

The interest in the frequency spectrum of the thermal  
vibrations: **Theory of the Vibrations of Sodium Chloride** with the  
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pushed into the background. But recent investigations,  
especially those of Max Born (1912, 1913, 1917) have shown  
that appreciable deviations from Debye's theory should occur  
according to **Ernst Walter Kellermann**. These deviations  
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A thesis in support of an application for the degree of  
D.Sc. in the University of Edinburgh.

1939.



## INTRODUCTION.

The interest in the frequency spectrum of the thermal vibrations in a crystal arose chiefly in connection 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.Karman (1912) has been pushed into the background. But recent investigations, especially those of Blackman (1938, 1935, 1937) 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.Karman in their original paper. They assumed only quasi-elastic forces between neighbouring particles. Later calculations have been made for ionic lattices, assuming <sup>the</sup> real forces in the crystal. 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) suggested a way of transforming these sums into more rapidly convergent expressions using a method /

method developed by Ewald (1921), 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 an one dimensional lattice making use of Epstein's Zeta functions. Herzfeld and Lyddane (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 Herzfeld and Lyddane. This applies especially to the case of the residual rays and the question whether the potential, from which the coupling coefficients are obtained, satisfies the Laplace equation or Poisson's equation.

In this paper we have used Ewald's method mentioned above, but interpreted and extended 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 /

it has not been too laborious to compute numerical values for 48 different modes of vibration.

In Sections II, III we give the derivation of these expressions by treating the problem as an electrostatic problem, neglecting the retardation; but the proper way of solving our problem is, to find a solution of Maxwell's equation for the electromagnetic field in the crystal. This will be done in Section IV. From this field the force exerted on a particle and the coupling coefficients can be obtained (Section V). We shall see 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 we define 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.

In Section VI the coupling coefficients for the Na Cl lattice are given and in Section VII the contribution due to the repulsive forces is calculated.

In Section VIII the equations for the coupling coefficients are checked by deriving from them formulæ for the elastic constants.

Finally /

Finally, in Section IX the coefficients have been calculated and in Section X the frequencies for 17 modes of vibrations, and the spectrum has been discussed.

The lattice is given by the lattice vectors  $\underline{a}_1, \underline{a}_2, \underline{a}_3$  which determine the cell of volume  $V_0$ . The cell contains  $Z$  particles, their position being given by the basis vectors  $\underline{u}_k = (u_{k1}, u_{k2}, u_{k3})$ . The equilibrium position of a particle  $(n, \underline{l})$  is given by the vector

$$(2.0) \quad \underline{r}_n^{\underline{l}} = \underline{a}^{\underline{l}} + \underline{u}_n, \quad \underline{a}^{\underline{l}} = l_1 \underline{a}_1 + l_2 \underline{a}_2 + l_3 \underline{a}_3$$

where  $\underline{l}$  stands for the three arbitrary integers  $l_1, l_2, l_3$ .

The distance vector between two lattice points  $(n, \underline{l}), (n', \underline{l}')$  is:

$$(2.1) \quad \underline{r}_{nn'}^{\underline{l}\underline{l}'} = \underline{r}_n^{\underline{l}} - \underline{r}_{n'}^{\underline{l}'} = \underline{a}^{\underline{l}} - \underline{a}^{\underline{l}'} + \underline{u}_n - \underline{u}_{n'}$$

These vectors depend only on the difference  $\underline{l} - \underline{l}'$  and can therefore be written  $\underline{r}_{nn'}^{\underline{l}\underline{l}'}$ .

We consider small independent displacements  $\underline{u}_n^{\underline{l}}$  of each particle from its equilibrium position

$$(2.2) \quad \underline{u}_n^{\underline{l}} = (u_{n1}^{\underline{l}}, u_{n2}^{\underline{l}}, u_{n3}^{\underline{l}})$$

so that the vector between the displaced particles is given by

$$(2.3) \quad \underline{r}_{nn'}^{\underline{l}\underline{l}'} = \underline{r}_{nn'}^{\underline{l}\underline{l}'} + \underline{u}_n^{\underline{l}} - \underline{u}_{n'}^{\underline{l}'}$$

## I. The Lattice Potential and the Coupling Coefficients

We use the notation of Born's 'Atomtheorie des festen Zustands' (1923) and repeat here some of its main points.

The lattice is given by the lattice vectors  $\underline{a}_1, \underline{a}_2, \underline{a}_3$  which determine the cell of volume  $\nu_0$ . The cell contains  $s$  particles, their position being given by the basis vectors  $\underline{r}_k$  ( $k = 1, \dots, s$ ). The equilibrium position of a particle  $(\kappa, \ell)$  is given by the vector

$$(1.0) \quad \underline{r}_{\kappa}^{\ell} = \underline{a}^{\ell} + \underline{r}_{\kappa}, \quad \underline{a}^{\ell} = \ell_1 \underline{a}_1 + \ell_2 \underline{a}_2 + \ell_3 \underline{a}_3$$

where  $\ell$  stands for the three arbitrary integers  $\ell_1, \ell_2, \ell_3$

The distance vector between two lattice points  $(\kappa, \ell), (\kappa', \ell')$  is:

$$(1.1) \quad \underline{r}_{\kappa\kappa'}^{\ell\ell'} = \underline{r}_{\kappa}^{\ell} - \underline{r}_{\kappa'}^{\ell'} = \underline{a}^{\ell} - \underline{a}^{\ell'} + \underline{r}_{\kappa} - \underline{r}_{\kappa'}$$

These vectors depend only on the difference  $\ell - \ell'$  and can therefore be written  $\underline{r}_{\kappa\kappa'}^{\ell-\ell'}$ .

We consider small independent displacements  $\underline{u}_{\kappa}^{\ell}$  of each particle from its equilibrium position

$$(1.2) \quad \underline{u}_{\kappa}^{\ell} = (u_{\kappa x}^{\ell}, u_{\kappa y}^{\ell}, u_{\kappa z}^{\ell})$$

so that the vector between the displaced particles is given by

$$(1.3) \quad \underline{r}_{\kappa\kappa'}^{\ell\ell'} = \underline{r}_{\kappa\kappa'}^{\ell-\ell'} + \underline{u}_{\kappa}^{\ell} - \underline{u}_{\kappa'}^{\ell'}$$

We /

We consider only central forces. The potential  $\phi_{\kappa\kappa'}(|r|)$  between a particle of kind  $\kappa$  and a particle of kind  $\kappa'$  is only a function of the distance  $|r|$  between them. The total potential energy of the lattice is

$$(1.4) \quad \Phi = \frac{1}{2} \sum_{\kappa\kappa'} \sum_{\ell\ell'} \phi_{\kappa\kappa'}(|r_{\kappa\kappa'}^{\ell\ell'}|)$$

Here the dash indicates that the terms  $\ell=\ell', \kappa=\kappa'$  should be omitted.

This sum, of course, diverges for an infinite lattice. For a finite piece of the crystal the surface layers play a different part from the interior, but these surface effects are energetically small compared with the contribution of the volume and can be neglected except where they are a subject of special study. Then the energy density

$$(1.5) \quad u = \frac{1}{Nv_a} \Phi \quad (N = \text{number of cells})$$

remains finite.

We expand the energy in the neighbourhood of the equilibrium position in powers of the displacements  $u_{\kappa}$  and obtain (neglecting surface effects)

$$(1.6) \quad \Phi = \Phi_0 + \Phi_1 + \Phi_2 + \dots$$

where

$$(1.7) \quad /$$

$$\begin{aligned}
 \Phi_0 &= \frac{1}{2} \sum_{\kappa\kappa'} \sum_{\ell\ell'} \Phi_{\kappa\kappa'}^{\ell-\ell'} = \frac{1}{2} N \sum_{\kappa\kappa'} \sum_{\ell} \Phi_{\kappa\kappa'}^{\ell} \\
 \Phi_1 &= \frac{1}{2} \sum_{\kappa\kappa'} \sum_{\ell\ell'} \sum_x [(\Phi_{\kappa\kappa'}^{\ell-\ell'})_x (u_{\kappa x}^{\ell} - u_{\kappa' x}^{\ell'})] \\
 (1.7) \quad &= \sum_{\kappa} \sum_{\ell'} \sum_x [\sum_{\kappa'} \sum_{\ell'} (\Phi_{\kappa\kappa'}^{\ell-\ell'})_x] u_{\kappa x}^{\ell} \\
 \Phi_2 &= \frac{1}{4} \sum_{\kappa\kappa'} \sum_{\ell\ell'} \sum_{xy} (\Phi_{\kappa\kappa'}^{\ell-\ell'})_{xy} (u_{\kappa x}^{\ell} - u_{\kappa' x}^{\ell'}) (u_{\kappa y}^{\ell} - u_{\kappa' y}^{\ell'}) .
 \end{aligned}$$

Here we have used the fact that the potential energy and its derivatives in equilibrium depend only on the difference  $\ell - \ell'$  so that one can introduce the notation

$$\begin{aligned}
 \Phi_{\kappa\kappa'}^{\ell} &= \Phi_{\kappa\kappa'} (|\dot{\gamma}_{\kappa\kappa'}^{\ell}|) \\
 (1.8) \quad (\Phi_{\kappa\kappa'}^{\ell})_x &= \left[ \frac{\partial}{\partial x} \Phi_{\kappa\kappa'}(\gamma) \right]_{\gamma = \dot{\gamma}_{\kappa\kappa'}^{\ell}} \\
 (\Phi_{\kappa\kappa'}^{\ell})_{xy} &= \left[ \frac{\partial^2}{\partial x \partial y} \Phi_{\kappa\kappa'}(\gamma) \right]_{\gamma = \dot{\gamma}_{\kappa\kappa'}^{\ell}}
 \end{aligned}$$

The transformation performed in (1.7) uses the fact that

$$(1.9) \quad (\Phi_{\kappa\kappa'}^{\ell})_x = - (\Phi_{\kappa'\kappa}^{-\ell})_x$$

and

$$(1.10) \quad (\Phi_{\kappa\kappa'}^{\ell})_{xy} = (\Phi_{\kappa'\kappa}^{-\ell})_{xy}$$

One can now simplify the expression of  $\Phi_2$  (1.7) by defining the originally undefined quantities  $(\Phi_{\kappa\kappa}^{\ell})_{xy}$  by the equation

$$(1.11) \quad \sum_{\kappa'} \sum_{\ell} (\Phi_{\kappa\kappa'}^{\ell})_{xy} = 0$$

and /



and obtains

$$(1.12) \quad \Phi_2 = -\frac{1}{2} \sum_{\kappa\kappa'} \sum_{\ell\ell'} \sum_{xy} (\Phi_{\kappa\kappa'})_{xy}^{(\ell-\ell')} u_{\kappa x}^{\ell} u_{\kappa' y}^{\ell'}$$

Now in the equilibrium  $\Phi_1$  vanishes, or with (1.7)

$$(1.13) \quad \sum_{\kappa'} \sum_{\ell'} (\Phi_{\kappa\kappa'})_x^{(\ell-\ell')} = 0 \quad (\kappa = 1, 2, \dots, s)$$

The second order terms lead to the equation of motion

$$(1.14) \quad m_{\kappa} \ddot{u}_{\kappa x}^{\ell} + \frac{\partial \Phi_2}{\partial u_{\kappa x}^{\ell}} = m_{\kappa} \ddot{u}_{\kappa x}^{\ell} - \sum_{\kappa'} \sum_{\ell'} \sum_{y} (\Phi_{\kappa\kappa'})_{xy}^{(\ell-\ell')} u_{\kappa' y}^{\ell'} = 0$$

Here the dot denotes differentiation with regard to time and  $m_{\kappa}$  is the mass of the particles of type  $\kappa$ .

