag{4.12}$$

Then one gets for the coupling force in the equation of motion (4.4)

$$F_{\kappa x} = \sum_{\kappa'}{}^C\begin{bmatrix}\kappa & \kappa' \\ x & x\end{bmatrix}_{\mathbf{k}=0} U_{\kappa' x} = \frac{4\pi}{3}e_\kappa\sum_{\kappa'}e_{\kappa'}\,U_{\kappa' x} = \frac{4\pi}{3}e_\kappa p_x,$$

which is the well-known expression for the Lorenz-Lorentz force.

The question whether the sum $\sum_x{}^C\begin{bmatrix}\kappa & \kappa' \\ x & x\end{bmatrix}$ is equal to zero or to $4\pi\dfrac{e_\kappa e_{\kappa'}}{v_a}$, i.e. whether the potential from which the coupling coefficients are derived satisfies Poisson's or Laplace's equation has been discussed before, but has never been cleared in a satisfactory way. The definite result of the foregoing derivation is that it proves without artificial assumptions the apparent discontinuity (cf. p. 519) of this potential as function of the wave vector $\mathbf{k}$. Lyddane and Herzfeld (1938) agree with Born that for $\mathbf{k} = 0$ the sum $\sum_x\begin{bmatrix}\kappa & \kappa' \\ x & x\end{bmatrix}_{\mathbf{k}=0}$ is really equal to $4\pi\dfrac{e_\kappa e_{\kappa'}}{v_a}$ and thus derived from a potential corresponding to a uniform charge distribution -1 per cell, but in order to explain the different properties of the potential for $\mathbf{k} \neq 0$ they assume that for all other wavelengths one has to perform a displacement of the uniform charge distribution, which gives rise to surface charges which just compensate the term $4\pi/v_a$ so that the above sum is equal to zero. This argument is not only rather artificial, since the displaced uniform charge -1 has no physical significance, but leads also to consequences which are only partly correct. They obtain two different frequencies for the residual rays, one for "transverse" waves which corresponds to the value hitherto found—and also in this paper—and one for "longitudinal" waves.

5. The coupling coefficients of the NaCl lattice

In the case of NaCl there are two different particles in the cell ($s = 2$); but, as far as symmetry is concerned, it may be regarded as a simple lattice, i.e. the Na sites are entirely equivalent to the Cl sites. Therefore, to any lattice vector $\mathbf{r}_{\kappa\kappa'}^l$ there corresponds another one of the same magnitude and in the opposite direction. The same is true for the reciprocal lattice. For this reason the coupling coefficients are all real, as may be seen from (1·10); in this sum all imaginary terms cancel so that

$$\left.\begin{array}{l}\begin{bmatrix}\kappa & \kappa' \\ x & y\end{bmatrix} = \sum_l (\phi_{\kappa\kappa'}^l)_{xy} \cos 2\pi(\mathbf{k}, \mathbf{r}_{\kappa\kappa'}^l), \\[2mm] \begin{bmatrix}\kappa & \kappa \\ x & y\end{bmatrix} = \sum_l (\phi_{\kappa\kappa}^l)_{xy} \cos 2\pi(\mathbf{k}, \mathbf{a}^l);\end{array}\right\} \tag{5·0}$$

and since $\mathbf{r}_{\kappa\kappa'} = -\mathbf{r}_{\kappa'\kappa}$,

$$\begin{bmatrix}\kappa & \kappa' \\ x & y\end{bmatrix} = \begin{bmatrix}\kappa' & \kappa \\ x & y\end{bmatrix}. \tag{5·1}$$

From (4·5) it can be seen that the coefficients are entirely symmetrical in x and y so that

$$\begin{bmatrix}\kappa & \kappa' \\ x & y\end{bmatrix} = \begin{bmatrix}\kappa & \kappa' \\ y & x\end{bmatrix}. \tag{5·2}$$

Furthermore, the NaCl lattice is entirely symmetrical in Na and Cl (if the repulsive forces between all but nearest neighbours are neglected); therefore

$$\begin{bmatrix}1 & 1 \\ x & y\end{bmatrix} = \begin{bmatrix}2 & 2 \\ x & y\end{bmatrix}. \tag{5·3}$$

The cell vectors of the NaCl lattice are

$$\left.\begin{array}{ll}\mathbf{a}_1 = r_0(0, 1, 1), & \mathbf{r}_{21} = -\mathbf{r}_{12} = r_0(1, 1, 1), \\[1mm] \mathbf{a}_2 = r_0(1, 0, 1), & v_a = 2r_0^3, \\[1mm] \mathbf{a}_3 = r_0(1, 1, 0), & \end{array}\right\} \tag{5·4}$$

where r_0 is the distance between nearest neighbours or the lattice constant and v_a the volume of the cell. A lattice vector is therefore of the form

$$\left.\begin{array}{ll}\mathbf{a}^l = r_0(l_2+l_3, \; l_3+l_1, \; l_1+l_2) = r_0(l_x, l_y, l_z), & \sum_x l_x \text{ even,} \\[2mm] \mathbf{r}_{21}^l = r_0(l_2+l_3+1, \; l_3+l_1+1, \; l_1+l_2+1) = r_0(m_x, m_y, m_z), & \sum_x m_x \text{ odd.}\end{array}\right\} \tag{5·5}$$

Here l_1, l_2, l_3 cover all integer numbers. Therefore, l_x, l_y, l_z cover all sets of integers for which $l_x+l_y+l_z = \sum_x l_x$ is even and m_x, m_y, m_z cover all sets of integers for which $\sum_x m_x$ is odd.

The reciprocal vectors are given by (1·13). With (5·4) they are

$$\left.\begin{aligned}
\mathbf{b}_1 &= \frac{1}{2r_0}(-1,\,1,\,1),\\
\mathbf{b}_2 &= \frac{1}{2r_0}(1,\,-1,\,1),\\
\mathbf{b}_3 &= \frac{1}{2r_0}(1,\,1,\,-1),
\end{aligned}\right\} \tag{5·6}$$

so that a vector in the reciprocal lattice is given by

$$\begin{aligned}
\mathbf{b}_h &= \frac{1}{2r_0}(h_2+h_3-h_1,\ h_3+h_1-h_2,\ h_1+h_2-h_3)\\
&= \frac{1}{2r_0}(h_x,\,h_y,\,h_z),\quad h_x,\,h_y,\,h_z \text{ all odd or all even,}
\end{aligned} \tag{5·7}$$

where h_x, h_y, h_z cover all sets of integers which are either all odd or all even, i.e. the reciprocal lattice is body-centred, as is well known.

The sums (2·15) representing the coupling coefficients may now be written in dimensionless form by writing ϵ/r_0 for the parameter E and substituting for the wave vector $\mathbf{k}$:

$$\left.\begin{aligned}
\mathbf{k} &= k_1\mathbf{b}_1+k_2\mathbf{b}_2+k_3\mathbf{b}_3 = \frac{1}{2r_0}(q_x,\,q_y,\,q_z),\\
q_x &= k_2+k_3-k_1,\ q_y = k_3+k_1-k_2,\ q_z = k_1+k_2-k_3,
\end{aligned}\right\} \tag{5·8}$$

$$\left.\begin{aligned}
\frac{v_a}{e^2}\,{}^C\!\begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix} &= -G^{11}_{xy}+\underset{l}{H}_{xy}+\frac{8}{3\sqrt{\pi}}\epsilon^3\delta_{xy},\\
\frac{v_a}{e^2}\,{}^C\!\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix} &= G^{12}_{xy}-\underset{m}{H}_{xy},
\end{aligned}\right\} \tag{5·9}$$

where

$$\left.\begin{aligned}
G^{11}_{xy} &= 4\pi\sum_h \frac{(h_x+q_x)\,(h_y+q_y)}{(\mathbf{h}+\mathbf{q})^2}\,e^{-\frac{\pi^2}{4\epsilon^2}(\mathbf{h}+\mathbf{q})^2},\\
G^{12}_{xy} &= 4\pi\sum_h \frac{(h_x+q_x)\,(h_y+q_y)}{(\mathbf{h}+\mathbf{q})^2}\,e^{-\frac{\pi^2}{4\epsilon^2}(\mathbf{h}+\mathbf{q})^2}\cos\pi(h_x+h_y+h_z),\\
\underset{l}{H}_{xy} &= 2\sum_l \left[-f(l)\,\delta_{xy}+g(l)\frac{l_x l_y}{l^2}\right]\cos\pi(\mathbf{q},\,\mathbf{l}),\\
f(l) &= \frac{2}{\sqrt{\pi}}\epsilon\frac{e^{-\epsilon^2 l^2}}{l^2}+\frac{\psi(\epsilon l)}{l^3},\\
g(l) &= \frac{4}{\sqrt{\pi}}\epsilon^3\,e^{-\epsilon^2 l^2}+\frac{6}{\sqrt{\pi}}\epsilon\frac{e^{-\epsilon^2 l^2}}{l^2}+\frac{3\psi(\epsilon l)}{l^3},\\
\psi(\epsilon l) &= 1-\frac{2}{\sqrt{\pi}}\int_0^{\epsilon l} e^{-\xi^2}\,d\xi,\\
l &= |l| = \sqrt{(l_x^2+l_y^2+l_z^2)}.
\end{aligned}\right\} \tag{5·10}$$

These equations only hold for $k \neq (0, 0, 0)$.

For some wave vectors $\mathbf{k}$ the calculation can be reduced appreciably by considering the cubic symmetry.

(1) $q_x = q_y = q_z$. This case is symmetrical in x, y, z. Therefore from (4·9) it follows that

$$^C\!\begin{bmatrix} \kappa & \kappa' \\ x & x \end{bmatrix} = {}^C\!\begin{bmatrix} \kappa & \kappa' \\ y & y \end{bmatrix} = {}^C\!\begin{bmatrix} \kappa & \kappa' \\ z & z \end{bmatrix} = 0, \quad q_x = q_y = q_z. \tag{5·11}$$

(2) $q_z = 0$ (or $q_z = 1$)*. In this case in G_{xz} the two terms (h_x, h_y, h_z) and $(h_x, h_y, -h_z)$ just cancel and $G_{xz} = 0$. Putting $\epsilon = \infty$, H_{xz} also vanishes (the coupling coefficients are, of course, independent of ϵ). Therefore

$$^C\!\begin{bmatrix} 1 & 1 \\ x & z \end{bmatrix} = {}^C\!\begin{bmatrix} 1 & 2 \\ x & z \end{bmatrix} = {}^C\!\begin{bmatrix} 1 & 1 \\ y & z \end{bmatrix} = {}^C\!\begin{bmatrix} 1 & 2 \\ y & z \end{bmatrix} = 0, \quad q_z = 0. \tag{5·12}$$

(3) Consider two wave vectors which differ only in the sign of the z-component. In this case put $\epsilon = 0$ so that only a contribution from H_{xz}* is obtained (cf. (5·10)a); it follows that

$$\left. \begin{array}{ll} \begin{bmatrix} 1 & 1 \\ x & z \end{bmatrix}_{\mathbf{k}} = -\begin{bmatrix} 1 & 1 \\ x & z \end{bmatrix}_{\mathbf{k}'}, & \begin{bmatrix} 1 & 2 \\ x & z \end{bmatrix}_{\mathbf{k}} = -\begin{bmatrix} 1 & 2 \\ x & z \end{bmatrix}_{\mathbf{k}'}, \\[2ex] \begin{bmatrix} 1 & 1 \\ y & z \end{bmatrix}_{\mathbf{k}} = -\begin{bmatrix} 1 & 1 \\ y & z \end{bmatrix}_{\mathbf{k}'}, & \begin{bmatrix} 1 & 2 \\ y & z \end{bmatrix}_{\mathbf{k}} = -\begin{bmatrix} 1 & 2 \\ y & z \end{bmatrix}_{\mathbf{k}'}, \quad q_x = q'_x, \quad q_y = q'_y, \quad q_z = -q'_z, \end{array} \right\} \tag{5·13}$$

whereas all other coefficients are the same for both wave vectors.