Consider now one of the independent normal modes of vibration with frequency  $\omega$  and wave vector  $\underline{k}$ , where  $k = \frac{1}{\lambda}$ . The displacements of the particles are then given by

$$(1.15) \quad u_{\kappa}^{\ell} = \underline{u}_{\kappa} e^{-i\omega t + 2\pi i (\underline{k}, \underline{r}_{\kappa}^{\ell})}$$

Inserting this value into (1.14) we find

$$(1.16) \quad \omega^2 m_{\kappa} u_{\kappa x} e^{2\pi i (\underline{k}, \underline{r}_{\kappa}^{\ell})} + \sum_{\kappa'} \sum_{\ell'} \sum_{y} (\Phi_{\kappa\kappa'})_{xy}^{(\ell-\ell')} u_{\kappa' y} e^{2\pi i (\underline{k}, \underline{r}_{\kappa'}^{\ell'})} = 0$$

or multiplying by  $e^{-2\pi i (\underline{k}, \underline{r}_{\kappa}^{\ell})}$

$$(1.17) \quad \omega^2 m_{\kappa} u_{\kappa x} + \sum_{\kappa'} \sum_{y} [\Phi_{\kappa\kappa'}]_{xy} u_{\kappa' y} = 0$$

where

$$(1.18) \quad /$$

$$(1.18) \quad [\kappa \kappa']_{xy} = \sum_{\ell} (\phi_{\kappa \kappa'}^{\ell})_{xy} e^{2\pi i (\underline{k}, \underline{r}_{\kappa'}^{\ell} - \underline{r}_{\kappa}^{\ell})}$$

is independent of  $\ell$  Therefore with (1.9):

$$(1.19) \quad [\kappa \kappa']_{xy} = \sum_{\ell} (\phi_{\kappa \kappa'}^{\ell})_{xy} e^{2\pi i (\underline{k}, \underline{r}_{\kappa'}^{\ell})}$$

and from (1.11) follows the relation

$$(1.20) \quad \sum_{\kappa'} [\kappa \kappa']_{xy} \kappa = 0$$

If the potential energy consists of different parts, for instance one corresponding to the Coulomb force (index  $C$ ) and one corresponding to repulsive forces (index  $R$ ), the coefficients of the equation of motion are the sum of the corresponding contributions, i.e.

$$(1.21) \quad [\kappa \kappa']_{xy} = {}^C [\kappa \kappa']_{xy} + {}^R [\kappa \kappa']_{xy}$$

The equations (1.17) hold for an infinite lattice as the coefficients (1.18) converge if the force decreases rapidly enough. The choice of the wave vectors  $\underline{k}$  is restricted by the bounding conditions of the surface. Since for a large crystal the bounding conditions do not affect the frequencies (cf. Born, 1923, P.592) we use the arbitrary bounding condition of the 'cyclical lattice', by postulating that the displacements be periodic in a volume having the same shape as the elementary cell and containing  $n^3 N$  cells. This leads to the /

the conditions

$$(1.22) \quad n(\underline{k}, \underline{a}_1) = \rho_1; \quad n(\underline{k}, \underline{a}_2) = \rho_2; \quad n(\underline{k}, \underline{a}_3) = \rho_3 \quad (\rho_i \text{ integers})$$

They are satisfied if

$$(1.23) \quad \underline{k} = k_1 \underline{b}_1 + k_2 \underline{b}_2 + k_3 \underline{b}_3$$

where the  $\underline{b}_i$  are the reciprocal lattice vectors defined by

$$(1.24) \quad (\underline{a}_i, \underline{b}_j) = \delta_{ij}$$

and

$$(1.25) \quad k_1 = \frac{\rho_1}{n}; \quad k_2 = \frac{\rho_2}{n}; \quad k_3 = \frac{\rho_3}{n} \quad (\rho_1, \rho_2, \rho_3 = 0, 1, 2, \dots, n-1)$$

## II. The Coupling Coefficients for Coulomb Interaction.

We consider an ionic lattice, as for example the Na Cl lattice. Then the main contribution to the interaction is due to the Coulomb forces of the ions, the potential of which we write

$$(2.0) \quad \varphi_{k'k}(|r|) = e_{k'} e_k f(r) \quad ; \quad f(r) = \frac{1}{|r|}$$

Here  $e_k$  is the charge of the  $k^{\text{th}}$  type of ion at the lattice points  $\mathbf{r}_k^0$ .

In this section we shall assume that we are allowed to treat the problem of thermal oscillations as an electrostatic problem.

Using the notation

$$(2.1) \quad \frac{\partial^2 \varphi}{\partial x \partial y} = f_{xy}$$

the second derivation of the potential energy of a particle  $k$  in the zero cell due to a particle  $k'$  in the cell  $\ell$  is given by

$$(2.2) \quad (\varphi_{k'k})_{xy} = e_{k'} e_k f_{xy}(\mathbf{r}_{k'k}^{\ell})$$

and those due to a particle  $k$  in the cell  $\ell$

$$(2.3) \quad (\varphi_{kk})_{xy} = e_k^2 f_{xy}(a^{\ell})$$

Therefore the contribution of the Coulomb force to the coupling coefficients /

coefficients (1.19) is

$$(2.4) \quad C [{}_{xy}^{kk'}] = e_{k'} e_k \sum f_{xy}({}_{k'}^{\circ} \ell) e^{2\pi i(\underline{k}, \underline{y}_{k'}^{\circ})}, \quad k \neq k' \quad (a)$$

When we come to the coefficients  $[{}_{xy}^{kk}]$  it must be remembered that the zero term ( $\ell = 0, 0, 0$ ) in the sum is defined by (1.11); this term is not equal to  $e_k^2 f_{xy}(0)$  which is infinite. It will be denoted by  $(\varphi_{kk}^{\circ})_{xy}$ ; thus we get

$$(2.5) \quad [{}_{xy}^{kk}] = e_k^2 \lim_{r \rightarrow 0} \left[ \sum_{\ell} f_{xy}(1r - \underline{\alpha}^{\ell}) e^{2\pi i(\underline{k}, \underline{\alpha}^{\ell})} - f_{xy}(r) \right] + (\varphi_{kk}^{\circ})_{xy}$$

For a wave vector  $\underline{k} = 0$  the coupling coefficients (2.4) and (2.5) are

$$(2.6) \quad [{}_{xy}^{kk'}]_{k=0} = \sum_{\ell} (\varphi_{k'k}^{\ell})_{xy}$$

$$[{}_{xy}^{kk}]_{k=0} = \sum_{\ell} (\varphi_{kk}^{\ell})_{xy} = \sum'_{\ell} (\varphi_{kk}^{\ell})_{xy} + (\varphi_{kk}^{\circ})_{xy}$$

Therefore, the zero term  $(\varphi_{kk}^{\circ})_{xy}$  defined by (1.11) can be expressed by (cf. (1.20))

$$(2.7) \quad (\varphi_{kk}^{\circ})_{xy} = - \sum_{k' \neq k} [{}_{xy}^{kk'}]_{k=0} - [{}_{xy}^{kk}]'_{k=0}$$

$$[{}_{xy}^{kk}]'_{k=0} = \sum'_{\ell} (\varphi_{kk}^{\ell})_{xy}$$

This formula holds for any <sup>central</sup> force and any lattice. But for Coulomb forces and a lattice of cubical symmetry it can easily be /

(a) We shall drop the index  $C$  in the sections II, III, IV as in those sections no other coefficients are considered. Also, we shall drop the index  $\circ$  in  ${}_{k'}^{\circ} \ell$  since no mistake can occur.

be shown that the zero term vanishes, for it represents the force exerted on the particle  $(k, l)$  if it is displaced by a small amount, all other particles being kept at their equilibrium positions. This is evident from (1.14) if we put all  $\underline{u}_{k'}^{l'} = 0$  except  $\underline{u}_k^l$ . This force is then derived from the electrostatic potential due to all other charges and satisfies Laplace's equation

$$\Delta \varphi = \frac{d^2 \varphi}{dx^2} + \frac{d^2 \varphi}{dy^2} + \frac{d^2 \varphi}{dz^2} = 0$$

Furthermore, it possesses cubical symmetry with the position  $\underline{y}_k^l$  of the particle  $(k, l)$  as centre of symmetry. Therefore

$$\frac{d^2 \varphi}{dx^2} = \frac{d^2 \varphi}{dy^2} = \frac{d^2 \varphi}{dz^2} = 0 \quad \text{for } \underline{y} = \underline{y}_k^l$$

Further, we conclude from the cubical symmetry that at the centre of symmetry  $\frac{d^2 \varphi}{dx dy} = - \frac{d^2 \varphi}{dx dy}$  and therefore

$$\frac{d^2 \varphi}{dx dy} = \frac{d^2 \varphi}{dy dz} = \frac{d^2 \varphi}{dz dx} = 0 \quad \text{for } \underline{y} = \underline{y}_k^l$$

Thus there is no Coulomb force for small displacements and  $(\varphi_{kk}^0)_{xy}$  vanishes, i.e.  $[\begin{smallmatrix} kk \\ xy \end{smallmatrix}]' = [\begin{smallmatrix} kk \\ xy \end{smallmatrix}]$

We now introduce the function

$$(2.8) \quad \int f(|\underline{r} - \underline{a}^l|) e^{2\pi i(\underline{k}, \underline{a}^l)} = F^k(\underline{r}) = F^k(x, y, z)$$

and in the same way a function

$$(2.9) \quad /$$

$$(2.9) \quad \int_{\underline{z}} f_{xy} (y - \underline{a}^{\ell}) e^{2\pi i (\underline{k}, \underline{a}^{\ell})} = F_{xy}^k(\underline{y}) = F_{xy}^k(x, y, z)$$

We shall express the coefficients (2.4) and (2.5) by means of these functions and then show that it is possible to find a very rapidly convergent representation of the sums (2.8) and (2.9).

If that is possible, it is permissible to exchange summation and differentiation in (2.9) so that

$$(2.10) \quad F_{xy}^k = \frac{\partial^2}{\partial x \partial y} F^k$$

Furthermore, since  $|\underline{y}_{kk'} - \underline{a}^{\ell}| = |\underline{y}_{k'k}|$  cf. (1.0), (1.1) and  $f(\underline{y}) = \frac{1}{|\underline{y}|}$  (2.0), we can write (2.4) using (2.9) (a)

$$(2.11) \quad \begin{aligned} [{}_{xy}^{kk'}] &= e_{k'k} e_k \int_{\underline{z}} f_{xy} (|\underline{y}_{k'k} + \underline{a}^{\ell}|) e^{2\pi i (\underline{k}, \underline{y}_{k'k} + \underline{a}^{\ell})} \\ &= e_k e_{k'} e^{-2\pi i (\underline{k}, \underline{y}_{kk'})} F_{xy}^k(\underline{y}_{kk'}) \quad , \quad \underline{y}_{kk'} = -\underline{y}_{k'k} \end{aligned}$$

(2.5) becomes

$$(2.11) \quad [{}_{xy}^{kk}] = e_k^2 \lim_{\underline{y} \rightarrow 0} [F_{xy}^k(\underline{y}) - f_{xy}(\underline{y})]$$

$F_{xy}^k(\underline{y})$  may, therefore, be considered as a kind of potential function from which the coupling coefficients are obtained.

(a) Thompson (1935) has not defined the coefficients  $[{}_{xy}^{kk'}]$  correctly. He leaves out the exponential function  $\exp\{-2\pi i (\underline{k}, \underline{y}_{kk'})\}$  c.f. (2.11).

### III. The Ewald-Transformation.

A method of transformation of lattice sums into quickly convergent expressions has been developed by Ewald (1921, 1938). In applying this method we shall use the notation of the reciprocal lattice.

This lattice is described by the lattice vectors  $\underline{b}_1, \underline{b}_2, \underline{b}_3$  so that any lattice point is given by

$$(3.0) \quad \underline{b}_h = h_1 \underline{b}_1 + h_2 \underline{b}_2 + h_3 \underline{b}_3 \quad (h_j \text{ integers})$$

Here the  $\underline{b}_j$  are defined by the equation (1.24) which has the solution

$$(3.1) \quad \underline{b}_1 = \frac{1}{v_a} [\underline{a}_2 \times \underline{a}_3] ; \quad \underline{b}_2 = \frac{1}{v_a} [\underline{a}_3 \times \underline{a}_1] ; \quad \underline{b}_3 = \frac{1}{v_a} [\underline{a}_1 \times \underline{a}_2]$$

Any arbitrary radius vector in the reciprocal lattice is given by

$$(3.2) \quad \underline{b}_\eta = \sum_j \eta_j \underline{b}_j$$

Where the  $\eta_j$  are not necessarily integers.

In general we understand by a lattice sum of a function

$\bar{f}(r)$  the expression:

$$(3.3) \quad \bar{F}(r) = \sum_{\underline{a}'} \bar{f}(r - \underline{a}')$$

This sum has obviously the periodicity of the lattice and we can develop it into a Fourier series

$$(3.4) \quad /$$



$$(3.4) \quad \int_{\underline{a}^{\ell}} \bar{f}(\underline{r} - \underline{a}^{\ell}) = \sum_{\underline{k}} \bar{F}_{\underline{k}} e^{2\pi i (\underline{k}, \underline{r})}$$

with the Fourier coefficients  $\bar{F}_{\underline{k}}$ .

If we have a sum

$$(3.5) \quad \bar{F}^{\underline{k}}(\underline{r}) = \sum_{\ell} \bar{f}(\underline{r} - \underline{a}^{\ell}) e^{2\pi i (\underline{k}, \underline{a}^{\ell})}$$

we can write this in the form

$$(3.6) \quad \bar{F}^{\underline{k}}(\underline{r}) = e^{2\pi i (\underline{k}, \underline{r})} \sum_{\ell} \bar{f}(\underline{r} - \underline{a}^{\ell}) e^{2\pi i (\underline{k}, \underline{a}^{\ell} - \underline{r})}$$

Therefore,  $\bar{F}^{\underline{k}}$  is a periodic function which is modulated by a wave  $e^{2\pi i (\underline{k}, \underline{r})}$ . We can then write the sum as a Fourier series (cf. Ewald, 1938)

$$(3.7) \quad \sum_{\ell} \bar{f}(\underline{r} - \underline{a}^{\ell}) e^{2\pi i (\underline{k}, \underline{a}^{\ell} - \underline{r})} = \sum_{\underline{k}'} \bar{F}_{\underline{k}'} e^{2\pi i (\underline{k}', \underline{r})}$$

The Fourier coefficients  $\bar{F}_{\underline{k}'}^{\underline{k}}$  are given by

$$(3.8) \quad \bar{F}_{\underline{k}'}^{\underline{k}} = \frac{1}{v_a} \int_{\square} \sum_{\ell} \bar{f}(\underline{r} - \underline{a}^{\ell}) e^{2\pi i (\underline{k}', \underline{a}^{\ell} - \underline{r}) - 2\pi i (\underline{k}, \underline{a}^{\ell})} d\underline{v}$$

$$d\underline{v} = dx_1 dx_2 dx_3$$

where the integration extends over one cell. The lattice sum over all these integrals is, of course, identical with the integral over the whole of space; observing that  $(\underline{k}' - \underline{k}, \underline{a}^{\ell})$  is always an integer, we obtain for (3.8)

$$(3.9) \quad \bar{F}_{\underline{k}'}^{\underline{k}} = \frac{1}{v_a} \int \bar{f}(\underline{r}) e^{-2\pi i (\underline{k}' - \underline{k}, \underline{r})} d\underline{v}$$

where the integration now extends over the whole of space.

If /

If now we represent  $\bar{f}(\underline{r})$  by a Fourier integral

$$(3.10) \quad \bar{f}(\underline{r}) = \int \bar{\varphi}(\underline{b}) e^{2\pi i(\underline{b}, \underline{r})} d\nu_{\underline{b}}, \quad d\nu_{\underline{b}} = db_x db_y db_z$$

then

$$(3.11) \quad \bar{\varphi}(\underline{b}) = \int \bar{f}(\underline{r}) e^{-2\pi i(\underline{b}, \underline{r})} d\nu$$

Comparing this expression with (3.9) we see that the Fourier coefficients  $\bar{F}_k^h$  can be expressed in terms of the Fourier transformed  $\bar{\varphi}(\underline{b})$  of  $\bar{f}(\underline{r})$ :

$$(3.12) \quad \bar{F}_k^h = \frac{1}{v_a} \bar{\varphi}(\underline{b}_k + \underline{k})$$

Substituting this value for  $\bar{F}_k^h$  in (3.7) we obtain the following Fourier development for the lattice sum (3.5)

$$(3.13) \quad \bar{F}^h(\underline{r}) = \sum_{\underline{k}} \bar{f}(\underline{r} - \underline{a}^k) e^{2\pi i(\underline{k}, \underline{a}^k)} = \frac{1}{v_a} \sum_{\underline{k}} \bar{\varphi}(\underline{b}_k + \underline{k}) e^{2\pi i(\underline{b}_k + \underline{k}, \underline{r})}$$

Following Ewald's method, we apply this result to the function

$$(3.14) \quad \bar{f}(\underline{r}) = \frac{2}{\sqrt{\pi}} e^{-\varepsilon^2 \underline{r}^2}$$

where  $\varepsilon$  is a parameter. The importance of this function is that the integration over the parameter  $\varepsilon$  gives us exactly the potential function  $f(\underline{r}) = \frac{1}{|\underline{r}|}$

$$(3.15) \quad \int_0^{\infty} \bar{f}(\underline{r}) d\varepsilon = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-\varepsilon^2 \underline{r}^2} d\varepsilon = \frac{1}{\underline{r}} = f(\underline{r})$$

The Fourier transformed (3.11) of  $\bar{f}(\underline{r})$  is given by

$$(3.16) \quad /$$

$$\begin{aligned}
 (3.16) \quad \bar{\varphi}(\underline{b}) &= \frac{2}{\sqrt{\pi}} \int \varepsilon^{-\varepsilon^2 \underline{r}^2 - 2\pi i (\underline{b}, \underline{r})} d\underline{v} \\
 &= \frac{2}{\sqrt{\pi}} \varepsilon^{-\frac{\pi^2 \underline{b}^2}{\varepsilon^2}} \int \varepsilon^{-(\varepsilon \underline{r} + i\frac{\underline{b}}{\varepsilon})^2} d\underline{v} \\
 &= 2\pi \frac{\varepsilon^{-\frac{\pi^2 \underline{b}^2}{\varepsilon^2}}}{\varepsilon^3}
 \end{aligned}$$

Inserting  $\bar{f}(\underline{r}-\underline{a}^l)$  and  $\bar{\varphi}(\underline{b}_\lambda+\underline{k})$  from (3.14) and (3.16) respectively into (3.13) we obtain

$$\begin{aligned}
 (3.17) \quad \bar{F}^k(\underline{r}) &= \frac{2}{\sqrt{\pi}} \int \varepsilon^{-\varepsilon^2 (\underline{r}-\underline{a}^l)^2 + 2\pi i (\underline{k}, \underline{a}^l)} \\
 &= \frac{2\pi}{\varepsilon^3} \sum_{\underline{k}} \frac{1}{\varepsilon^3} \varepsilon^{-\frac{\pi^2}{\varepsilon^2} (\underline{b}_\lambda+\underline{k})^2 + 2\pi i (\underline{b}_\lambda+\underline{k}, \underline{r})}
 \end{aligned}$$

This formula is identical with that obtained by Ewald by means of the transformation of Theta functions (cf. Born, 1923, p.765).

If now we integrate  $\bar{F}^k(\underline{r})$  over the parameter  $\varepsilon$ , we obtain with (3.15) the potential function  $F^k(\underline{r})$  defined by (2.8).

$$(3.18) \quad \int_0^\infty \bar{F}^k(\underline{r}) d\varepsilon = F^k(\underline{r})$$

Now the sum in the first representation of  $\bar{F}^k$  in (3.17) converges rapidly for large values of  $\varepsilon$ , but not for small values. The sum in the second expression in (3.17) converges rapidly for small values of  $\varepsilon$ , but not for large ones.

Following Ewald, we divide the integration into two parts

$\int_0^\infty = \int_0^E + \int_E^\infty$  and take as integrand in the first integral the second representation of  $\bar{F}^k$  in (3.17) and in the second integral the first one. We obtain

$$(3.19) \quad /$$

$$(3.19) \quad F^k(\underline{y}) = \frac{2\pi}{v_a} \int_0^E \sum_k \frac{d\varepsilon}{\varepsilon^3} e^{-\frac{\pi^2}{E^2} (\underline{b}_k + \underline{k})^2 + 2\pi i (\underline{b}_k + \underline{k}, \underline{y})} + \frac{2}{\sqrt{\pi}} \int_E^\infty \sum_k e^{-\varepsilon^2 (\underline{y} - \underline{a}^k)^2 + 2\pi i (\underline{k}, \underline{a}^k)} d\varepsilon$$

The first term in (3.19) can be integrated directly, the second term may be expressed by means of the Gauss function

$$(3.20) \quad G(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-\xi^2} d\xi, \quad G(\infty) = 1$$

Then

$$(3.21) \quad \frac{2}{\sqrt{\pi}} \int_E^\infty d\varepsilon e^{-\varepsilon^2 (\underline{y} - \underline{a}^k)^2} = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{d\beta}{|\underline{y} - \underline{a}^k|} e^{-\beta^2} - \frac{2}{\sqrt{\pi}} \int_0^{\varepsilon |\underline{y} - \underline{a}^k|} \frac{d\beta}{|\underline{y} - \underline{a}^k|} e^{-\beta^2} = \frac{1 - G(\varepsilon |\underline{y} - \underline{a}^k|)}{|\underline{y} - \underline{a}^k|} \quad (\beta = \varepsilon |\underline{y} - \underline{a}^k|)$$

Thus we finally obtain  $F^k(\underline{y})$

$$(3.22) \quad F^k(\underline{y}) = \frac{1}{\pi v_a} \sum_k \frac{1}{(\underline{b}_k + \underline{k})^2} e^{-\frac{\pi^2}{E^2} (\underline{b}_k + \underline{k})^2 + 2\pi i (\underline{b}_k + \underline{k}, \underline{y})} + \sum_k \frac{1 - G(\varepsilon |\underline{y} - \underline{a}^k|)}{|\underline{y} - \underline{a}^k|} e^{2\pi i (\underline{k}, \underline{a}^k)}$$

We can choose  $\varepsilon$  in such a way that the two series in (3.22) converge rapidly, so that the interchange of differentiation and summation in (2.9), (2.10) is justified.

Inserting this representation of  $F^k(\underline{y})$  in (2.11) and (2.12) the coupling coefficients are obtained in a rapidly convergent form.