(4) Consider two wave vectors $\mathbf{k}$, $\mathbf{k}'$ which are identical apart from an interchange of the components of q_x, q_y. Taking again $\epsilon = 0$, then

$$\left. \begin{array}{ll} \begin{bmatrix} 1 & 1 \\ x & x \end{bmatrix}_{\mathbf{k}} = \begin{bmatrix} 1 & 1 \\ y & y \end{bmatrix}_{\mathbf{k}'}, & \begin{bmatrix} 1 & 2 \\ x & x \end{bmatrix}_{\mathbf{k}} = \begin{bmatrix} 1 & 2 \\ y & y \end{bmatrix}_{\mathbf{k}'}, \\[2ex] \begin{bmatrix} 1 & 1 \\ y & y \end{bmatrix}_{\mathbf{k}} = \begin{bmatrix} 1 & 1 \\ x & x \end{bmatrix}_{\mathbf{k}'}, & \begin{bmatrix} 1 & 2 \\ y & y \end{bmatrix}_{\mathbf{k}} = \begin{bmatrix} 1 & 2 \\ x & x \end{bmatrix}_{\mathbf{k}'}, \quad q_x = q'_y, \quad q_y = q'_x, \quad q_z = q'_z, \end{array} \right\} \tag{5·14}$$

all the other coefficients being equal.

* This can also be seen by considering the function H_{xz} only ($\epsilon = 0$). For $x \neq z$ we find developing

$$\cos \pi(\mathbf{q}, \mathbf{l}) = \cos \pi(q_x l_x + q_y l_y + q_z l_z),$$

$$H_{xz} = -2 \sum_l g(l) \frac{l_x l_z}{l^2} \sin \pi \, q_x l_x \sin \pi \, q_z l_z \cos \pi \, q_y l_y. \tag{5·10a}$$

All other terms arising from the development of $\cos \pi(\mathbf{q}, \mathbf{l})$ cancel because of symmetry (l_x, l_z assume the same positive and negative values).

We see at once from (5·10)a that for $q_z = 1$ (or $q_z = 0$), $H_{xz} = 0$ and therefore

$$^C\!\begin{bmatrix} 1 & 1 \\ x & z \end{bmatrix} = {}^C\!\begin{bmatrix} 1 & 2 \\ x & z \end{bmatrix} = {}^C\!\begin{bmatrix} 1 & 1 \\ y & z \end{bmatrix} = {}^C\!\begin{bmatrix} 1 & 2 \\ y & z \end{bmatrix} = 0, \text{ for } q_z = 1.$$

It is not surprising that these bracket coefficients vanish, for in the reciprocal lattice the point given by the position vector $q_x = q_y = 0$, $q_z = 1$ is symmetrically situated with respect to all lattice points. If q_x, $q_y \neq 0$ the symmetry in the z-direction is not destroyed, and it will be seen from G_{xx} ($\epsilon = \infty$) that the coefficients in question vanish on account of this symmetry.

From the condition of the cyclic lattice (1·15), (1·16) it follows that k_1, k_2, k_3 range from 0 to 1. In order to obtain a fair survey of the coefficients as functions of the wave vector, I divide this range into tenths and consider the vector components

$$k_i = \frac{p_i}{10}, \quad (p_1, p_2, p_3 \text{ integers}). \tag{5·15}$$

In order to make full use of the symmetric properties of the coefficients it is more convenient to consider the region of allowed wave vectors in the q_x, q_y, q_z space. Since the reciprocal lattice is of the body-centred type this region is of the form of an octahedron with its vertices cut off (cf. for example, Sommerfeld and Bethe 1933, figure 27). The boundaries are given by the equations

$$q_x \pm q_y \pm q_z = \pm\tfrac{3}{2}; \quad q_x = \pm1, \quad q_y = \pm1, \quad q_z = \pm1. \tag{5·16}$$

In view of the properties (5·13) just considered one may restrict the calculation to positive values of q_x, q_y, q_z. All other coefficients may then be obtained from (5·13). Furthermore, in view of (5·14) the calculation can be restricted to sets of numbers such that $q_x \geqslant q_y \geqslant q_z$. Thus only those values of $\mathbf{q}$ such that

$$\left.\begin{aligned} 0 \leqslant q_z \leqslant q_y \leqslant q_x \leqslant 1, \\ q_x + q_y + q_z \leqslant \tfrac{3}{2}, \end{aligned}\right\} \tag{5·17}$$

need be considered.

It will be convenient to introduce as in (5·15) whole numbers p_x, p_y, p_z given by (5·7)

$$p_x = p_2 + p_3 - p_1, \quad p_y = p_3 + p_1 - p_2, \quad p_z = p_1 + p_2 - p_3, \tag{5·18}$$

the sets of whole numbers p_x, p_y, p_z are either all odd or all even and satisfy the conditions

$$\left.\begin{aligned} 0 \leqslant p_z \leqslant p_y \leqslant p_x \leqslant 10, \\ p_x + p_y + p_z \leqslant 15. \end{aligned}\right\} \tag{5·19}$$

There are forty-eight sets of numbers of this type.

I could, of course, also divide the range in the q_x, q_y, q_z space into tenths. But this would give more sets of numbers p_x, p_y, p_z, i.e. a closer division of our range which is not necessary for our purposes. If, on the other hand, I divided it into fifths, it would give too small a choice.

6. The repulsive forces

Apart from the Coulomb forces there are other forces present in an ionic lattice, mainly the repulsive forces which prevent the lattice from collapsing, and also the van der Waals forces. Let us collect all those other forces in a potential $v(r)$. These forces decrease very rapidly with the distance, with the exception of the Van der Waals forces (cf. (Lennard-)Jones and Ingham 1925). But, as Born and Mayer (1932) have shown, these forces form only a very small percentage of the potential $v(r)$, so that it is sufficient

to consider only the interaction between nearest neighbours. In the NaCl lattice each ion is surrounded by six nearest neighbours so that the energy per cell is given by

$$\tfrac{1}{2}\Phi_0 = -\alpha\frac{e^2}{r_0} + 6v(r_0), \tag{6.0}$$

where α is the Madelung constant and r_0 the distance between nearest neighbours.

The first two derivatives of $v(r)$ can be obtained from the condition of equilibrium and the compressibility; putting for abbreviation

$$2\left[\frac{dv(r)}{dr}\right]_{r=r_0} = \frac{e^2}{2r_0^2}B, \\ 2\left[\frac{d^2v(r)}{dr^2}\right]_{r=r_0} = \frac{e^2}{2r_0^3}A, \tag{6.1}$$

the condition of equilibrium is

$$\frac{d\tfrac{1}{2}\Phi_0}{dr_0} = 0 = \alpha\frac{e^2}{r_0^2} + \tfrac{3}{2}B\frac{e^2}{r_0^2},$$

so that

$$B = -\frac{2\alpha}{3} = -1.165, \tag{6.2}$$

using Madelung's constant $\alpha = 1.7476$.

The compressibility is given by

$$\frac{1}{\kappa} = \frac{1}{9v_a}r_0^2\frac{d^2\tfrac{1}{2}\Phi_0}{dr_0^2} = \frac{1}{18r_0}\frac{d^2\tfrac{1}{2}\Phi_0}{dr_0^2} = \frac{1}{18r_0}\left[-2\alpha\frac{e^2}{r_0^3} + \tfrac{3}{2}A\frac{e^2}{r_0^3}\right], \quad v_a = 2r_0^3,$$

so that

$$A = \frac{12r_0^4}{\kappa e^2} + \tfrac{4}{3}\alpha. \tag{6.3}$$

A depends, of course, on the particular crystal considered. Here NaCl has been chosen where $\kappa = 4.16 \times 10^{-12}$ cm.^{2}/dyne, $r_0 = 2.814 \times 10^{-8}$ cm. With $e = 4.8 \times 10^{-10}$ e.s.u., I get

$$A = 10.18 \quad \text{(for NaCl)}. \tag{6.4}$$

Consider now that part of the coupling coefficients which is due to the repulsive forces. This part is given by (1.10), (1.12),

$$^R\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} = \sum_l (v_{\kappa\kappa'}^l)_{xy}\, e^{2\pi i(\mathbf{k}, \mathbf{r}_{\kappa'\kappa}^l)}. \tag{6.5}$$

In the case $\kappa' \neq \kappa$ the sum (6.5) extends over the six nearest neighbours given by the vectors

$$r_0(\pm 1, \quad 0, \quad 0), \\ r_0(\quad 0, \pm 1, \quad 0), \\ r_0(\quad 0, \quad 0, \pm 1). \tag{6.6}$$

The differentiation in (6·5) yields with the definition (6·1)

$$^{R}\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix} = \frac{1}{2}\frac{e^2}{v_a}\sum_{l}\left[A\frac{x_{12}^{l}y_{12}^{l}}{(r_{12}^{l})^2}+B\left(\delta_{xy}-\frac{x_{12}^{l}y_{12}^{l}}{(r_{12}^{l})^2}\right)\right]e^{2\pi i(\mathbf{k},\mathbf{r}_{12})}. \tag{6·7}$$

The sum over the vectors (6·6) gives

$$^{R}\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix} = 0, \quad x \neq y; \quad ^{R}\begin{bmatrix} 1 & 2 \\ x & x \end{bmatrix}\frac{v_a}{e^2} = A\cos 2\pi k_x r_0 + B(\cos 2\pi k_y r_0 + \cos 2\pi k_z r_0). \tag{6·8}$$

In the case $\kappa' = \kappa$ only the zero term in (6·5) remains, all other terms representing interaction between distant ions:

$$^{R}\begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix} = (v_{\kappa\kappa}^0)_{xy}. \tag{6·9}$$

This expression is independent of $\mathbf{k}$ and can therefore be calculated from (1·11)

$$^{R}\begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix} + ^{R}\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix}_{k=0} = 0,$$

so that

$$^{R}\begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix} = 0, \quad x \neq y; \quad ^{R}\begin{bmatrix} 1 & 1 \\ x & x \end{bmatrix}\frac{v_a}{e^2} = -(A+2B). \tag{6·10}$$

If for $\mathbf{k}$ the dimensionless vector $\mathbf{q}$ given by (5·8) is introduced, (6·8) and (6·10) may be written

$$\left.\begin{array}{l} ^{R}\begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix} = ^{R}\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix} = 0, \\[2mm] ^{R}\begin{bmatrix} 1 & 1 \\ x & x \end{bmatrix}\frac{v_a}{e^2} = -(A+2B), \quad ^{R}\begin{bmatrix} 1 & 2 \\ x & x \end{bmatrix}\frac{v_a}{e^2} = A\cos \pi q_x + B(\cos \pi q_y + \cos \pi q_z). \end{array}\right\} \tag{6·11}$$

7. The elastic constants

Born (1923) has shown that the coupling coefficients in the equation of motion are connected with the elastic constants.

The latter are defined by Born (1923, p. 547)

$$[xy\,\bar{x}\bar{y}] = \frac{1}{2v_a}\sum_{\kappa\kappa'}\sum_{l}(\phi_{\kappa\kappa'}^{l})_{xy}\,\bar{x}_{\kappa\kappa'}^{l}\,\bar{y}_{\kappa\kappa'}^{l}. \tag{7·0}$$

The elastic constants in the usual notation are related to the bracket symbols (7·0) for a crystal of cubic symmetry as follows:

$$\left.\begin{array}{l} [xxxx] = c_{11}, \\ [xxyy] = c_{12}, \\ [xyxy] = c_{44}. \end{array}\right\} \tag{7·1}$$

The Cauchy relation $$c_{12} = c_{44} \tag{7·2}$$

holds; this is a consequence of the assumption of central forces in a simple lattice with central symmetry about every particle.

One finds exactly the expressions (7·0) if the coupling coefficients (1·10) are developed in a power series of the inverse wave-length; with $2\pi\mathbf{k} = \tau\mathbf{s}$, where $\mathbf{s}$ is a unit vector, one finds

$$\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} = \begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(0)} + \begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(1)} \tau + \begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(2)} \tau^2 + \dots, \tag{7·3}$$

where

$$\begin{aligned}
\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(0)} &= \sum_l (\phi^l_{\kappa'\kappa})_{xy}, \\
\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(1)} &= i \sum_l (\mathbf{s}, \mathbf{r}^l_{\kappa'\kappa})(\phi^l_{\kappa'\kappa})_{xy}, \\
\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(2)} &= -\tfrac{1}{2}\sum_l (\mathbf{s}, \mathbf{r}^l_{\kappa'\kappa})^2 (\phi^l_{\kappa'\kappa})_{xy} = -\tfrac{1}{2}\sum_l \sum_{\bar{x},\bar{y}} s_{\bar{x}} s_{\bar{y}} \bar{x}^l_{\kappa'\kappa} \bar{y}^l_{\kappa'\kappa} (\phi^l_{\kappa'\kappa})_{xy}.
\end{aligned} \right\} \tag{7·4}$$

Comparing (7·3) with (7·0) one notices that

$$-v_a \sum_{\bar{x},\bar{y}} s_{\bar{x}} s_{\bar{y}} [xy\,\bar{x}\bar{y}] = \sum_{\kappa\kappa'} \begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(2)}. \tag{7·5}$$

In order to calculate $^C\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(2)}$, develop the expressions (5·9), (5·10) for the coupling coefficients of the NaCl lattice. The result is

$$\begin{aligned}
\sum_{\kappa\kappa'} {}^C\begin{bmatrix} \kappa & \kappa' \\ x & x \end{bmatrix} &= 2\Big\{ {}^C\begin{bmatrix} 1 & 1 \\ x & x \end{bmatrix}^{(2)} + {}^C\begin{bmatrix} 1 & 2 \\ x & x \end{bmatrix}^{(2)} \Big\} \\
&= -\frac{e^2}{r_0}\Big\{ s_x^2\Big[\frac{2}{\pi}\sum_h \chi_x(h) + \sum_l \Big[\Big(f(l)+g(l)\frac{l_x^2}{l^2}\Big)l_x^2\Big] - \sum_m\Big[\Big(f(m)+g(m)\frac{m_x^2}{m^2}\Big)m_x^2\Big]\Big] \\
&\quad + s_y^2\Big[\frac{2}{\pi}\sum_h \chi_y(h) + \sum_l\Big[\Big(f(l)+g(l)\frac{l_y^2}{l^2}\Big)l_y^2\Big] - \sum_m\Big[\Big(f(m)+g(m)\frac{m_y^2}{m^2}\Big)m_y^2\Big]\Big] \\
&\quad + s_z^2\Big[\frac{2}{\pi}\sum_h \chi_z(h) + \sum_l\Big[\Big(f(l)+g(l)\frac{l_z^2}{l^2}\Big)l_z^2\Big] - \sum_m\Big[\Big(f(m)+g(m)\frac{m_z^2}{m^2}\Big)m_z^2\Big]\Big]\Big\},
\end{aligned} \tag{7·6}$$

where

$$\chi_y(h) = \frac{4}{h^2} e^{-\frac{\pi^2 h^2}{4\epsilon^2}}\Big[4\frac{h_x^2 h_y^2}{h^4} - \frac{h_x^2}{h^2} + \frac{\pi^2}{\epsilon^2}\Big(\frac{h_x^2 h_y^2}{h^2} - \frac{h_x^2}{4}\Big) + \frac{\pi^4}{\epsilon^4}\frac{h_x^2 h_y^2}{8} + \delta_{xy}\Big(1 - 4\frac{h_x^2}{h^2} - \frac{\pi^2}{\epsilon^2}h_x^2\Big)\Big]. \tag{7·7}$$

Similarly one obtains for $^C\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(2)}$

$$\begin{aligned}
\sum_{\kappa\kappa'} {}^C\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}^{(2)} &= 2\Big\{ {}^C\begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix}^{(2)} + {}^C\begin{bmatrix} 1 & 2 \\ x & y \end{bmatrix}^{(2)} \Big\} \\
&= -2\frac{e^2}{r_0} s_x s_y\Big[\frac{1}{\pi}\sum_h \bar{\chi}(h) + \sum_l g(l)\frac{l_x^2 l_y^2}{l^2} - \sum_m g(m)\frac{m_x^2 m_y^2}{m^2}\Big], \tag{7·8}
\end{aligned}$$

where
$$\bar{\chi}(h) = \frac{4}{h^2} e^{-\frac{\pi^2 h^2}{4\epsilon^2}} \left[8\frac{h_x^2 h_y^2}{h^4} - 2\frac{h_x^2 + h_y^2}{h^2} + 1 + 2\frac{\pi^2}{\epsilon^2}\left(\frac{h_x^2 h_y^2}{h^2} - \tfrac{1}{4}(h_x^2 + h_y^2)\right) + \frac{\pi^4}{\epsilon^4}\frac{h_x^2 h_y^2}{4}\right]. \quad (7\cdot9)$$

Comparing $(7\cdot6)$, $(7\cdot8)$ with $(7\cdot5)$ one finds that part of the elastic constants which is due to the Coulomb forces:

$$\begin{aligned}
{}^{C}c_{11} = {}^{C}[xxxx] &= \frac{e^2}{v_a r_0}\left\{\frac{2}{\pi}\sum_h \chi_x(h) + \sum_l\left[f(l) + g(l)\frac{l_x^2}{l^2}\right]l_x^2 - \sum_m\left[f(m) + g(m)\frac{m_x^2}{m^2}\right]m_x^2\right\}, \\
{}^{C}c_{12} = {}^{C}[xxyy] &= \frac{e^2}{v_a r_0}\left\{\frac{2}{\pi}\sum_h \chi_y(h) + \sum_l\left[f(l) + g(l)\frac{l_x^2}{l^2}\right]l_y^2 - \sum_m\left[f(m) + g(m)\frac{m_x^2}{m^2}\right]m_y^2\right\}, \\
{}^{C}c_{44} = {}^{C}[xyxy] &= \frac{e^2}{v_a r_0}\left\{\frac{1}{\pi}\sum_h \bar{\chi}(h) + \sum_l g(l)\frac{l_x^2 l_y^2}{l^2} - \sum_m g(m)\frac{m_x^2 m_y^2}{m^2}\right\}.
\end{aligned} \quad (7\cdot10)$$

That part of the elastic constants which is due to the repulsive forces can be calculated in the same way. From $(6\cdot8)$, $(6\cdot10)$ one has

$$\begin{aligned}
\sum_{\kappa\kappa'}{}^{R}\begin{bmatrix}\kappa & \kappa' \\ x & x\end{bmatrix}^{(2)} &= 2\left\{{}^{R}\begin{bmatrix}1 & 1 \\ x & x\end{bmatrix}^{(2)} + {}^{R}\begin{bmatrix}1 & 2 \\ x & x\end{bmatrix}^{(2)}\right\} = \frac{e^2}{r_0}\{-As_x^2 - B(s_y^2 + s_z^2)\}, \\
\sum_{\kappa\kappa'}{}^{R}\begin{bmatrix}\kappa & \kappa' \\ x & y\end{bmatrix}^{(2)} &= 0,
\end{aligned} \quad (7\cdot11)$$

so that
$$ {}^{R}c_{11} = \frac{e^2}{v_a r_0}\frac{A}{2}, \quad {}^{R}c_{12} = \frac{e^2}{v_a r_0}\frac{B}{2}, \quad {}^{R}c_{44} = 0. \quad (7\cdot12)$$

The Cauchy relation need not be satisfied for the individual contributions of the Coulomb and repulsive forces, but only for the sum, if the condition of equilibrium is taken into account.*

The numerical calculation gives

$$\begin{aligned}
{}^{C}c_{11} &= -2\cdot56\frac{e^2}{2r_0^4}; & {}^{R}c_{11} &= 5\cdot09\frac{e^2}{2r_0^4}; & c_{11} &= 2\cdot53\frac{e^2}{2r_0^4}; \\
{}^{C}c_{12} &= 1\cdot28\frac{e^2}{2r_0^4}; & {}^{R}c_{12} &= -0\cdot583\frac{e^2}{2r_0^4}; & c_{12} &= 0\cdot695\frac{e^2}{2r_0^4}; \\
{}^{C}c_{44} &= 0\cdot696\frac{e^2}{2r_0^4}; & {}^{R}c_{44} &= 0; & c_{44} &= 0\cdot696\frac{e^2}{2r_0^4}.
\end{aligned}$$

* The reason is seen from the direct derivation of the elastic constants; they are given by Born (1923, p. 548)

$$[xy\bar{x}\bar{y}] = \frac{1}{2v_a}\sum_{\kappa\kappa'}\sum_l[\delta_{xy}P^l_{\kappa\kappa'}\bar{x}^l_{\kappa\kappa'}\bar{y}^l_{\kappa\kappa'} + Q^l_{\kappa\kappa'}x^l_{\kappa\kappa'}y^l_{\kappa\kappa'}\bar{x}^l_{\kappa\kappa'}\bar{y}^l_{\kappa\kappa'}],$$

where
$$P^l_{\kappa\kappa'} = \left[\frac{1}{r}\left(\frac{d\phi_{\kappa\kappa'}}{dr}\right)\right]_{r^l_{\kappa\kappa'}}, \quad Q^l_{\kappa\kappa'} = \left[\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi_{\kappa\kappa'}}{dr}\right)\right]_{r^l_{\kappa\kappa'}}.$$

The equilibrium condition leads to the disappearance of the term $P^l_{\kappa\kappa'}$, if ϕ is the total potential, and

$$[xy\bar{x}\bar{y}] = \frac{1}{2v_a}\sum_{\kappa\kappa'}\sum_l Q^l_{\kappa\kappa'}x^l_{\kappa\kappa'}y^l_{\kappa\kappa'}\bar{x}^l_{\kappa\kappa'}\bar{y}^l_{\kappa\kappa'}$$

is symmetric in all the four indices x, y, $\bar{x}$, $\bar{y}$ and can be written $[xy\bar{x}\bar{y}] = [xxyy]$. But this does not hold for the Coulomb part of the potential separately.

The value $^{C}c_{11}$ calculated by Madelung's method has been given by Born (1920); he finds the value $-2 \cdot 55 \dfrac{e^2}{2r_0^4}$. Since the numerical calculations are confined to an accuracy of 1 %, the two values agree with each other.