For  $\kappa' \neq \kappa$  we find

$$(3.23) \quad [{}_{xy}^{\kappa\kappa'}] = \varepsilon_\kappa \varepsilon_{\kappa'} \left\{ -\frac{4\pi}{v_a} \sum_k \frac{(\underline{b}_{\kappa x} + \underline{b}_{\kappa'}) (\underline{b}_{\kappa y} + \underline{b}_{\kappa'})}{(\underline{b}_k + \underline{k})^2} e^{-\frac{\pi^2}{E^2} (\underline{b}_k + \underline{k})^2 - 2\pi i (\underline{b}_k + \underline{k}, \underline{y}_{\kappa\kappa'})} + E^2 \sum_k \left[ \Psi'(E |\underline{y}_{\kappa\kappa'}^k|) \frac{\delta_{xy}}{|\underline{y}_{\kappa\kappa'}^k|} + (E \Psi''(E |\underline{y}_{\kappa\kappa'}^k|) - \Psi'(E |\underline{y}_{\kappa\kappa'}^k|)) \frac{1}{|\underline{y}_{\kappa\kappa'}^k|} \right] e^{2\pi i (\underline{k}, \underline{y}_{\kappa\kappa'}^k)} \right\}$$

where /

where

$$(3.24) \quad \frac{1-G(x)}{x} = \Psi(x), \quad \Psi'(x) = \frac{\partial \Psi}{\partial x}, \quad \Psi''(x) = \frac{\partial^2 \Psi}{\partial x^2}$$

For  $k \neq k$  we use for  $\bar{f}(\underline{r})$  in (2.12) the integral representation (3.14) and split it also into two integrals with the dividing point  $E$ . We obtain easily

$$(3.25) \quad \begin{aligned} [\kappa \kappa]_{xy} &= \ell_k^2 \lim_{\gamma \rightarrow 0} \frac{\partial^2}{\partial x \partial y} \{ F^k(\underline{r}) - f(\underline{r}) \} \\ &= \ell_k^2 \lim_{\gamma \rightarrow 0} \frac{\partial^2}{\partial x \partial y} \left\{ \frac{1}{\pi \nu a} \sum_{\underline{k}} \frac{1}{(\underline{b}_k + \underline{k})^2} e^{-\frac{\pi^2}{E^2} (\underline{b}_k + \underline{k})^2 + 2\pi i (\underline{b}_k + \underline{k}, \underline{r})} \right. \\ &\quad \left. + \sum \frac{1-G(E|\underline{r}-\underline{a}^i)}{|\underline{r}-\underline{a}^i|} e^{2\pi i (\underline{k}, \underline{a}^i)} - \left( \frac{G(E|\underline{r})}{|\underline{r}|} + \frac{1-G(E|\underline{r})}{|\underline{r}|} \right) \right\} \end{aligned}$$

The last term ~~cancel~~ cancels the zero term of the second sum. We shall indicate its subtraction by an accent on the summation sign.

Developing the integrand of  $G(E|\underline{r})$  into a power series in  $\underline{r}$ , we find easily that

$$(3.26) \quad \lim_{\gamma \rightarrow 0} \frac{\partial^2}{\partial x \partial y} \left( \frac{G(E\underline{r})}{\underline{r}} \right) = -\frac{4}{3\sqrt{\pi}} E^3 \delta_{xy}$$

So we obtain

$$(3.27) \quad \begin{aligned} [\kappa \kappa]_{xy} &= \ell_k^2 \left\{ -\frac{4\pi}{\nu a} \sum_{\underline{k}} \frac{(\underline{b}_{kx} + k_x)(\underline{b}_{ky} + k_y)}{(\underline{b}_k + \underline{k})^2} e^{-\frac{\pi^2}{E^2} (\underline{b}_k + \underline{k})^2} \right. \\ &\quad \left. + E^2 \sum_{\underline{k}} \left[ \Psi'(E|\underline{a}^i) \frac{\delta_{xy}}{|\underline{a}^i|} + \left( E \Psi''(E|\underline{a}^i) - \Psi'(E|\underline{a}^i) \frac{a_x^i a_y^i}{|\underline{a}^i|^2} \right) e^{2\pi i (\underline{k}, \underline{a}^i)} \right] \right. \\ &\quad \left. + \frac{4}{3\sqrt{\pi}} E^3 \delta_{xy} \right\} \end{aligned}$$

For a wave vector  $\underline{k} = (0, 0, 0)$  we observe that there is a divergence in the potential function  $F^k(\underline{r})$  (3.22) for  $\underline{b}_k = (0, 0, 0)$ . We shall see in section IV that this divergence /

divergence is due to the electrostatic derivation of the coupling coefficients; it disappears in the correct electrodynamic treatment, to which we shall turn in the next two sections.

#### IV. The Electromagnetic Field.

In the introduction we pointed out that the electrostatic derivation of the coupling coefficients needs justification, because the vibrations of ions is in general accompanied by an electromagnetic field. We must, therefore, start from Maxwell's equations and find the proper solution of these equations for our problem. This has been done by Born (1923, p.760; see also Born and Goeppert-Mayer, 1933, P.770). He has calculated the electromagnetic field of the crystal by a superposition of spherical waves arising from the vibrating point charges. (This corresponds to the introduction of the 'optical' potentials instead of the electrostatic potentials (cf. Ewald, 1921). We 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.

We shall see that the coupling coefficients will again be expressible as the second derivatives of a potential function, to which we can apply the same transformation used in the preceding section. As a matter of fact, we shall find that in general the potentials are the same so that we can use the results of the preceding section without modification. Only in the case of infinitely long waves a slight modification will be necessary; this can be applied immediately by comparing the /

the electromagnetic formula with the representation (3.23), (3.27) of the electrostatic values with  $\underline{\epsilon} = \infty$ . We shall see that this modification will remove the divergent term in the potential function (3.22).

The case of infinitely long waves ( $\underline{k} = (0, 0, 0)$ ) has already been treated by Born (1923, p.728,773). It leads to the frequency of the residual rays.

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. Starting from a finite crystal with  $n^3 = N$  cells and a finite wave length, one has to do with a double limit:  $N \rightarrow \infty$  and  $\lambda \rightarrow \infty$ . Now for finite wave lengths and a finite crystal we have in general

$$r_0 \leq \lambda \ll n r_0 \quad (r_0 \text{ lattice constant})$$

Here we must proceed clearly first to the limit  $N \rightarrow \infty$ . For infinite wave lengths on the other hand, we must first put  $\lambda = \infty$  and then proceed to the limit  $N \rightarrow \infty$ . If, however, we reverse the order of the limit we obtain obviously those very long waves which are of the order of the dimensions of the whole crystal, but not the infinite waves proper.

We shall now proceed to the calculation of the electromagnetic field. This field can be represented by the field of /



of vibrating dipoles plus an electrostatic field. We assume a fixed charge  $-\epsilon_{\kappa}$  at the lattice points and a charge  $+\epsilon_{\kappa}$  displaced by an amount  $\underline{u}_{\kappa}^{\ell}$  given by (1.15)

$$\underline{u}_{\kappa}^{\ell} = \underline{u}_{\kappa} e^{-i\omega t} e^{2\pi i(\underline{k}, \underline{r}_{\kappa}^{\ell})}$$

The dipole has, therefore, the moment  $\epsilon_{\kappa} \underline{u}_{\kappa}^{\ell}$ . However, we have to compensate the charge  $-\epsilon_{\kappa}$  by another fixed charge  $+\epsilon_{\kappa}$  at the lattice points  $\underline{r}_{\kappa}^{\ell}$ . These fixed charges give rise to an electrostatic potential which is identical with the electrostatic potential of the lattice at rest. In Section II we have seen that for lattices of cubical symmetry and for small displacements this potential does not give rise to a force. For lattices of other types this electrostatic potential supplies the zero term  $(\varphi_{\kappa\kappa}^0)_{\underline{x}\underline{y}}$  (cf. (2.7)) as is obvious from the discussion of this term in Section II. Restricting the calculation to cubical lattices we may disregard this term.

The electromagnetic field can be described by the Hertz vector

$$(4.0) \quad \underline{Z} = \underline{\int} e^{-i\omega t} e^{2\pi i(\underline{k}, \underline{r})}$$

which is the sum of Hertz's solutions for the various vibrating dipoles. The vector  $\underline{\int}$  is a function of space. It has been determined by Born (1923, P.761); he finds

$$(4.1) \quad \underline{\int} = \sum_{\kappa} \rho_{\kappa} \underline{S}(\underline{r} - \underline{r}_{\kappa}) \quad , \quad \rho_{\kappa} = \epsilon_{\kappa} \underline{u}_{\kappa}$$

where /

where  $\mathcal{S}$  is the Fourier series

$$(4.2) \quad \mathcal{S} = \frac{1}{\pi v_a} \sum_k \frac{e^{2\pi i (\underline{b}_k, \underline{r})}}{(\underline{b}_k + \underline{k})^2 - k_0^2}$$

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

$\lambda_0$  is the wave length in vacuum corresponding to the frequency  $\omega_0$ .

We separate the zero term of the series (4.2) which represents the mean value of the electromagnetic field

$$(4.3) \quad \mathcal{S} = \bar{\mathcal{S}} + \tilde{\mathcal{S}}$$

$$\bar{\mathcal{S}} = \frac{1}{\pi v_a} \frac{1}{k^2 - k_0^2} = \frac{1}{\pi v_a} \frac{n^2/k^2}{n^2 - 1}$$

$$\tilde{\mathcal{S}} = \frac{1}{\pi v_a} \sum_k' \frac{e^{2\pi i (\underline{b}_k, \underline{r})}}{(\underline{b}_k + \underline{k})^2 - k_0^2}$$

where we have introduced the refractive index  $n = \frac{k}{k_0} = \frac{1}{\lambda}$

The Hertz vector corresponding to the mean electromagnetic field is, according to (4.1), (4.0) given by

$$(4.4) \quad \underline{\bar{Z}} = \frac{1}{\pi} \underline{P} \frac{n^2/k^2}{n^2 - 1}$$

where

$$(4.5) \quad \underline{P} = \underline{P}_0 e^{-i\omega t} e^{2\pi i (\underline{k}, \underline{r})}$$

$$\underline{P}_0 = \frac{1}{v_a} \sum_k \underline{P}_k$$

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

From the Hertz vector (4.4) we obtain the mean electromagnetic field vectors

$$(4.6) \quad /$$

$$\begin{aligned}
 \underline{\bar{E}} &= \text{grad div } \underline{\bar{Z}} - \frac{1}{c^2} \frac{\partial^2 \underline{\bar{Z}}}{\partial t^2} = 4\pi \frac{1}{n^2-1} \{ \underline{\rho} - n^2 \underline{s} (\underline{\rho}, \underline{s}) \} \\
 (4.6) \quad \underline{\bar{H}} &= \frac{1}{c} \text{curl } \frac{\partial \underline{\bar{Z}}}{\partial t} = 4\pi \frac{n}{n^2-1} (\underline{s} \times \underline{\rho}) \\
 \underline{k} &= |k| \underline{s}
 \end{aligned}$$

Here  $\underline{s}$  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  $\underline{B} = \underline{H}$  and splitting up  $\underline{D}$  into  $\underline{E} + 4\pi \underline{\rho}$  as has been pointed out by Born (1933, p.776).

In order to discuss the formulae (4.6) we must consider the magnitude of  $n = \frac{k}{k_0} = \frac{\lambda_0}{\lambda}$ ; this will enable us to differentiate between the two distinct cases  $k=0$  and  $k \neq 0$ .