In table 1 the results are compared with the experimental values.* The units are dynes/cm.$^2 \times 10^{11}$.

TABLE 1

	Exp.	Theor.
c_{11}	4·95	4·65
c_{12}	1·4	1·28
$\frac{1}{3}(c_{11}+2c_{12})$	2·58 ⎫	2·40
$1/\kappa$	2·40 ⎭	
c_{44}	1·28	1·28

The theoretical value of the reciprocal compressibility $(2 \cdot 40 \times 10^{11}$ dynes/cm.$^2)$ satisfies, of course, exactly the relation $\dfrac{3}{\kappa} = c_{11}+2c_{12}$ with the theoretical values of c_{11} and c_{12}, and coincides with the experimental value since this value has been used for the determination of the constant A. But it differs from the experimental elasticity constants. This is an incongruity not of the theory, but of the experimental results. In fact, the measurements of c_{12} are rather inaccurate (it has been measured only within 10 % error). Therefore the experimental values agree with the theoretical values within the limits of error.

The perfect agreement of the experimental and theoretical values of c_{44} are a strong confirmation of the theory; for, the theoretical value of c_{44} does not depend on A (or κ), but only on the lattice constant.

8. Numerical results for the coupling coefficients

For the purpose of numerical calculation of the coupling coefficients the adjustable parameter ϵ in equation (5·10) has been chosen equal to 1. All terms smaller than 1 % of the largest term in each series were neglected. Since the series in question converge rapidly this gives an accuracy of 1 %–2 %.

All coefficients have been calculated independently from each other so that the equations (4·9) could be used to check the results. These equations were satisfied in each case within 1 %. The only exceptions are $\mathbf{p} = (6, 6, 0)$ and $\mathbf{p} = (6, 6, 2)$. In these cases the final coefficients are the differences between two nearly equal quantities and therefore the error is larger than 1 %, but as in this case the electrical part is much smaller than the repulsive part of the coefficients, the total error is again not larger than 1 % so that it is not worth while to increase the accuracy of the electric part.

* The elastic constants have been calculated from the elastic moduli $\varDelta_{ij}$ given in *Landolt-Börnstein*, 1935, 3 Erg.Bd. 1, 74.

Apart from this, each coefficient has been checked independently either by calculating the coefficients belonging to the wave vector $(q_x, q_y, -q_z)$ which involves a different order in the evaluation of the terms of the series or by repeating the calculation with a different value of ϵ. Each coefficient has therefore been calculated twice by means of numerically different series. The agreement in each case was within 1%.

The results are given in tables 2, 2a, which contain that part of the coupling coefficients which is due to the Coulomb force. The values are given in units of e^2/v_a and depend therefore only on the lattice structure, but not on the volume. In the first

column the wave vector of the mode of vibration is given in units of $\dfrac{1}{10}\dfrac{1}{2r_0}$; the numbers

describing the wave vector are identical with the components p_x, p_y, p_z introduced in (5·19). Table 3 contains the total coupling coefficients for NaCl, obtained by summing the contributions of the Coulomb force and the repulsive force (cf. (1·12)). The latter contribution, of course, depends on the properties of the Na and Cl ions. The coefficients are given again in units of e^2/v_a.

Since the coefficients ${}^{R}\!\left[\begin{smallmatrix} \kappa & \kappa' \\ x & y \end{smallmatrix}\right] = 0$; $x \neq y$ (cf. (6·8)), the bracket symbols

$$ {}^{C}\!\left[\begin{matrix} \kappa & \kappa' \\ x & y \end{matrix}\right] = \left[\begin{matrix} \kappa & \kappa' \\ x & y \end{matrix}\right] $$

are already the total coefficients and therefore table 2a and table 3 represent the whole set of the coefficients for the equation of motion.

9. Evaluation of the frequencies

In the case of NaCl ($s = 2$) the equations of motion for any given wave vector $\mathbf{k}$ constitute a system of six homogeneous equations for the amplitudes $\mathbf{U}_\kappa$ of the vibration. For a non-trivial solution the determinant of the system must vanish. This leads to the secular equation for the frequencies:

$$
\begin{vmatrix}
\begin{Bmatrix} 1 & 1 \\ x & x \end{Bmatrix}-\lambda & \begin{Bmatrix} 1 & 2 \\ x & x \end{Bmatrix} & \begin{Bmatrix} 1 & 1 \\ x & y \end{Bmatrix} & \begin{Bmatrix} 1 & 2 \\ x & y \end{Bmatrix} & \begin{Bmatrix} 1 & 1 \\ x & z \end{Bmatrix} & \begin{Bmatrix} 1 & 2 \\ x & z \end{Bmatrix} \\[2mm]
\begin{Bmatrix} 2 & 1 \\ x & x \end{Bmatrix} & \begin{Bmatrix} 2 & 2 \\ x & x \end{Bmatrix}-\lambda & \begin{Bmatrix} 2 & 1 \\ x & y \end{Bmatrix} & \begin{Bmatrix} 2 & 2 \\ x & y \end{Bmatrix} & \begin{Bmatrix} 2 & 1 \\ x & z \end{Bmatrix} & \begin{Bmatrix} 2 & 2 \\ x & z \end{Bmatrix} \\[2mm]
\begin{Bmatrix} 1 & 1 \\ y & x \end{Bmatrix} & \begin{Bmatrix} 1 & 2 \\ y & x \end{Bmatrix} & \begin{Bmatrix} 1 & 1 \\ y & y \end{Bmatrix}-\lambda & \begin{Bmatrix} 1 & 2 \\ y & y \end{Bmatrix} & \begin{Bmatrix} 1 & 1 \\ y & z \end{Bmatrix} & \begin{Bmatrix} 1 & 2 \\ y & z \end{Bmatrix} \\[2mm]
\begin{Bmatrix} 2 & 1 \\ y & x \end{Bmatrix} & \begin{Bmatrix} 2 & 2 \\ y & x \end{Bmatrix} & \begin{Bmatrix} 2 & 1 \\ y & y \end{Bmatrix} & \begin{Bmatrix} 2 & 2 \\ y & y \end{Bmatrix}-\lambda & \begin{Bmatrix} 2 & 1 \\ y & z \end{Bmatrix} & \begin{Bmatrix} 2 & 2 \\ y & z \end{Bmatrix} \\[2mm]
\begin{Bmatrix} 1 & 1 \\ z & x \end{Bmatrix} & \begin{Bmatrix} 1 & 2 \\ z & x \end{Bmatrix} & \begin{Bmatrix} 1 & 1 \\ z & y \end{Bmatrix} & \begin{Bmatrix} 1 & 2 \\ z & y \end{Bmatrix} & \begin{Bmatrix} 1 & 1 \\ z & z \end{Bmatrix}-\lambda & \begin{Bmatrix} 1 & 2 \\ z & z \end{Bmatrix} \\[2mm]
\begin{Bmatrix} 2 & 1 \\ z & x \end{Bmatrix} & \begin{Bmatrix} 2 & 2 \\ z & x \end{Bmatrix} & \begin{Bmatrix} 2 & 1 \\ z & y \end{Bmatrix} & \begin{Bmatrix} 2 & 2 \\ z & y \end{Bmatrix} & \begin{Bmatrix} 2 & 1 \\ z & z \end{Bmatrix} & \begin{Bmatrix} 2 & 2 \\ z & z \end{Bmatrix}-\lambda
\end{vmatrix} = 0. \quad (9\cdot0)
$$

TABLE 2

p_x	p_y	p_z	$c\begin{bmatrix}1&1\\x&x\end{bmatrix}\dfrac{v_a}{e^2}$	$c\begin{bmatrix}1&1\\y&y\end{bmatrix}\dfrac{v_a}{e^2}$	$c\begin{bmatrix}1&1\\z&z\end{bmatrix}\dfrac{v_a}{e^2}$	$c\begin{bmatrix}1&2\\x&x\end{bmatrix}\dfrac{v_a}{e^2}$	$c\begin{bmatrix}1&2\\y&y\end{bmatrix}\dfrac{v_a}{e^2}$	$c\begin{bmatrix}1&2\\z&z\end{bmatrix}\dfrac{v_a}{e^2}$
10	5	0*	−0·785	+1·594	−0·785	+10·981	0	−10·981
10	4	0	−1·812	+1·640	+0·181	+12·166	−2·313	− 9·856
10	2	2	−2·938	+1·468	+1·468	+13·448	−6·725	− 6·725
10	2	0	−3·606	+1·961	+1·638	+14·214	−6·071	− 8·142
10	0	0	−4·330	+2·160	+2·160	+15·043	−7·520	− 7·520
9	5	1	−0·714	+1·453	−0·714	+10·530	0	−10·530
9	3	3	−1·583	+0·795	+0·795	+11·513	−5·758	− 5·758
9	3	1	−2·699	+1·663	+0·987	+12·860	−4·439	− 8·473
9	1	1	−4·047	+2·022	+2·022	+14·430	−7·214	− 7·214
8	6	0	+0·059	+1·195	−1·298	+ 8·549	+3·003	−11·548
8	4	2	−1·471	+1·142	+0·339	+10·375	−2·375	− 8·003
8	4	0	−1·975	+1·450	+0·535	+11·079	−1·692	− 9·391
8	2	2	−3·184	+1·595	+1·595	+12·524	−6·263	− 6·263
8	2	0	−3·911	+2·031	+1·882	+13·402	−5·633	− 7·779
8	0	0	−4·738	+2·366	+2·366	+14·386	−7·193	− 7·193
7	5	3	−0·286	+0·571	−0·286	+ 6·838	0	− 6·838
7	5	1	−0·894	+0·846	+0·062	+ 8·148	+1·342	− 9·479
7	3	3	−1·859	+0·932	+0·932	+ 9·281	−4·642	− 4·642
7	3	1	−3·049	+1·527	+1·526	+10·970	−3·368	− 7·605
7	1	1	−4·699	+2·350	+2·350	+13·021	−6·512	− 6·512
6	6	2	+0·140	+0·140	−0·274	+ 4·312	+4·312	− 8·615
6	6	0	+0·017	+0·017	−0·022	+ 5·004	+5·004	− 9·997
6	4	4	−0·552	+0·279	+0·279	+ 4·933	−2·470	− 2·470
6	4	2	−1·594	+0·621	+0·976	+ 7·120	−0·548	− 6·566
6	4	0	−2·090	+0·684	+1·428	+ 8·025	+0·192	− 8·201
6	2	2	−3·594	+1·803	+1·803	+ 9·933	−4·964	− 4·964
6	2	0	−4·563	+2·066	+2·500	+11·200	−4·360	− 6·844
6	0	0	−5·782	+2·891	+2·891	+12·683	−6·344	− 6·344
5	5	5	0	0	0	0	0	0
5	5	3	−0·228	−0·228	+0·450	+ 2·379	+2·379	− 4·761
5	5	1	−0·600	−0·600	+1·214	+ 3·929	+3·929	− 7·845
5	3	3	−1·659	+0·836	+0·836	+ 5·252	−2·628	− 2·628
5	3	1	−3·050	+0·840	+2·224	+ 7·467	−1·198	− 6·267
5	1	1	−5·526	+2·764	+2·764	+10·591	−5·299	− 5·299
4	4	4	0	0	0	0	0	0
4	4	2	−0·751	−0·751	+1·502	+ 2·351	+2·351	− 4·702
4	4	0	−1·220	−1·220	+2·455	+ 3·406	+3·406	− 6·799
4	2	2	−3·115	+1·561	+1·561	+ 5·892	−2·945	− 2·945
4	2	0	−4·642	+1·414	+3·228	+ 7·850	−2·137	− 5·717
4	0	0	−6·987	+3·512	+3·512	+10·623	−5·313	− 5·313
3	3	3	0	0	0	0	0	0
3	3	1	−1·352	−1·352	+2·706	+ 2·407	+2·407	− 4·813
3	1	1	−5·377	+2·684	+2·684	+ 7·282	−3·641	− 3·641
2	2	2	0	0	0	0	0	0
2	2	0	−1·893	−1·893	+3·796	+ 2·421	+2·421	− 4·820
2	0	0	−8·013	+3·997	+3·997	+ 8·994	−4·491	− 4·491
1	1	1	0	0	0	0	0	0
0	0	0	—	—	—	—	—	—

* The vector (10, 5, 0) is really not a vector within our choice. I have, however, considered it, since it is one of the corner points of our phase space.

TABLE 2a

p_x	p_y	p_z	$\begin{bmatrix}1 & 1\\ x & y\end{bmatrix}\frac{v_a}{e^2}$	$\begin{bmatrix}1 & 1\\ x & z\end{bmatrix}\frac{v_a}{e^2}$	$\begin{bmatrix}1 & 1\\ y & z\end{bmatrix}\frac{v_a}{e^2}$	$\begin{bmatrix}1 & 2\\ x & y\end{bmatrix}\frac{v_a}{e^2}$	$\begin{bmatrix}1 & 2\\ x & z\end{bmatrix}\frac{v_a}{e^2}$	$\begin{bmatrix}1 & 2\\ y & z\end{bmatrix}\frac{v_a}{e^2}$
10	5	0	0	0	0	0	0	0
10	4	0	0	0	0	0	0	0
10	2	2	0	0	−1.038	0	0	−0.393
10	2	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0
9	5	1	−1.009	−0.322	−1.009	+0.438	0	−0.438
9	3	3	−0.856	−0.856	−2.099	+0.251	+0.251	−0.856
9	3	1	−0.883	−0.335	−0.762	+0.450	+0.120	−0.267
9	1	1	−0.356	−0.356	−0.281	+0.197	+0.197	−0.083
8	6	0	−1.796	0	0	+0.803	0	0
8	4	2	−1.946	−1.201	−1.815	+0.810	+0.238	−0.570
8	4	0	−1.985	0	0	+1.050	0	0
8	2	2	−1.288	−1.288	−1.077	+0.634	+0.634	−0.244
8	2	0	−1.344	0	0	+0.793	0	0
8	0	0	0	0	0	0	0	0
7	5	3	−2.810	−2.303	−2.810	+0.742	0	−0.742
7	5	1	−2.868	−0.870	−1.030	+1.423	+0.075	−0.191
7	3	3	−2.422	−2.422	−2.190	+0.918	+0.918	−0.308
7	3	1	−2.620	−0.974	−0.829	+1.522	+0.434	−0.051
7	1	1	−1.093	−1.093	−0.320	+0.688	+0.688	+0.006
6	6	2	−3.177	−1.937	−1.937	+1.293	−0.172	−0.172
6	6	0	−3.234	0	0	+1.697	0	0
6	4	4	−3.299	−3.299	−3.205	+0.694	+0.694	−0.203
6	4	2	−3.606	−2.145	−1.588	+1.866	+0.693	+0.116
6	4	0	−3.806	0	0	+2.346	0	0
6	2	2	−2.546	−2.546	−1.291	+1.532	+1.532	+0.242
6	2	0	−2.772	0	0	+1.911	0	0
6	0	0	0	0	0	0	0	0
5	5	5	−3.615	−3.615	−3.615	0	0	0
5	5	3	−3.833	−2.980	−2.980	+1.506	+0.436	+0.436
5	5	1	−4.202	−1.174	−1.174	+2.510	+0.276	+0.276
5	3	3	−3.582	−3.582	−2.642	+1.853	+1.853	+0.794
5	3	1	−4.273	−1.546	−1.098	+2.974	+0.911	+0.439
5	1	1	−1.963	−1.963	−0.481	+1.483	+1.483	−0.236
4	4	4	−3.668	−3.668	−3.668	+1.330	+1.330	+1.330
4	4	2	−4.560	−2.590	−2.590	+2.932	+1.259	+1.259
4	4	0	−5.088	0	0	+3.695	0	0
4	2	2	−3.720	−3.720	−2.034	+2.760	+2.760	+1.270
4	2	0	−4.464	0	0	+3.637	0	0
4	0	0	0	0	0	0	0	0
3	3	3	−3.810	−3.810	−3.810	+2.511	+2.511	+2.511
3	3	1	−5.363	−1.872	−1.872	+4.359	+1.398	+1.398
3	1	1	−3.243	−3.243	−1.111	+2.869	+2.869	+0.937
2	2	2	−3.986	−3.986	−3.986	+3.421	+3.421	+3.421
2	2	0	−6.038	0	0	+5.531	0	0
2	0	0	0	0	0	0	0	0
1	1	1	−4.132	−4.132	−4.132	+3.993	+3.993	+3.993
0	0	0	0	0	0	0	0	0

TABLE 3

p_x	p_y	p_z	$\begin{bmatrix} 1 & 1 \\ x & x \end{bmatrix}\dfrac{v_a}{e^2}$	$\begin{bmatrix} 1 & 1 \\ y & y \end{bmatrix}\dfrac{v_a}{e^2}$	$\begin{bmatrix} 1 & 1 \\ z & z \end{bmatrix}\dfrac{v_a}{e^2}$	$\begin{bmatrix} 1 & 2 \\ x & x \end{bmatrix}\dfrac{v_a}{e^2}$	$\begin{bmatrix} 1 & 2 \\ y & y \end{bmatrix}\dfrac{v_a}{e^2}$	$\begin{bmatrix} 1 & 2 \\ z & z \end{bmatrix}\dfrac{v_a}{e^2}$
10	5	0	− 8·635	−6·256	−8·635	− 0·364	0	+0·364
10	4	0	− 9·662	−6·210	−7·669	+ 0·461	+0·833	+1·129
10	2	2	−10·788	−6·382	−6·382	+ 1·383	+1·734	+1·734
10	2	0	−11·456	−5·889	−6·212	+ 1·927	+2·165	+2·261
10	0	0	−12·180	−5·690	−5·690	+ 2·533	+2·660	+2·660
9	5	1	− 8·564	−6·397	−8·564	− 0·260	0	+0·260
9	3	3	− 9·433	−7·055	−7·055	+ 0·461	+0·649	+0·649
9	3	1	−10·549	−6·187	−6·863	+ 1·385	+1·545	+1·632
9	1	1	−11·897	−5·828	−5·828	+ 2·532	+2·468	+2·468
8	6	0	− 7·791	−6·655	−9·148	− 0·492	−0·366	−0·066
8	4	2	− 9·321	−6·708	−7·511	+ 0·837	+0·771	+0·816
8	4	0	− 9·825	−6·400	−7·315	+ 1·318	+1·232	+1·372
8	2	2	−11·034	−6·255	−6·255	+ 2·403	+1·973	+1·973
8	2	0	−11·761	−5·189	−5·968	+ 3·059	+2·380	+2·401
8	0	0	−12·588	−5·484	−5·484	+ 3·820	+2·764	+2·764
7	5	3	− 8·136	−7·279	−8·136	+ 0·169	0	−0·169
7	5	1	− 8·744	−7·004	−7·788	+ 1·056	+0·919	+0·888
7	3	3	− 9·709	−6·918	−6·918	+ 1·927	+1·342	+1·342
7	3	1	−10·899	−6·323	−6·324	+ 3·193	+2·193	+2·077
7	1	1	−12·549	−5·500	−5·500	+ 4·821	+2·747	+2·747
6	6	2	− 7·710	−7·710	−8·124	+ 0·583	+0·583	+0·341
6	6	0	− 7·833	−7·833	−7·872	+ 1·053	+1·053	+0·903
6	4	4	− 8·402	−7·571	−7·571	+ 1·067	+0·676	+0·676
6	4	2	− 9·444	−7·229	−6·874	+ 2·672	+2·015	+1·670
6	4	0	− 9·940	−7·166	−6·422	+ 3·354	+2·533	+1·979
6	2	2	−11·444	−6·047	−6·047	+ 4·902	+2·689	+2·689
6	2	0	−12·413	−5·784	−5·350	+ 5·947	+3·071	+2·753
6	0	0	−13·632	−4·959	−4·959	+ 7·207	+3·031	+3·031
5	5	5	− 7·850	−7·850	−7·850	0	0	0
5	5	3	− 8·078	−8·078	−7·400	+ 1·694	+1·694	+1·223
5	5	1	− 8·450	−8·450	−6·636	+ 2·821	+2·821	+1·837
5	3	3	− 9·509	−7·014	−7·014	+ 3·882	+2·671	+2·671
5	3	1	−10·900	−7·010	−5·626	+ 5·683	+3·678	+2·730
5	1	1	−13·376	−5·086	−5·086	+ 8·375	+3·275	+3·275
4	4	4	− 7·850	−7·850	−7·850	+ 2·426	+2·426	+2·426
4	4	2	− 8·601	−8·601	−6·348	+ 4·195	+4·195	+2·814
4	4	0	− 9·070	−9·070	−5·395	+ 5·027	+5·027	+2·661
4	2	2	−10·965	−6·289	−6·289	+ 7·153	+3·989	+3·989
4	2	0	−12·492	−6·436	−4·622	+ 8·889	+4·574	+3·161
4	0	0	−14·837	−4·338	−4·338	+11·439	+3·342	+3·342
3	3	3	− 7·850	−7·850	−7·850	+ 4·614	+4·614	+4·614
3	3	1	− 9·202	−9·202	−5·144	+ 6·598	+6·598	+3·499
3	1	1	−13·227	−5·166	−5·166	+11·050	+4·248	+4·248
2	2	2	− 7·850	−7·850	−7·850	+ 6·351	+6·351	+6·351
2	2	0	− 9·743	−9·743	−4·054	+ 8·550	+8·550	+3·475
2	0	0	−15·863	−3·853	−3·853	+14·900	+3·582	+3·582
1	1	1	− 7·850	−7·850	−7·850	+ 7·466	+7·466	+7·466
0	0	0	—	—	—	—	—	—

Here
$$\begin{Bmatrix} \kappa & \kappa' \\ x & y \end{Bmatrix} = -\frac{1}{\sqrt{m_\kappa}\sqrt{m_{\kappa'}}}\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} \tag{9.1}$$

is introduced so that
$$\lambda = \omega^2. \tag{9.2}$$

The determinant is symmetric since
$$\begin{Bmatrix} \kappa & \kappa' \\ x & y \end{Bmatrix} = \begin{Bmatrix} \kappa' & \kappa \\ y & x \end{Bmatrix},$$

as follows from (5·1), (5·2).

For the calculation of the roots of the equation (9·0) which gives the frequencies of the crystal I have used a method given by Aitken (1937). (I wish to thank Dr A. C. Aitken for advising me to use this method, which was a very great help in these calculations.)

It is, however, not always necessary to consider determinants of the sixth order. In our choice of wave vectors (p_x, p_y, p_z) the determinant (9·0) splits up very frequently into determinants of a lower order. Considering all these cases one obtains a satisfactory survey over the frequency spectrum if the wave vector is described, not with the help of (p_x, p_y, p_z), but by its components (p_1, p_2, p_3) (cf. (5·18)).