The frequency of the fastest vibrations occurring in crystals is of the order  $\sim 10^{13} \text{ sec}^{-1}$  and the corresponding smallest wave length  $\lambda_0 = \frac{1}{k_0} \sim 10^{-3} \text{ cm}$ . This is very large compared with the lattice distance ( $\sim 10^{-8} \text{ cm}$ ). For the thermal vibrations of the crystal one can consider the wave length  $\lambda$  as very small compared with the length  $\lambda_0$  of the light wave of the same frequency in vacuo. We can put therefore  $n \approx \infty$ . The only exception is  $k=0$ ; in this case  $n$  vanishes since  $\frac{1}{k_0} \neq 0$  (cf. 4.2;  $\omega_0 \neq 0$ )

Therefore, in the case  $k=0$  (4.6) becomes

$$(4.7) \quad \underline{\bar{E}} = -4\pi \underline{\rho}, \quad \underline{\bar{H}} = 0 \quad k=0, k_0 \text{ not neglected}$$

and /

and in the case  $k \neq 0$

$$(4.8) \quad \bar{\underline{E}} = -4\pi \underline{s} (\underline{D}, \underline{s}) , \quad \bar{\underline{H}} = 0 ; k \neq 0, k_0 \text{ neglected}$$

The solution (4.0) for the Hertz vector is not necessarily the correct solution of our problem. We have assumed that the motion of the dipoles is given by (1.15) without enquiring into the reaction forces, which are due to the emission of radiation. Only, if we can show that no radiation is emitted by the crystal, the solution (4.0), (4.1), (4.2) is correct. We can see, 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. It can be seen at once (cf. Born 1933, P.643) from the expression for the total moment itself

$$(4.9) \quad \sum_{\underline{\ell}} \sum_{\underline{k}} \underline{p}_{\underline{k}}^{\underline{\ell}} = \sum_{\underline{\ell}} \sum_{\underline{k}} \underline{e}_{\underline{k}} \underline{u}_{\underline{k}}^{\underline{\ell}} = e^{-i\omega t} \sum_{\underline{k}} \underline{e}_{\underline{k}} \underline{u}_{\underline{k}} e^{2\pi i(\underline{k}, \underline{r}_{\underline{k}})} \sum_{\underline{\ell}} e^{2\pi i(\underline{k}, \underline{r}_{\underline{\ell}})}$$

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

We 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  $\underline{b}_3$ , so that

$$(4.10) \quad \begin{array}{ll} (\underline{r}, \underline{b}_3) > 0 & \text{inside the crystal} \\ (\underline{r}, \underline{b}_3) < 0 & \text{outside the crystal} \end{array}$$

The /

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

$$(4.11) \quad \underline{Z}^{(in)} = \underline{Z}^{(0)} + \underline{Z}^{(1)}$$

$$\underline{Z}^{(out)} = \underline{Z}^{(2)}$$

where  $\underline{Z}^{(in)}$  and  $\underline{Z}^{(out)}$  are the Hertz vectors inside and outside the crystal. Here the vectors  $\underline{Z}^{(j)}$  ( $j = 0, 1, 2$ ) are determined with the help of equations (4.0), (4.1) by the functions  $S^{(j)}$  given by

$$(4.12) \quad S^{(0)} = \frac{1}{v_a} \sum_k \frac{e^{2\pi i (\underline{b}_k, \underline{r})}}{(\underline{b}_k + \underline{k})^2 - k_0^2}$$

$$S^{(1)} = \frac{2i}{v_a} \sum_{\substack{\underline{l}_1, \underline{l}_2 \\ -\infty \\ \infty}} e^{2\pi i [\underline{l}_1 (\underline{r}, \underline{b}_1) + \underline{l}_2 (\underline{r}, \underline{b}_2) + \eta_1 (\underline{r}, \underline{b}_3)]} \frac{b_3^2 (\eta_1 - \eta_2) (1 - e^{-2\pi i \eta_1})}{b_3^2 (\eta_1 - \eta_2) (1 - e^{-2\pi i \eta_1})}$$

$$S^{(2)} = \frac{2i}{v_a} \sum_{\substack{\underline{l}_1, \underline{l}_2 \\ -\infty \\ \infty}} e^{2\pi i [\underline{l}_1 (\underline{r}, \underline{b}_1) + \underline{l}_2 (\underline{r}, \underline{b}_2) + \eta_2 (\underline{r}, \underline{b}_3)]} \frac{b_3^2 (\eta_1 - \eta_2) (1 - e^{-2\pi i \eta_2})}{b_3^2 (\eta_1 - \eta_2) (1 - e^{-2\pi i \eta_2})}$$

In  $S^{(0)}$  we recognise the expression (4.2) for the infinite lattice.

The constants  $\eta_1, \eta_2$  in (4.12) are the two solutions of the equation

$$(4.13) \quad (\underline{l}_1 \underline{b}_1 + \underline{l}_2 \underline{b}_2 + \eta \underline{b}_3 + \underline{k})^2 = k_0^2$$

These are given by

$$(4.14) \quad \eta_{1,2} = \frac{1}{b_3} \left[ -(\underline{b}_3, \underline{q}) \pm \sqrt{(\underline{b}_3, \underline{q})^2 + b_3^2 (k_0^2 - q^2)} \right]$$

$$\underline{q} = \underline{l}_1 \underline{b}_1 + \underline{l}_2 \underline{b}_2 + \underline{k}$$

We consider first the case when either  $\underline{l}_1$  or  $\underline{l}_2$  or both are different /

different from zero. Writing  $\underline{k}$  as

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

where  $-\frac{1}{2} \leq k_i \leq \frac{1}{2}$  (cf. Section VI), we see that  $\underline{q}$  cannot be parallel to  $\underline{b}_3$ , so that

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

Since  $k_0 \ll |b_j|$  it follows that  $k_0$  in (4.14) may be neglected, so that the square root is imaginary and  $\eta_{1,2}$  are conjugate complex. In this case we have to use for  $\eta_1$  the solution with positive imaginary part, and for  $\eta_2$  the solution with negative imaginary part. If we insert such complex solution in (4.12) it follows with (4.10) that  $S^{(1)}$  and  $S^{(2)}$  decrease exponentially with the distance from the surface. They represent only small surface effects and may be neglected.

We now turn to the zero terms of the series  $S^{(1)}$  and  $S^{(2)}$  (i.e.  $l_1 = l_2 = 0$ ). Then the solution (4.14) reduces to

$$(4.15) \quad \eta_{1,2} = \frac{1}{b_3^2} \left[ -(\underline{b}_3, \underline{k}) \pm \sqrt{(\underline{b}_3, \underline{k})^2 + b_3^2 (k_0^2 - k^2)} \right], \text{ for } l_1 = l_2 = 0$$

If  $k \neq 0$ , so that  $k_0 \ll k$ , we may neglect  $k_0$  again and the solutions  $\eta_{1,2}$  are again conjugate complex, if  $\underline{k}$  is not parallel to  $\underline{b}_3$ . In this case we obtain again exponentially decreasing expressions. The only exception is when  $\underline{k}$  is parallel to  $\underline{b}_3$ . In this case we obtain from (4.15)

$$(4.16) \quad \eta_{1,2} = \frac{-k \pm k_0}{|b_3|} \quad \text{for } (\underline{b}_3, \underline{k}) = |b_3| |k|$$

and /

and

$$(4.17) \quad \eta_{1,2} \cdot \underline{b}_3 = -\underline{k} \pm \underline{k}_0$$

Inserting these values in (4.12) we obtain with (4.0), (4.1) the Hertz vectors  $\underline{Z}^{(1)}$ ,  $\underline{Z}^{(2)}$  corresponding to the zero terms of  $S^{(1)}$ ,  $S^{(2)}$

$$(4.18) \quad \underline{Z}^{(1)} = \frac{i}{v_a} e^{-i\omega t} \frac{e^{2\pi i(\underline{y}, \underline{k}_0)}}{|b_3| k_0 (1 - e^{2\pi i(k-k_0)/|b_3|})} \sum_{\underline{k}} \rho_{\underline{k}} e^{2\pi i(\underline{y}_{\underline{k}}, \underline{k} - \underline{k}_0)}$$

$$\underline{Z}^{(2)} = \frac{i}{v_a} e^{-i\omega t} \frac{e^{-2\pi i(\underline{y}, \underline{k}_0)}}{|b_3| k_0 (1 - e^{2\pi i(k+k_0)/|b_3|})} \sum_{\underline{k}} \rho_{\underline{k}} e^{2\pi i(\underline{y}_{\underline{k}}, \underline{k} + \underline{k}_0)}$$

Since  $k_0 \ll k$ ,  $k_0 \ll |b_3|$  and  $(\underline{y}_{\underline{k}}, \underline{k}_i) \sim 1$ , it follows that  $(\underline{y}_{\underline{k}}, \underline{k}_0) \ll 1$ . We obtain to the first order in  $k_0$

$$(4.19) \quad \underline{Z}^{(1)} = \frac{i}{v_a} \frac{e^{-i\omega t} e^{2\pi i(\underline{y}, \underline{k}_0)}}{|b_3| k_0} \frac{\sum_{\underline{k}} \rho_{\underline{k}}}{1 - e^{2\pi i k / |b_3|}}$$

$$\underline{Z}^{(2)} = \frac{i}{v_a} \frac{e^{-i\omega t} e^{-2\pi i(\underline{y}, \underline{k}_0)}}{|b_3| k_0} \frac{\sum_{\underline{k}} \rho_{\underline{k}}}{1 - e^{2\pi i k / |b_3|}}$$

In this case we obtain indeed an outgoing radiation field.

But the effect of this field is negligible. This may be seen either by calculating the force from  $\underline{Z}^{(1)}$  or by calculating the energy flow of the outgoing radiation <sup>from  $\underline{Z}^{(2)}$</sup>  and comparing it with the energy of the oscillator. If we calculate this by means of (4.6) we obtain only values of the magnitude  $\frac{k_0}{|b_3|}$  which can be neglected.

The field of the crystal is, therefore, completely determined by  $S^{(0)}$  (4.12) or (4.2) which gives the right solution /

solution for our problem for  $k \neq 0$ .

We have now only to consider the case  $k = 0$ . We obtain for the zero term of the Hertz vectors  $\underline{Z}^{(1)}$ ,  $\underline{Z}^{(2)}$  once more the expression (4.18) and need only put  $k = 0$ . But in this case  $\frac{k_0}{|k_0|}$  in the exponential function of the denominator cannot be neglected. Expanding this exponential we find, instead of (4.19)

$$(4.20) \quad \begin{aligned} \underline{Z}^{(1)} &= \frac{1}{2\pi v_a} \frac{e^{-i\omega t} e^{2\pi i(x, k_0)}}{k_0^2} \sum_{\kappa} \rho_{\kappa} \\ \underline{Z}^{(2)} &= \frac{1}{2\pi v_a} \frac{e^{-i\omega t} e^{-2\pi i(y, k_0)}}{k_0^2} \sum_{\kappa} \rho_{\kappa} \end{aligned}$$

$\underline{Z}^{(2)}$  represents again an outgoing wave, but the amplitude contains  $\frac{1}{k_0^2}$  and therefore it cannot be neglected. However, this case of infinitely long waves, i.e. long waves compared with the dimensions of the whole crystal has already been treated by Born (1933, p.777). He shows that in this case one has to omit the zero term in the Fourier series (4.2) which gives rise only to the mean Maxwell field  $-4\pi \rho$  (cf. 4.7) and that then the modified expression (4.2) gives the right solution of our problem for  $k = 0$ .

The force on the particle  $(x, t)$  is then determined by the Hertz vector



## V. The Coupling Coefficients of the Electromagnetic Interaction.

We can now write down the Hertz vector for all states of vibrations of the crystal, cf. (4.0), (4.1), (4.2). Since  $k_0$  is small compared to the vectors of the reciprocal lattice,  $k_0$  may be neglected in (4.2) except for the zero term  $k_n = (0, 0, 0)$ . As long as  $k \neq 0$ ,  $k_0$  may be neglected also in the zero term, as we have just shown. For  $k = 0$  on the other hand the zero term must be omitted. Therefore we find for  $S$

$$(5.0) \quad S = \frac{1}{\pi v_a} \sum' \frac{e^{2\pi i(k_n, r)}}{(k_n + k)^2}$$

where the dash indicated that for  $k = 0$ , the zero term  $k_n = 0$  must be omitted.