In a large number of cases the determinant (9·0) can easily be split up into a product of three determinants.

(1) $\mathbf{p} = (p_x, 0, 0)$ or $\mathbf{p} = (0, p_2, p_3)$; $p_2 = p_3$. Variation of p_x, i.e. of p_2, p_3, therefore, means going along the diagonal of the ground plane of the phase space. We have with (5·12), (5·11), (6·11)
$$\begin{Bmatrix} \kappa & \kappa' \\ y & y \end{Bmatrix} = \begin{Bmatrix} \kappa & \kappa' \\ z & z \end{Bmatrix}, \quad \begin{Bmatrix} \kappa & \kappa' \\ x & y \end{Bmatrix} = \begin{Bmatrix} \kappa & \kappa' \\ y & z \end{Bmatrix} = \begin{Bmatrix} \kappa & \kappa' \\ z & x \end{Bmatrix} = 0.$$

I introduce for abbreviation the notation
$$a = \begin{Bmatrix} 1 & 1 \\ x & x \end{Bmatrix}, \quad b = \begin{Bmatrix} 2 & 2 \\ x & x \end{Bmatrix}, \quad c = \begin{Bmatrix} 1 & 2 \\ x & x \end{Bmatrix};$$
$$a' = \begin{Bmatrix} 1 & 1 \\ y & y \end{Bmatrix} = \begin{Bmatrix} 1 & 1 \\ z & z \end{Bmatrix}, \quad b' = \begin{Bmatrix} 2 & 2 \\ y & y \end{Bmatrix} = \begin{Bmatrix} 2 & 2 \\ z & z \end{Bmatrix}, \quad c' = \begin{Bmatrix} 1 & 2 \\ y & y \end{Bmatrix} = \begin{Bmatrix} 1 & 2 \\ z & z \end{Bmatrix}. \tag{9.3}$$

The determinant can then be written as the product
$$\begin{vmatrix} a-\lambda & c \\ c & b-\lambda \end{vmatrix} \begin{vmatrix} a'-\lambda & c' \\ c' & b'-\lambda \end{vmatrix}^2 = 0, \tag{9.4}$$

with the solutions
$$\lambda^l_{1,2} = (\omega^l_{1,2})^2 = \frac{e^2}{v_a}\left[\frac{a+b}{2} \pm \sqrt{\left\{\left(\frac{a+b}{2}\right)^2 - (ab-c^2)\right\}}\right],$$
$$\lambda^{tr}_{1,2} = (\omega^{tr}_{1,2})^2 = \frac{e^2}{v_a}\left[\frac{a'+b'}{2} \pm \sqrt{\left\{\left(\frac{a'+b'}{2}\right)^2 - (a'b'-c'^2)\right\}}\right]. \tag{9.5}$$

By inspection of the equation of motion it is easily seen that the first two of these frequencies correspond to longitudinal waves. The second two give transverse waves. They have to be counted twice since the corresponding determinant in (9·4) is squared, giving the two independent directions of polarization of the transverse waves.

(2) For a wave vector $(10, p_y, 0)$ it follows from (5·12), (6·11) that the determinant splits up into three. The vibrations are in the x, y and z directions. In the case $(10, p_y, 0)$ one has in general three different determinants. Only in the case $(10, 5, 0)$ one has, because of the symmetry

$$\begin{bmatrix} \kappa & \kappa' \\ x & x \end{bmatrix}_{(10, 5, 0)} = \begin{bmatrix} \kappa & \kappa' \\ z & z \end{bmatrix}_{(10, 5, 0)} \quad \text{(cf. table 3),} \tag{9·6}$$

two different determinants, but the frequencies $\omega^x_{1,2}$ have to be counted twice.

The frequencies for the cases $(10, 5, 0)$, $(10, 0, 0)$, $(5, 5, 5)$ and $(0, 0, 0)$ have already been calculated by Lyddane and Herzfeld. Their values for the electric part of the coefficients agree with ours, but there is a difference in the constants A and B which is due to the repulsive forces. These authors obtain for A: 10·606, B: 1·073 (cf. (6·4)). This is due to the fact that they use the repulsive potential of Born and Mayer (1932) for the calculation of these constants, thus neglecting the Van der Waals (London) forces, which are roughly included in our general expression:

(3) $\quad \mathbf{p} = (p_x, p_y, p_z)$; $\quad p_x = p_y = p_z$ or $\quad \mathbf{p} = (p_1, p_2, p_3)$; $\quad p_1 = p_2 = p_3$.

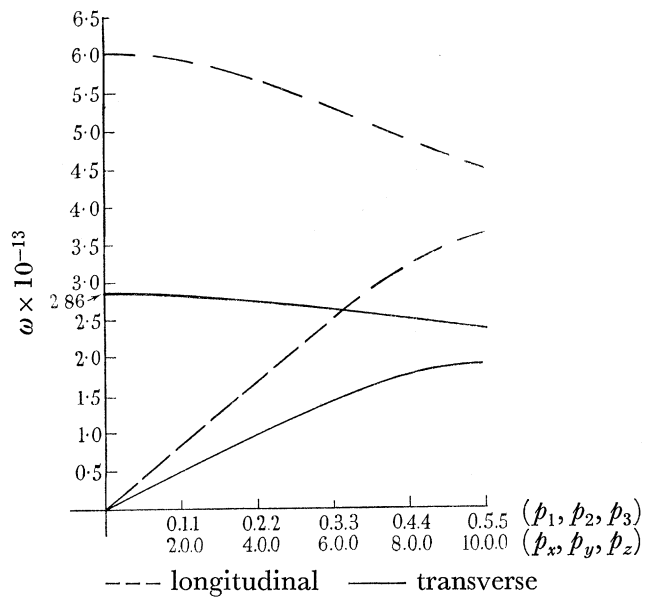Clearly, variation of the p_i means moving along the main diagonal of the phase space. The following identities hold:

$$\left.\begin{aligned} a &= \begin{Bmatrix} 1 & 1 \\ x & x \end{Bmatrix} = \begin{Bmatrix} 1 & 1 \\ y & y \end{Bmatrix} = \begin{Bmatrix} 1 & 1 \\ z & z \end{Bmatrix}, & d &= \begin{Bmatrix} 1 & 1 \\ x & y \end{Bmatrix} = \begin{Bmatrix} 1 & 1 \\ y & z \end{Bmatrix} = \begin{Bmatrix} 1 & 1 \\ z & x \end{Bmatrix}, \\ b &= \begin{Bmatrix} 2 & 2 \\ x & x \end{Bmatrix} = \begin{Bmatrix} 2 & 2 \\ y & y \end{Bmatrix} = \begin{Bmatrix} 2 & 2 \\ z & z \end{Bmatrix}, & e &= \begin{Bmatrix} 2 & 2 \\ x & y \end{Bmatrix} = \begin{Bmatrix} 2 & 2 \\ y & z \end{Bmatrix} = \begin{Bmatrix} 2 & 2 \\ z & x \end{Bmatrix}, \\ c &= \begin{Bmatrix} 1 & 2 \\ x & x \end{Bmatrix} = \begin{Bmatrix} 1 & 2 \\ y & y \end{Bmatrix} = \begin{Bmatrix} 1 & 2 \\ z & z \end{Bmatrix}, & f &= \begin{Bmatrix} 1 & 2 \\ x & y \end{Bmatrix} = \begin{Bmatrix} 1 & 2 \\ y & z \end{Bmatrix} = \begin{Bmatrix} 1 & 2 \\ z & x \end{Bmatrix}. \end{aligned}\right\} \tag{9·7}$$

The secular determinant gives

$$\begin{vmatrix} a+2d-\lambda & c+2f \\ c+2f & b+2e-\lambda \end{vmatrix} \begin{vmatrix} a-d-\lambda & c-f \\ c-f & b-e-\lambda \end{vmatrix}^2 = 0. \tag{9·8}$$

Again two longitudinal and twice two transverse waves are obtained with the frequencies:

$$\left.\begin{aligned} \lambda^l_{1,2} &= (\omega^l_{1,2})^2 = \frac{e^2}{v_a}\left[\frac{\alpha+\beta}{2} \pm \sqrt{\left\{\left(\frac{\alpha+\beta}{2}\right)^2 - (\alpha\beta-\gamma^2)\right\}}\right], \\ \lambda^{tr}_{1,2} &= (\omega^{tr}_{1,2})^2 = \frac{e^2}{v_a}\left[\frac{\alpha'+\beta'}{2} \pm \sqrt{\left\{\left(\frac{\alpha'+\beta'}{2}\right)^2 - (\alpha'\beta'-\gamma'^2)\right\}}\right], \\ \alpha &= a+2d, \qquad \alpha' = a-d, \\ \beta &= b+2e, \qquad \beta' = b-e, \\ \gamma &= c+2f, \qquad \gamma' = c-f. \end{aligned}\right\} \tag{9·9}$$

(4) $(p_x, p_y, 0)$. The determinant splits up into two, of the fourth and the second order respectively. The latter characterises a transverse vibration in the z direction.

(5) $(p_x = p_y, p_z)$. The determinant splits up into one of the fourth and one of the second order. The transverse vibration is perpendicular to the diagonal $x = y$.

(6) $(p_x = p_y, 0)$. Here the determinant splits up into three. The following coefficients are equal:

$$a = \begin{Bmatrix} 1 & 1 \\ x & x \end{Bmatrix} = \begin{Bmatrix} 1 & 1 \\ y & y \end{Bmatrix}, \quad d = \begin{Bmatrix} 1 & 1 \\ x & y \end{Bmatrix}, \quad \bar{a} = \begin{Bmatrix} 1 & 1 \\ z & z \end{Bmatrix},$$

$$b = \begin{Bmatrix} 2 & 2 \\ x & x \end{Bmatrix} = \begin{Bmatrix} 2 & 2 \\ y & y \end{Bmatrix}, \quad e = \begin{Bmatrix} 2 & 2 \\ x & y \end{Bmatrix}, \quad \bar{b} = \begin{Bmatrix} 2 & 2 \\ z & z \end{Bmatrix}, \tag{9.10}$$

$$c = \begin{Bmatrix} 1 & 2 \\ x & x \end{Bmatrix} = \begin{Bmatrix} 1 & 2 \\ y & y \end{Bmatrix}, \quad f = \begin{Bmatrix} 1 & 2 \\ x & y \end{Bmatrix}, \quad \bar{c} = \begin{Bmatrix} 1 & 2 \\ z & z \end{Bmatrix}.$$

All other coefficients vanish. The secular equation is

$$\begin{vmatrix} a+d-\lambda & c+f \\ c+f & b+e-\lambda \end{vmatrix} \quad \begin{vmatrix} a-d-\lambda & c-f \\ c-f & b-e-\lambda \end{vmatrix} \quad \begin{vmatrix} \bar{a}-\lambda & \bar{c} \\ \bar{c} & \bar{b}-\lambda \end{vmatrix} = 0. \tag{9.11}$$

Two longitudinal and four transverse waves are obtained with the frequencies

$$\lambda_{1,2}^{l} = (\omega_{1,2}^{l})^2 = \frac{e^2}{v_a}\left[\frac{\alpha+\beta}{2} \pm \sqrt{\left\{\left(\frac{\alpha+\beta}{2}\right)^2 - (\alpha\beta-\gamma^2)\right\}}\right],$$

$$\lambda_{1,2}^{tr} = (\omega_{1,2}^{tr})^2 = \frac{e^2}{v_a}\left[\frac{\alpha'+\beta'}{2} \pm \sqrt{\left\{\left(\frac{\alpha'+\beta'}{2}\right)^2 - (\alpha'\beta'-\gamma'^2)\right\}}\right],$$

$$\lambda_{3,4}^{tr} = (\omega_{3,4}^{tr})^2 = \frac{e^2}{v_a}\left[\frac{\bar{a}+\bar{b}}{2} \pm \sqrt{\left\{\left(\frac{\bar{a}+\bar{b}}{2}\right)^2 - (\bar{a}\bar{b}-\bar{c}^2)\right\}}\right], \tag{9.12}$$

$$\alpha = a+d, \qquad \alpha' = a-d,$$
$$\beta = b+e, \qquad \beta' = b-e,$$
$$\gamma = c+f, \qquad \gamma' = c-f.$$

The direction of polarization of the transverse waves is the z axis $(\omega_{3,4}^{tr})$ and one of the diagonals in the xy plane $(\omega_{1,2}^{tr})$ respectively.

In general, two of the vibrations will be quasi-longitudinal and four quasi-transverse. The numerical values of all the frequencies are collected in table 5; I have also plotted (figures 1–8) the frequencies belonging to the vectors

(p_1, p_2, p_3):   from $(0, 0, 0)$ to $(0, 5, 5)$,

                ,, $(0, 0, 0)$,, $(5, 5, 5)$,

from $(0, 1, 1)$ to $(0, 1, 5)$, from $(2, 3, 3)$ to $(2, 3, 6)$,

  ,, $(1, 1, 1)$,, $(1, 1, 5)$,   ,, $(3, 3, 3)$,, $(3, 3, 6)$,

  ,, $(2, 2, 2)$,, $(2, 2, 6)$,   ,, $(3, 4, 4)$,, $(3, 4, 7)$.

FIGURE 1. **p**: (0.0.0) to (0.5.5)

FIGURE 2. **p**: (0.0.0) to (5.5.5)
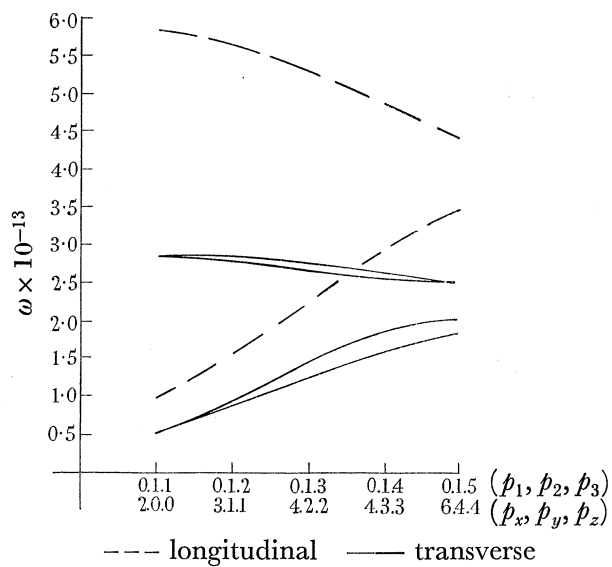
FIGURE 3. **p**: (0.1.1) to (0.1.5)
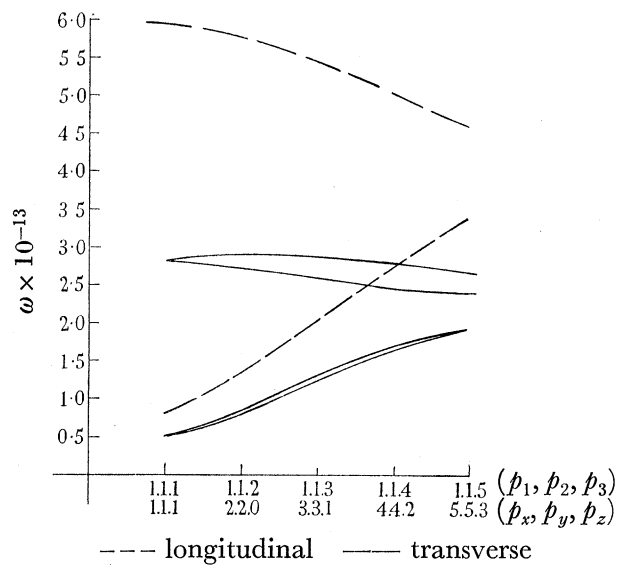
FIGURE 4. **p**: (1.1.1) to (1.1.5)
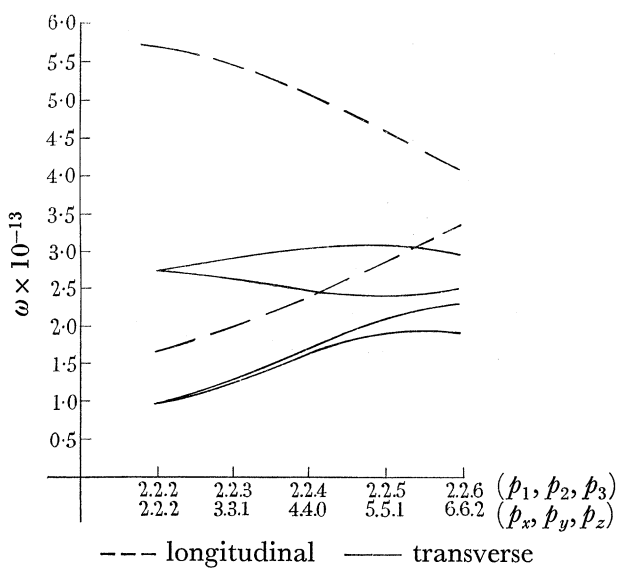
FIGURE 5. **p**: (2.2.2) to (2.2.6)
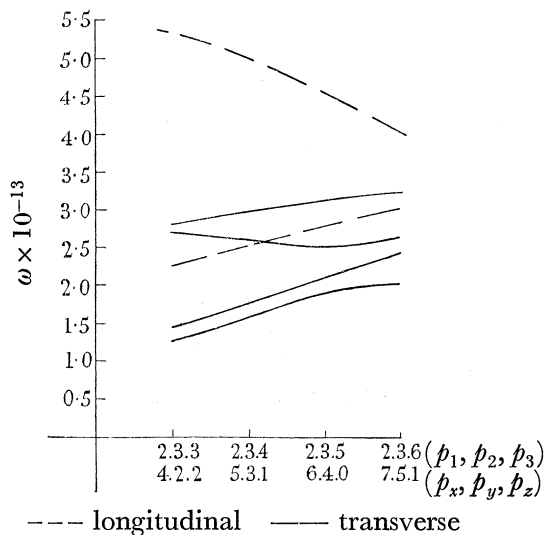
FIGURE 6. **p**: (2.3.3) to (2.3.6)

In the figures the vector components are described both in terms of the p_x, p_y, p_z and of the p_1, p_2, p_3. The units are 10^{13} sec.$^{-1}$. For the longitudinal as well as for the transverse vibrations the figures show the well-known picture of the "optical" and "acoustic" branches. It can be seen that the branches of the transverse frequencies in figures 1 and 2 (where those frequencies have to be counted twice (cf. pp. 540, 541)) split up in the more general case into two branches each.

This degeneration, as shown in figures 1 and 2, is, of course, due to neglecting higher order terms in the development of the energy (1·5). For the same reason it must be understood that in those cases where two branches of the frequencies intersect each other, say for instance two transverse frequency branches, this degeneration would be removed by taking account of higher terms in the development of the energy. The cross-point would be dissolved in such a way that the two lower parts of the original branches would be connected, and the two higher parts as well.
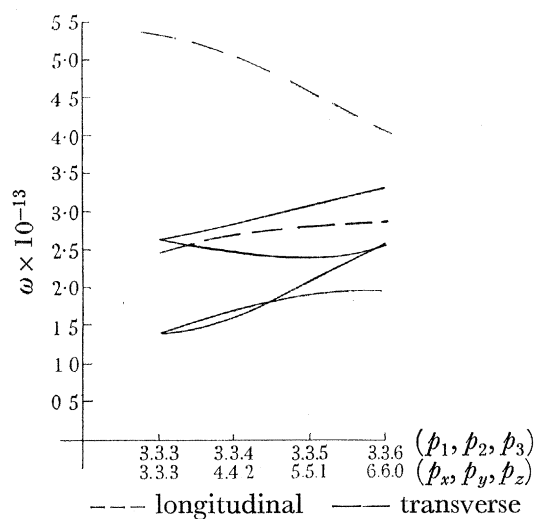
FIGURE 7. $\mathbf{p}$: (3.3.3) to (3.3.6)
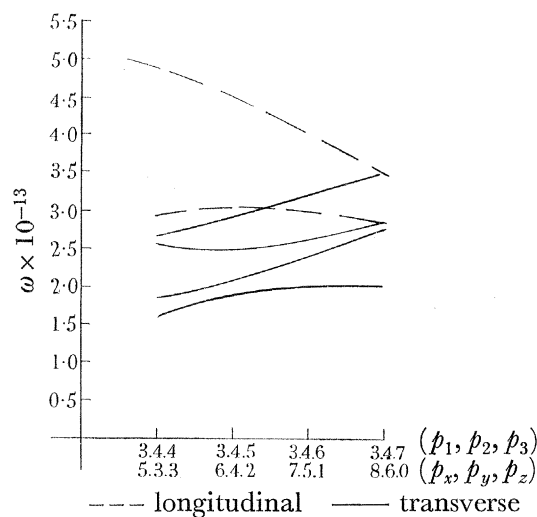
FIGURE 8. $\mathbf{p}$: (3.4.4) to (3.4.7)

For the case $(0, 0, 0)$ of the residual ray we obtain uniquely the frequency

$$\omega = \sqrt{\frac{e^2}{v_a}\left[A + 2B - \frac{4\pi}{3}\right]} = 2\cdot86 \times 10^{13} \text{ sec.}^{-1}.$$

Lyddane and Herzfeld (1938) obtain the same limiting frequency for transverse waves and beside this a limiting frequency

$$\omega = \sqrt{\frac{e^2}{v_a}\left[A + 2B + \frac{8\pi}{3}\right]} = 6\cdot02 \times 10^{13} \text{ sec.}^{-1}$$

for "longitudinal" waves. The numerical values here are slightly smaller than those of Lyddane and Herzfeld due to the different choice of A, B (cf. p. 541). But, as shown in §4, one cannot accept this second frequency as one of residual rays which is, therefore, given in square brackets in table 5.