In evaluating the field acting on the dipole  $(\kappa, \ell)$  we must subtract the field of the dipole itself. The moment of the dipole is

$$(5.1) \quad p_\kappa^\ell = e_\kappa \underline{r}_\kappa^\ell = p_\kappa e^{-i\omega t} e^{2\pi i(k, r_\kappa^\ell)}$$

and therefore its Hertz vector

$$(5.2) \quad \underline{Z}_\kappa^\ell = p_\kappa e^{-i\omega t} e^{2\pi i(k, r_\kappa^\ell)} \frac{1}{|\underline{r} - \underline{r}_\kappa^\ell|}$$

The force on the particle  $(\kappa, \ell)$  is then determined by the Hertz vector

$$\underline{Z}_\kappa^{\ell*} = \underline{Z} - \underline{Z}_\kappa^\ell$$

or /

or from (4.0), (4.1) and (5.0)

$$(5.3) \quad \underline{Z}_{\kappa}^{\ell*} = e^{-i\omega t} e^{2\pi i(\underline{k}, \underline{r}_{\kappa}^{\ell})} \sum_{\kappa'} \rho_{\kappa'} \left\{ S(\underline{r}-\underline{r}_{\kappa'}) e^{2\pi i(\underline{k}, \underline{r}-\underline{r}_{\kappa}^{\ell})} - \frac{\delta_{\kappa\kappa'}}{|\underline{r}-\underline{r}_{\kappa}^{\ell}|} \right\}$$

Since  $S$  is periodic in the lattice (cf. 5.0), we introduce the potential functions

$$(5.4) \quad \Psi^{\underline{k}}(\underline{r}) = S(\underline{r}) e^{2\pi i(\underline{k}, \underline{r})} = \frac{1}{\pi v_a} \sum_{\underline{k}'} \frac{e^{2\pi i(\underline{k}_0 + \underline{k}, \underline{r})}}{(\underline{k}_0 + \underline{k})^2}$$

$$\bar{\Psi}^{\underline{k}}(\underline{r}) = \Psi^{\underline{k}}(\underline{r}) - \frac{1}{|\underline{r}|}$$

and obtain for the Hertz vector (5.3)

$$(5.5) \quad \underline{Z}_{\kappa}^{\ell*} = e^{-i\omega t} e^{2\pi i(\underline{k}, \underline{r}_{\kappa}^{\ell})} \left\{ \rho_{\kappa} \bar{\Psi}^{\underline{k}}(\underline{r}-\underline{r}_{\kappa}^{\ell}) + \sum_{\kappa' \neq \kappa} \rho_{\kappa'} \Psi^{\underline{k}}(\underline{r}-\underline{r}_{\kappa}^{\ell}) e^{2\pi i(\underline{k}, \underline{r}_{\kappa}^{\ell})} \right\}$$

The electromagnetic field vectors can now be obtained from (4.6)

The magnetic field gives only a second order contribution to the force and may be neglected. The electric field is

$$(5.6) \quad \underline{E}_{\kappa x}^{\ell*} = \text{grad}_x \text{div} \underline{Z}_{\kappa}^{\ell*} - \frac{1}{c^2} \ddot{\underline{Z}}_{\kappa x}^{\ell*}$$

$$= e^{-i\omega t} e^{2\pi i(\underline{k}, \underline{r}_{\kappa}^{\ell})} \left\{ \sum_{\underline{y}} \rho_{\kappa y} \frac{\partial^2}{\partial x \partial y} \bar{\Psi}^{\underline{k}}(\underline{r}-\underline{r}_{\kappa}^{\ell}) + \sum_{\kappa' \neq \kappa} \sum_{\underline{y}} \rho_{\kappa' y} \frac{\partial^2}{\partial x \partial y} \Psi^{\underline{k}}(\underline{r}-\underline{r}_{\kappa}^{\ell}) e^{2\pi i(\underline{k}, \underline{r}_{\kappa}^{\ell})} \right\} + \frac{\omega^2}{c^2} \underline{Z}_{\kappa x}^{\ell*}$$

According to (5.4) the terms due to the  $\text{grad div} \underline{Z}_{\kappa}^{\ell*}$  obtain factors  $(\underline{k}_0 + \underline{k})_x \cdot (\underline{k}_0 + \underline{k})_y$  whereas the last term in

(5.6) has the factor  $\frac{\omega^2}{c^2} = 4\pi^2 \hbar \omega^2$ . It can therefore be

neglected. Putting  $\underline{r} = \underline{r}_{\kappa}^{\ell}$  and multiplying with the charge

$\rho_{\kappa}$  we obtain the force on the particle  $(\kappa, \ell)$ . We insert

this /

this expression in the equation of motion and cancel the factor  $\exp\{-i\omega t\} \cdot \exp\{2\pi i(\underline{k}, \underline{r}^k)\}$  . we find with

$$\underline{p}_k = e_k \underline{u}_k$$

$$(5.7) \quad m_k \omega^2 u_{kx} + \sum_{k'} \sum_y [{}_{xy}^{kk'}] u_{k'y} = 0$$

$$(5.8) \quad [{}_{xy}^{kk'}] = e_k e_{k'} \psi_{xy}^k(\underline{r}_{kk'}) e^{-2\pi i(\underline{k}, \underline{r}_{kk'})}$$

$$[{}_{xy}^{kk}] = e_k^2 \bar{\psi}_{xy}^k(0)$$

where the indices  $xy$  denote again differentiation.

Comparing this expression with (2.11), (2.12) we see that the coupling coefficients are identical with those derived in Section II $\bar{z}$ , except that the function  $F^k(\underline{r})$  must be replaced by  $\psi^k(\underline{r})$ . In order to compare these two functions, we take the parameter  $E$  in (3.22) equal to  $\infty$ . Then  $F^k$  is given by

$$(5.9) \quad F^k(\underline{r}) = \frac{1}{\pi v_a} \sum_k \frac{e^{2\pi i(\underline{k}, \underline{r})}}{(\underline{k}_x + \underline{k})^2}$$

This is identical with the expression (5.4) for  $\psi^k(\underline{r})$  with the exception of the case  $k=0$ . In this case the divergent zero term in  $F^k$  is omitted in  $\psi^k$ .

$$(5.10) \quad \psi^k(\underline{r}) = F^k(\underline{r}) \quad ; \text{ for } k \neq 0$$

$$\psi^0(\underline{r}) = \lim_{k \rightarrow 0} \left( F^k(\underline{r}) - \frac{1}{\pi v_a} \frac{e^{2\pi i(\underline{k}, \underline{r})}}{k^2} \right) \quad ; \text{ for } k=0.$$

Thus for  $k \neq 0$  the electrostatic derivation is justified.

$F^k$  is defined as a sum of potentials of point charges.

Therefore it satisfies Laplace's equation

$$(5.11) \quad /$$

$$(5.11) \quad \Delta F^k = \Delta \psi^k = 0 \quad ; k \neq 0$$

This was to be expected since we neglected  $k_0$ , i.e. the effect of the retardation. With (5.8) we get the relation

$$(5.12) \quad \left[ \begin{smallmatrix} k k' \\ x x \end{smallmatrix} \right] + \left[ \begin{smallmatrix} k k' \\ y y \end{smallmatrix} \right] + \left[ \begin{smallmatrix} k k' \\ z z \end{smallmatrix} \right] = \sum_x \left[ \begin{smallmatrix} k k' \\ x x \end{smallmatrix} \right] = 0$$

(cf. Born, 1923, p. 728)

For  $k=0$  on the other hand (5.10) gives

$$(5.13) \quad \Delta \psi^0 = \lim_{k \rightarrow 0} \left( \Delta F^k + \frac{4\pi}{2a} e^{2\pi i(k, r)} \right) = \frac{4\pi}{2a} \quad ; k=0$$

$$(5.14) \quad \sum_x \left[ \begin{smallmatrix} k k' \\ x x \end{smallmatrix} \right]_{k=0} = e_k e_{k'} \frac{4\pi}{2a}$$

This holds also for  $k'=k$  if one substitutes  $\bar{\psi}^0$  for  $\psi^0$  in (5.13). The potential  $\psi^0$  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

$$(5.16) \quad \left[ \begin{smallmatrix} k k' \\ x x \end{smallmatrix} \right]_{k=0} = e_k e_{k'} \frac{4\pi}{3v_0} \quad , \quad \left[ \begin{smallmatrix} k k' \\ x x \end{smallmatrix} \right]_{k=0} = e_k^2 \frac{4\pi}{3v_0}$$

$$\left[ \begin{smallmatrix} k k' \\ x y \end{smallmatrix} \right]_{k=0} = \left[ \begin{smallmatrix} k k' \\ x y \end{smallmatrix} \right]_{k=0} = \text{cycl.} = 0$$

Then we obtain the coupling force

$$(5.17) \quad F_{k_x} = \sum_{k'} \left[ \begin{smallmatrix} k k' \\ x x \end{smallmatrix} \right]_{k=0} U_{k'_x} = \frac{4\pi}{3} e_k \sum_{k'} e_{k'} U_{k'_x} = \frac{4\pi}{3} \rho_x e_k$$

which /

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

The question whether the sum  $\sum_x [\kappa_x \kappa'_x]$  is equal to 0 or to  $\epsilon \kappa \kappa' \frac{4\pi}{v_a}$  has been discussed before, but had not been cleared in a satisfactory way. Hertzfeld and Lyddam (1938) assume that for infinite waves it is equal to  $\epsilon \kappa \kappa' \frac{4\pi}{v_a}$  but that for all other wave lengths one has to displace the uniform charge distribution  $-1$ ; this would give rise to surface charges which just compensate the term  $\frac{4\pi}{v_a}$  so that the above sum is equal to zero. This argument leads to the correct result, which we have obtained above without any such assumptions; but it appears rather artificial, since the displaced uniform charge  $-1$  has no immediate physical significance.

## VI. The Coupling Coefficients of the NaCl-Lattice.

In the case of NaCl we have 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  $\underline{y}_{\kappa\kappa'}^{\ell}$  there corresponds another one of the same magnitude and in opposite direction. The same is true for the reciprocal lattice. For this reason the coupling coefficients are all real, as may be seen from (1.19); in this sum all imaginary terms cancel so that

$$(6.0) \quad \begin{aligned} \left[ \begin{array}{cc} \kappa\kappa' \\ x\gamma \end{array} \right] &= \sum_{\ell} (\Phi_{\kappa\kappa'}^{\ell})_{x\gamma} \cos 2\pi (\underline{k}, \underline{y}_{\kappa\kappa'}^{\ell}) \\ \left[ \begin{array}{cc} \kappa\kappa \\ x\gamma \end{array} \right] &= \sum_{\ell} (\Phi_{\kappa\kappa}^{\ell})_{x\gamma} \cos 2\pi (\underline{k}, \underline{a}^{\ell}) \end{aligned}$$

and since  $\underline{y}_{\kappa\kappa'} = -\underline{y}_{\kappa'\kappa}$

$$(6.1) \quad \left[ \begin{array}{cc} \kappa\kappa' \\ x\gamma \end{array} \right] = \left[ \begin{array}{cc} \kappa'\kappa \\ x\gamma \end{array} \right]$$

From (5.8) it can be seen that the coefficients are entirely symmetrical in  $x$  and  $\gamma$  so that

$$(6.2) \quad \left[ \begin{array}{cc} \kappa\kappa' \\ x\gamma \end{array} \right] = \left[ \begin{array}{cc} \kappa\kappa' \\ \gamma x \end{array} \right]$$

Furthermore, the NaCl lattice is entirely symmetrical in Na and Cl/

and Cl (if we neglect the repulsive forces between all but nearest neighbours); therefore

$$(6.3) \quad \begin{bmatrix} 1 & 1 \\ x & y \end{bmatrix} = \begin{bmatrix} 2 & 2 \\ x & y \end{bmatrix}$$

The cell vectors of the NaCl lattice are

$$(6.4) \quad \begin{aligned} \underline{a}_1 &= \gamma_0 (0, 1, 1) & \underline{y}_{21} &= -\underline{y}_{12} = \gamma_0 (1, 1, 1) \\ \underline{a}_2 &= \gamma_0 (1, 0, 1) & \underline{v}_a &= 2\gamma_0^3 \\ \underline{a}_3 &= \gamma_0 (1, 1, 0) \end{aligned}$$

where  $\gamma_0$  is the distance between nearest neighbours or the lattice constant and  $\underline{v}_a$  the volume of the cell. A lattice vector is therefore of the form

$$(6.5) \quad \begin{aligned} \underline{a}^l &= \gamma_0 (l_2 + l_3, l_3 + l_1, l_1 + l_2) = \gamma_0 (l_x, l_y, l_z), \quad \sum_x l_x = \text{even} \\ \underline{y}_{21}^l &= \gamma_0 (l_2 + l_3 + 1, l_3 + l_1 + 1, l_1 + l_2 + 1) = \gamma_0 (m_x, m_y, m_z), \quad \sum_x m_x = \text{odd} \end{aligned}$$

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 (3.1). With (6.4) we obtain

$$(6.6) \quad \begin{aligned} \underline{b}_1 &= \frac{1}{2\gamma_0} (-1, 1, 1) \\ \underline{b}_2 &= \frac{1}{2\gamma_0} (1, -1, 1) \\ \underline{b}_3 &= \frac{1}{2\gamma_0} (1, 1, -1) \end{aligned}$$

so that a vector in the reciprocal lattice is given by

$$(6.7) /$$

$$(6.7) \quad \underline{b}_k = \frac{1}{2v_0} (k_2 + k_3 - k_1, k_3 + k_1 - k_2, k_1 + k_2 - k_3) \\ = \frac{1}{2v_0} (k_x, k_y, k_z) \quad , \quad k_x, k_y, k_z \text{ all odd or all even}$$

where  $k_x, k_y, k_z$  cover all sets of integers which are either all odd or all even.

The sums<sup>(3.23), (3.27)</sup> representing the coupling coefficients may now be written dimensionless by writing  $\frac{\epsilon}{v_0}$  for the parameter  $E$  in (5.11) and substituting for the wave vector  $\underline{k}$  :

$$(6.8) \quad \underline{k} = k_1 \underline{b}_1 + k_2 \underline{b}_2 + k_3 \underline{b}_3 = \frac{1}{2v_0} (q_x, q_y, q_z) \\ q_x = k_2 + k_3 - k_1, \quad q_y = k_3 + k_1 - k_2, \quad q_z = k_1 + k_2 - k_3$$

$$(6.9) \quad \frac{v_0}{c^2} \epsilon_{xy}^{[1,2]} = G_{xy}^{21}(\underline{k}) - H_{xy}(\underline{k}) \\ \frac{v_0}{c^2} \epsilon_{xy}^{[1,1]} = -G_{xy}^{11}(\underline{k}) + H_{xy}(\underline{k}) + \frac{8}{3\sqrt{\pi}} \epsilon^3 \delta_{xy}$$

where

$$G_{xy}^{12}(\underline{k}) = 4\sqrt{\pi} \sum_{\underline{q}} \frac{(k_x + q_x)(k_y + q_y)}{(k_x + q_x)^2} e^{-\frac{\pi^2}{4\epsilon^2} (\underline{k} + \underline{q})^2} \cos \pi (k_x + k_y + k_z)$$

$$G_{xy}^{11}(\underline{k}) = 4\sqrt{\pi} \sum_{\underline{q}} \frac{(k_x + q_x)(k_y + q_y)}{(k_x + q_x)^2} e^{-\frac{\pi^2}{4\epsilon^2} (\underline{k} + \underline{q})^2}$$

$$(6.10) \quad H_{xy}(\underline{k}) = 2 \sum_{\underline{m}} \left[ -f(m) \delta_{xy} + g(m) \frac{m_x m_y}{m^2} \right] \cos \pi (\underline{q}, \underline{m})$$

$$f(m) = \frac{2}{\sqrt{\pi}} \epsilon \frac{e^{-\epsilon^2 m^2}}{m^2} + \frac{\Psi(m)}{m^3}$$

$$g(m) = \frac{4}{\sqrt{\pi}} \epsilon^3 e^{-\epsilon^2 m^2} + \frac{6}{\sqrt{\pi}} \epsilon \frac{e^{-\epsilon^2 m^2}}{m^2} + 3 \frac{\Psi(m)}{m^3}$$

$$\Psi(m) /$$



$$\Psi(m) = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\varepsilon m} e^{-\xi^2} d\xi$$

$$m = |\underline{m}| = (m_x^2 + m_y^2 + m_z^2)^{\frac{1}{2}}$$

These equations only hold for  $\underline{k} \neq (0, 0, 0)$

For some wave vectors  $\underline{k}$  we can reduce the calculation appreciably by considering the cubic symmetry.

1.)  $q_x = q_y = q_z$  . This case is symmetrical in  $x, y, z$ .

Therefore, we conclude from (5.13) that

$$(6.11) \quad \begin{matrix} C \\ \text{xx} \end{matrix} \begin{bmatrix} k & k' \\ x & x \end{bmatrix} = \begin{matrix} C \\ \text{yy} \end{matrix} \begin{bmatrix} k & k' \\ y & y \end{bmatrix} = \begin{matrix} C \\ \text{zz} \end{matrix} \begin{bmatrix} k & k' \\ z & z \end{bmatrix} = 0, \quad q_x = q_y = q_z.$$

2.)  $q_z = 0$  (or  $q_z = 1$ , cf. note p. 36a)<sup>1)</sup>

In this case in  $\int_{x_z}(\underline{k})$  the two terms  $h_x, h_y, h_z$  and  $h_x, h_y, -h_z$  just cancel and  $\int_{x_z}(\underline{k}) = 0$ . Putting  $\varepsilon = \infty$ , then  $H_{kz}^{(m)}$  also vanishes (the coupling coefficients are, of course, independent of  $\varepsilon$ ). Therefore

$$(6.12) \quad \begin{matrix} C \\ \text{xz} \end{matrix} \begin{bmatrix} 2' \\ xz \end{bmatrix} = \begin{matrix} C \\ \text{xz} \end{matrix} \begin{bmatrix} 1' \\ xz \end{bmatrix} = \begin{matrix} C \\ \text{yz} \end{matrix} \begin{bmatrix} 2' \\ yz \end{bmatrix} = \begin{matrix} C \\ \text{yz} \end{matrix} \begin{bmatrix} 1' \\ yz \end{bmatrix} = 0$$

3.) Consider two wave vectors  $\underline{k}, \underline{k}'$  which differ only in the sign of the  $z$ -component. If we put in this case  $\varepsilon = 0$  so that we obtain only a contribution from  $H_{kz}^{(1)}$  it follows that

$$(6.13) \quad \begin{matrix} C \\ \text{xz} \end{matrix} \begin{bmatrix} 2' \\ xz \end{bmatrix}_k = - \begin{matrix} C \\ \text{xz} \end{matrix} \begin{bmatrix} 2' \\ xz \end{bmatrix}_{k'}; \quad \begin{matrix} C \\ \text{xz} \end{matrix} \begin{bmatrix} 1' \\ xz \end{bmatrix}_k = - \begin{matrix} C \\ \text{xz} \end{matrix} \begin{bmatrix} 1' \\ xz \end{bmatrix}_{k'} \quad \begin{matrix} q_x = q_{x'} \\ q_y = q_{y'} \\ q_z = -q_{z'} \end{matrix}$$

whereas/

1.) This can also be seen by considering the function

$H_{xz}$  only ( $\varepsilon=0$ ). For  $x \neq z$  we find developing

$$\cos \pi(q, \underline{m}) = \cos \pi(q_x m_x + q_y m_y + q_z m_z)$$

$$(6.10)a \quad H_{xz} = -2 \sum_{\underline{m}} g(\underline{m}) \frac{m_x m_z}{m^2} \sin \pi q_x m_x \sin \pi q_z m_z \cos \pi q_y m_y$$

All other terms arising from the development of  $\cos \pi(q, \underline{m})$  cancel because of symmetry ( $m_x, m_z$  assume the same positive and negative values).

We see at once from (6.10)a that for  $q_z = 1$  (or  $q_z = 0$ )

$H_{xz} = 0$  and therefore

$$\left[ \begin{matrix} z' \\ xz \end{matrix} \right] = \left[ \begin{matrix} ' \\ xz \end{matrix} \right] = \left[ \begin{matrix} z' \\ yz \end{matrix} \right] = \left[ \begin{matrix} ' \\ yz \end{matrix} \right] = 0 \quad \text{for } q_z = 1 \text{ (or } q_z = 0)$$

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  $\int_{xz} (\varepsilon = \infty)$  that the coefficients in question vanish on account of this symmetry.

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

4.) Consider two wave vectors  $\underline{k}, \underline{k}'$  which are identical apart from an interchange of the components of  $q_x, q_y$ . Taking again  $\xi \rightarrow \infty$ , we see that

$$(6.14) \quad \begin{aligned} \begin{bmatrix} z' \\ xx \end{bmatrix}_k &= \begin{bmatrix} z' \\ yy \end{bmatrix}_{k'} & ; & \begin{bmatrix} ' \\ xx \end{bmatrix}_k &= \begin{bmatrix} ' \\ yy \end{bmatrix}_{k'} & \quad q_x = q_y' \\ \begin{bmatrix} z' \\ yy \end{bmatrix}_k &= \begin{bmatrix} z' \\ xx \end{bmatrix}_{k'} & ; & \begin{bmatrix} z' \\ yy \end{bmatrix}_k &= \begin{bmatrix} ' \\ xx \end{bmatrix}_{k'} & \quad q_y = q_x' \\ & & & & & \quad q_z = q_z' \end{aligned}$$

all the other coefficients being equal.

From the condition of the cyclic lattice (1.23), (1.25) 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, we divide this range into tenths and consider the vector components

$$(6.16) \quad k_i = \frac{\rho_i}{10} \quad , \quad (\rho_1, \rho_2, \rho_3 \text{ integers})$$

In order to make full use of the symmetry 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 bodycentered type this region is of the form of an octohedron with its vertices cut off/

cut off (cf. for example, Sommerfeld and Bethe, Handbuch der Physik, 1933, Vol. XXIV, 2, p. 402, fig. 27). The boundaries are given by the equations

$$(6.16) \quad q_x \pm q_y \pm q_z = \pm \frac{3}{2}, \quad q_x = \pm 1, \quad q_y = \pm 1, \quad q_z = \pm 1$$

In view of the symmetry properties just considered we may restrict the calculation to positive values of  $q_x, q_y, q_z$ . All other coefficients may then be obtained from (6.13). Furthermore, ~~if~~ in view of (6.14) we can restrict the calculation to sets of numbers such that  $q_x \geq q_y \geq q_z$ . Thus we need only consider values of  $q$  such that

$$(6.17) \quad \begin{aligned} 0 \leq q_z \leq q_y \leq q_x \leq 1 \\ q_x + q_y + q_z \leq \frac{3}{2} \end{aligned}$$

If we introduce as in (6.15) whole numbers  $\rho_x, \rho_y, \rho_z$  we obtain corresponding to (6.7)

$$(6.18) \quad \rho_x = \rho_2 + \rho_3 - \rho_1, \quad \rho_y = \rho_3 + \rho_1 - \rho_2, \quad \rho_z = \rho_1 + \rho_2 - \rho_3$$

and we have to calculate the coupling coefficients for all sets of whole number  $\rho_x, \rho_y, \rho_z$  which are either all odd or all even and satisfy the conditions

$$(6.19) \quad \begin{aligned} 0 \leq \rho_z \leq \rho_y \leq \rho_x \leq 10 \\ \rho_x + \rho_y + \rho_z \leq 15 \end{aligned}$$

There are/

## VII. 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. Let us collect all those other forces in a potential  $v(r)$ , and since these forces decrease very rapidly with the distance we need consider only the interaction between nearest neighbours. In the NaCl lattice each ion is surrounded by 6 nearest neighbours so that the energy per cell is given by

$$(7.0) \quad \frac{\Phi_0}{Z} = - \frac{\alpha e^2}{r_0} + 6 v(r_0)$$

where  $\alpha$  is the Madelung constant and  $r_0$  the distance between nearest neighbours.