TABLE 4. FREQUENCIES OF THE NaCl LATTICE

p_x	p_y	p_z	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
10	5	0	3·43	2·91*	2·75	2·35*	—	—
10	4	0	3·63	3·28	2·95	2·91	2·52	2·28
10	2	2	3·88	3·25	3·01	2·94	2·45	1·82
10	2	0	4·03	3·13	3·06	3·05	2·02	1·96
10	0	0	4·20	3·10	3·09*	1·77*	—	—
9	5	1	3·60	3·36	2·89	2·89	2·59	2·23
9	3	3	3·79	3·32	3·02	2·75	2·66	1·88
9	3	1	3·90	3·21	3·02	2·89	2·41	2·01
9	1	1	4·17	3·13	3·05	3·05	1·96	1·76
8	6	0	3·52	3·52	2·87	2·84	2·75	2·03
8	4	2	3·97	3·17	3·06	2·76	2·43	1·97
8	4	0	3·93	3·24	2·98	2·69	2·42	2·16
8	2	2	4·17	3·09	2·96	2·92	2·30	1·75
8	2	0	4·25	3·11	3·00	2·81	1·92	1·70
8	0	0	4·38	3·07*	2·99	1·69*	—	—
7	5	3	4·23	3·24	2·79	2·78	2·40	1·75
7	5	1	4·04	3·23	3·00	2·63	2·40	2·03
7	3	3	4·33	3·17	2·84	2·72	2·28	1·78
7	3	1	4·39	3·08	2·91	2·72	2·16	1·83
7	1	1	4·57	3·02	3·00	2·83	1·76	1·60
6	6	2	4·17	3·33	2·96	2·48	2·30	1·92
6	6	0	4·05	3·30	2·89	2·59	2·54	1·96
6	4	4	4·47	3·51	2·53	2·51	2·05	1·86
6	4	2	4·52	3·05	2·92	2·51	2·07	1·93
6	4	0	4·55	3·13	2·78	2·48	2·13	1·93
6	2	2	4·76	2·87	2·83	2·75	1·94	1·55
6	2	0	4·81	3·04	2·83	2·62	1·65	1·62
6	0	0	4·87	3·01*	2·59	1·42*	—	—
5	5	5	4·52	3·64	2·40*	1·93*	—	—
5	5	3	4·59	3·36	2·67	2·40	1·93	1·92
5	5	1	4·60	3·08	2·84	2·41	2·08	1·92
5	3	3	4·91	2·95	2·68	2·57	1·86	1·61
5	3	1	5·01	2·97	2·60	2·52	1·75	1·57
5	1	1	5·14	3·02	2·83	2·34	1·57	1·08
4	4	4	4·86	3·22	2·50*	1·77*	—	—
4	4	2	5·06	2·83	2·71	2·49	1·69	1·62
4	4	0	5·09	3·03	2·49	2·39	1·69	1·65
4	2	2	5·34	2·81	2·70	2·26	1·46	1·27
4	2	0	5·39	2·96	2·73	2·05	1·27	1·25
4	0	0	5·44	2·94*	1·90	1·03*	—	—
3	3	3	5·33	2·65*	2·48	1·42*	—	—
3	3	1	5·48	2·90	2·63	2·01	1·30	1·25
3	1	1	5·67	2·88	2·83	1·59	0·96	0·89
2	2	2	5·71	2·76*	1·67	1·00*	—	—
2	2	0	5·78	2·91	2·75	1·35	0·85	0·79
2	0	0	5·87	2·89*	1·02	0·54*	—	—
1	1	1	5·94	2·84*	0·84	0·51*	—	—
(0	0	0	[6·02]	2·86	0·00	—	—	—)

The frequencies belonging to a wave vector are ordered with regard to their absolute magnitude. The units are 10^{13} sec.$^{-1}$.

* To be counted twice.

10. The frequency spectrum

From the frequencies calculated, it is possible to obtain the frequency spectrum $N(\nu)$, which is required for many applications. I divide the ν scale into a number of equal intervals $\Delta\nu$ and count the number of calculated frequencies in each interval. In order to obtain the spectrum very accurately it is, of course, desirable to choose $\Delta\nu$ as small as possible. On the other hand, there is a lower limit for the size of $\Delta\nu$. First, there should be a fair number of frequencies in each interval; secondly, it is obviously pointless to decrease the interval beyond the accuracy with which the frequencies are

ν_R: residual rays frequency
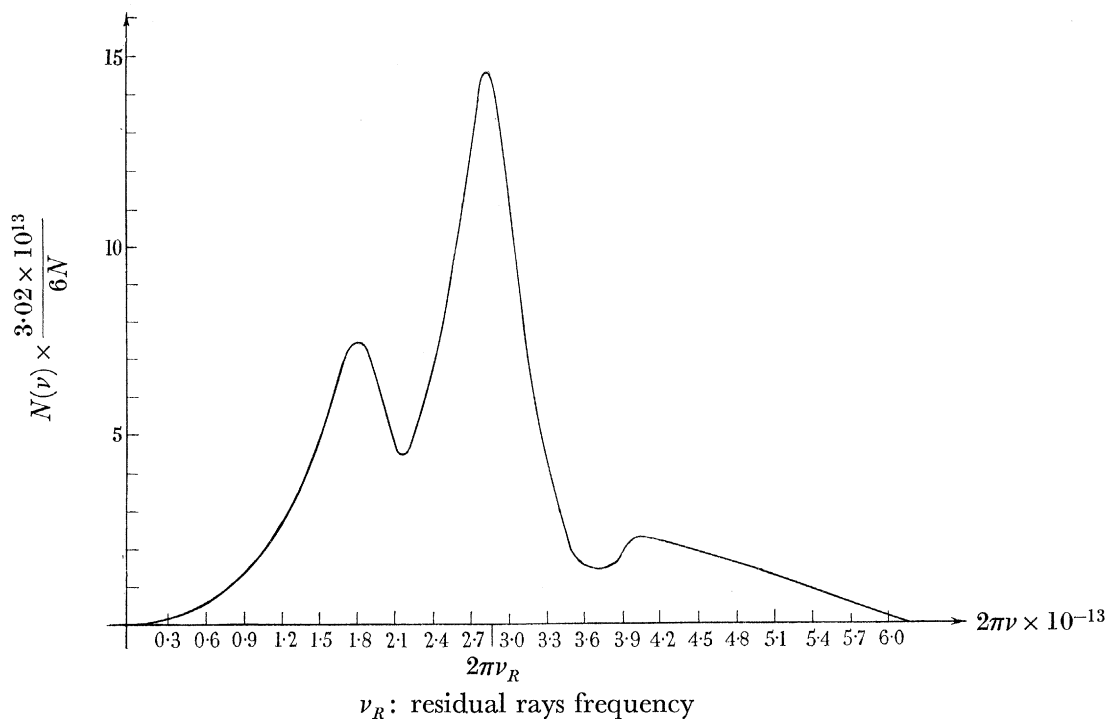
FIGURE 9. Frequency distribution $N(\nu)$.

calculated. I have chosen $\Delta\omega = 2\pi\Delta\nu = 0.3 \times 10^{13}$ sec.$^{-1}$ which corresponds to the accuracy of our calculation. In that case the average number of frequencies in each interval is about 14. Therefore, the spectrum obtained is accurate within a possible shift of some frequencies of not more than 0.3×10^{13} sec.$^{-1}$. Only at the ends of the spectrum the average number of frequencies per interval is too small as to give this accuracy. In this way three step-curves have been plotted, each of which is shifted against the other by a third of an interval $\Delta\omega$ in the scale of the ω's. The distribution curve (figure 9) is the approximation of these graphs by a smooth curve which is normalized so that the total number of frequencies is $3N$,

$$\int N(\nu)\, d\nu = 6N,$$

where $N(\nu)\, d\nu$ is the number of frequencies between ν and $\nu+d\nu$, and N is Avogadro's number.

One recognizes three maxima at $1\cdot8$, $2\cdot85$, and $4\cdot2 \times 10^{13}$ sec.$^{-1}$. These maxima are due to the different types of normal modes. I have analysed the frequency spectrum by drawing separate distribution curves for longitudinal optical (*l.o.*), longitudinal acoustic (*l.a.*), transverse optical (*t.o.*), and transverse acoustic (*t.a.*) waves respectively (although a strict classification into longitudinal and transverse waves is not always possible).

The corresponding graph is given in figure 10. The different maxima in the distribution curve (figure 9) correspond to these four kinds of vibrations; the maxima due to the longitudinal acoustic and the transverse optical frequencies coincide and give rise to the large maximum in figure 9 near the frequency of the residual rays.
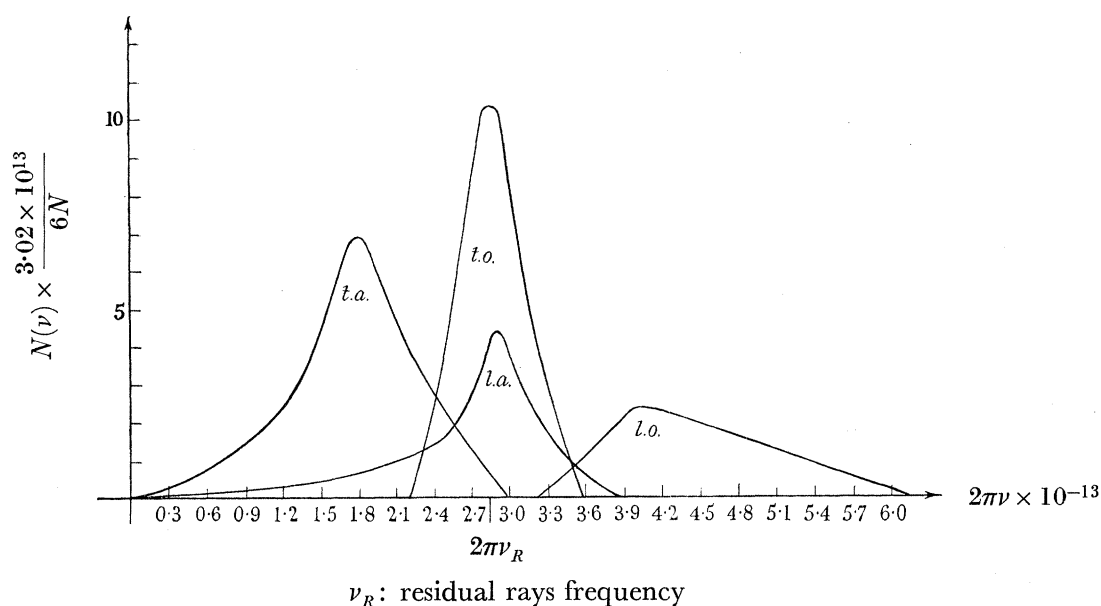

ν_R: residual rays frequency

FIGURE 10. Frequency distribution $N(\nu)$, analysed.

A more careful consideration of the frequency spectrum will be made in connexion with its application to the problem of the specific heat, which will follow shortly.*

I am very much indebted to Professor M. Born, who suggested this problem to me, for his advice on many occasions.

I am also very grateful to Dr K. Fuchs for many suggestions.

The numerical results were obtained with the help of a Muldivo calculating machine. I wish to thank Professor W. Oliver who kindly allowed me the use of the machine.

* *Note added in proof.* A slight numerical error has occurred in the computation of the figures 9 and 10. This, however, does not alter the result appreciably. The correct curves will be published in the paper on the specific heat.

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SUMMARY

According to Born's treatment of polar crystals, the frequency equation for a vibrating crystal contains in its coefficients lattice sums which are due to long range Coulomb forces. Using a method developed by Ewald it has been possible to find a quickly convergent form of those sums. The general formulae for the coefficients have been developed and a special application has been made to the case of sodium chloride. The coefficients and also the frequencies themselves have been calculated for 48 different states of vibration of the crystal which are chosen in such a way as to make possible a fair survey over the whole frequency spectrum of the crystal. It appears that the purely electrostatic derivation of the general formulae for the coefficients does not give information about the case of the residual rays. This can only be obtained by taking account of the electrodynamic boundary conditions, namely that the crystal as a whole must not emit radiation, which leads to the correct solution for the frequency of the residual rays. The formulae for the coefficients have also been used for the calculation of the elastic constants of sodium chloride.

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