We shall need the first two derivatives of  $v(r_0)$ . These can be obtained from the condition of equilibrium and the compressibility. We put for abbreviation

$$(7.1) \quad \begin{aligned} 2 \left( \frac{d v(r)}{d r} \right)_{r=r_0} &= \frac{e^2}{2 r_0^2} B \\ 2 \left( \frac{d^2 v(r)}{d r^2} \right)_{r=r_0} &= \frac{e^2}{2 r_0^3} A \end{aligned}$$

Then the condition of equilibrium is

$$\frac{d \Phi_0 / Z}{d r_0} = 0 = \frac{\alpha e^2}{r_0^2} + 3 \frac{e^2}{2 r_0^2} B$$

so that

$$(7.2) /$$

$$(7.2) \quad B = -\frac{2\alpha}{3}$$

The compressibility is given by

$$\frac{1}{\kappa} = \frac{1}{9v_a} r_0^2 \frac{d^2 \phi_0/2}{dr_0^2} = \frac{1}{18r_0} \frac{d^2 \phi_0/2}{dr_0^2} = \frac{1}{18r_0} \left[ -2 \frac{\alpha \epsilon^2}{r_0^3} + \frac{3}{2} \frac{\epsilon^2}{r_0^3} A \right]$$

( $v_a = 2r_0^3$ )

so that

$$(7.3) \quad A = \frac{12r_0^4}{\kappa \epsilon^2} + \frac{4}{3} \alpha$$

With  $\epsilon = 4.8 \cdot 10^{-10}$  e.s.u.,  $\alpha = 1.7476$ ,  $\kappa = 4.16 \cdot 10^{-12} \text{ cm}^2/\text{dyn}$ ,  $r_0 = 2.814 \cdot 10^{-8} \text{ cm}$

the values of  $A$  and  $B$  are

$$(7.4) \quad A = 10.18, \quad B = -1.165$$

We now proceed to calculate that part of the coupling coefficients which is due to the repulsive forces. This part is given by (1.21), (1.19)

$$(7.5) \quad R \left[ \begin{matrix} \kappa \kappa' \\ xy \end{matrix} \right] = \sum_{\epsilon} (v_{\kappa \kappa'})_{xy} e^{2\pi i (\frac{x}{\epsilon}, \frac{y}{\epsilon})}$$

Consider first the case  $\kappa' \neq \kappa$ ; we have to sum (7.5) over the 6 nearest neighbours given by the vectors

$$(7.6) \quad \begin{aligned} & r_0 (\pm 1, 0, 0) \\ & r_0 (0, \pm 1, 0) \\ & r_0 (0, 0, \pm 1) \end{aligned}$$

The differentiation in (7.5) yields with the definition (7.1)

$$(7.7) /$$

$$(7.7) \quad R \begin{bmatrix} 12 \\ xy \end{bmatrix} = \frac{1}{2} \frac{e^2}{v_a} \sum_{\underline{k}} \left[ A \frac{x_{12}^{\underline{k}} y_{12}^{\underline{k}}}{(v_{12}^{\underline{k}})^2} + B \left( \delta_{xy} - \frac{x_{12}^{\underline{k}} y_{12}^{\underline{k}}}{(v_{12}^{\underline{k}})^2} \right) \right] e^{2\pi i(\underline{k}, \underline{r}_{12})}$$

The sum over the vectors (7.6) gives

$$(7.8) \quad R \begin{bmatrix} 12 \\ xy \end{bmatrix} = 0, \quad R \begin{bmatrix} 12 \\ xx \end{bmatrix} \frac{v_a}{e^2} = A \omega 2\pi k_x r_0 + B(\omega 2\pi k_y r_0 + \omega 2\pi k_z r_0)$$

In the case  $k' = k$  only the zero term in (7.5) remains, all other terms representing interaction between distant ions.

$$(7.9) \quad R \begin{bmatrix} 11 \\ xy \end{bmatrix} = (v_{kk})_{xy}$$

This expression is independent of  $k$  and can therefore be calculated from (2.7)

$$R \begin{bmatrix} 11 \\ xy \end{bmatrix} + R \begin{bmatrix} 12 \\ xy \end{bmatrix}_{k=0} = 0$$

so that

$$(7.10) \quad R \begin{bmatrix} 11 \\ xy \end{bmatrix} = 0, \quad \frac{v_a}{e^2} R \begin{bmatrix} 11 \\ xx \end{bmatrix} = -(A + 2B)$$

If we introduce for  $\underline{k}$  the dimensionless vector  $\underline{q}$  given by

(6.8), (7.8) and (7.10) may be written:

$$(7.11) \quad R \begin{bmatrix} 11 \\ xy \end{bmatrix} = R \begin{bmatrix} 12 \\ xy \end{bmatrix} = 0$$

$$\frac{v_a}{e^2} R \begin{bmatrix} 11 \\ xx \end{bmatrix} = -(A + 2B), \quad \frac{v_a}{e^2} R \begin{bmatrix} 12 \\ xx \end{bmatrix} = A \omega \pi q_x + B(\omega \pi q_y + \omega \pi q_z)$$

### VIII. 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)

$$(8.0) \quad [xy \bar{x}\bar{y}] = \frac{1}{2Va} \sum_{\kappa\kappa'} \int_{\underline{e}} (\Phi_{\kappa\kappa'})_{xy} \bar{x}_{\kappa\kappa'}^c \bar{y}_{\kappa\kappa'}^c$$

The elastic constants in the usual notation are related to the bracket symbols (8.0) as follows

$$(8.1) \quad \begin{aligned} [xxxx] &= c_{11} \\ [xxyy] &= c_{12} \\ [xxzz] &= c_{13} \\ [xyxy] &= c_{44} \end{aligned}$$

From the cubic symmetry of the NaCl lattice it follows that  $x, y$  and  $z$  in (8.0) can be interchanged so that we get

$$c_{12} = c_{13} \quad \text{and the Cauchy relation}$$

$$(8.2) \quad c_{12} = c_{44}$$

We find exactly the expressions (8.0) if we develop the coupling coefficients (1.19) into a power series of the inverse wave length; with  $2\pi \underline{k} = \tau \underline{s}$  where  $\underline{s}$  is a unit vector we find

$$(8.3) /$$



$$(8.3) \quad [{}_{xy}^{kk'}] = [{}_{xy}^{kk'}]_{(0)} + [{}_{xy}^{kk'}]_{(1)} \tau + [{}_{xy}^{kk'}]_{(2)} \tau^2 + \dots$$

where

$$(8.4) \quad \begin{aligned} [{}_{xy}^{kk'}]_{(0)} &= \int_{\mathcal{Q}} (\Phi_{kk'}^{\ell})_{xy} \\ [{}_{xy}^{kk'}]_{(1)} &= i \int_{\mathcal{Q}} (\underline{s}, \underline{\Sigma}_{kk'}^{\ell}) (\Phi_{kk'}^{\ell})_{xy} \\ [{}_{xy}^{kk'}]_{(2)} &= -\frac{1}{2} \int_{\mathcal{Q}} (\underline{s}, \underline{\Sigma}_{kk'}^{\ell})^2 (\Phi_{kk'}^{\ell})_{xy} = -\frac{1}{2} \int_{\mathcal{Q}} \sum_{\bar{x}, \bar{y}} s_{\bar{x}} s_{\bar{y}} \bar{x}_{kk'}^{\ell} \bar{y}_{kk'}^{\ell} (\Phi_{kk'}^{\ell})_{xy} \end{aligned}$$

Comparing (8.3) with (8.0) one notices that

$$(8.5) \quad -\nu_a \sum_{\bar{x}, \bar{y}} s_{\bar{x}} s_{\bar{y}} [x\gamma \bar{x}\bar{y}] = \sum_{kk'} [{}_{xy}^{kk'}]_{(2)}$$

We now calculate  $[{}_{xx}^{kk'}]_{(2)}$  by developing the expressions (6.9), (6.10) for the coupling coefficients of the NaCl lattice.

We find the result:

$$(8.6) \quad \begin{aligned} \sum_{kk'} [{}_{xx}^{kk'}]_{(2)} &= 2 \left\{ [{}_{xx}^{11}]_{(2)} + [{}_{xx}^{12}]_{(2)} \right\} \\ &= -\frac{e^2}{\nu_0} \left\{ s_x^2 \left[ \frac{2}{\pi} \sum_k \chi_x(k) - \sum_m [(f(m)+g(m)) \frac{m_x^2}{m^2}] m_x^2 \right] \right. \\ &\quad \left. + \int_{\mathcal{Q}} [(f(\ell)+g(\ell)) \frac{\ell_x^2}{\ell^2}] \ell_x^2 \right\} \\ &\quad + s_y^2 \left[ \frac{2}{\pi} \sum_k \chi_y(k) - \sum_m [(f(m)+g(m)) \frac{m_y^2}{m^2}] m_y^2 \right] \\ &\quad \left. + \int_{\mathcal{Q}} [(f(\ell)+g(\ell)) \frac{\ell_y^2}{\ell^2}] \ell_y^2 \right\} \\ &\quad + s_z^2 \left[ \frac{2}{\pi} \sum_k \chi_z(k) - \sum_m [(f(m)+g(m)) \frac{m_z^2}{m^2}] m_z^2 \right] \\ &\quad \left. + \int_{\mathcal{Q}} [(f(\ell)+g(\ell)) \frac{\ell_z^2}{\ell^2}] \ell_z^2 \right\} \end{aligned}$$

where

$$(8.7) \quad \chi_{\gamma}(k) = \frac{4}{k^2} e^{-\frac{\pi^2 k^2}{4\varepsilon^2}} \left[ 4 \frac{k_x^2 k_y^2}{k^4} - \frac{k_x^2}{k^2} + \frac{\pi^2}{\varepsilon^2} \left( \frac{k_x^2 k_y^2}{k^2} - \frac{k_x^2}{4} \right) + \frac{\pi^4}{\varepsilon^4} \frac{k_x^2 k_y^2}{8} \right. \\ \left. + s_{xy} \left\{ 1 - \frac{4k_x^2}{k^2} - \frac{\pi^2}{\varepsilon^2} k_x^2 \right\} \right]$$

and for/

Similarly one obtains for  ${}^C [{}_{xy}^{kk'}]_{(2)}$

$$(8.8) \quad \sum_{kk'} {}^C [{}_{xy}^{kk'}]_{(2)} = 2 \left\{ {}^C [{}_{xy}^{21}]_{(2)} + {}^C [{}_{xy}^{11}]_{(2)} \right\} \\ = - \frac{2e^2}{v_0} s_x s_y \left[ \frac{1}{\pi} \sum_k \bar{\chi}(k) - \sum_m [g(m) \frac{m_x^2 m_y^2}{m^2}] + \sum_l [g(l) \frac{l_x^2 l_y^2}{l^2}] \right]$$

where

$$(8.9) \quad \bar{\chi}(k) = \frac{4}{k^2} e^{-\frac{\pi^2 k^2}{4\epsilon^2}} \left[ \frac{8k_x^2 k_y^2}{k^4} - 2 \left( \frac{k_x^2 + k_y^2}{k^2} \right) + 1 + \frac{2\pi^2}{\epsilon^2} \left( \frac{k_x^2 k_y^2}{k^2} - \frac{k_x^2}{4} - \frac{k_y^2}{4} \right) + \frac{\pi^4}{\epsilon^4} \frac{k_x^2 k_y^2}{4} \right]$$

Comparing (8.6), (8.8) with (8.5) we find that part of the elastic constants which is due to the Coulomb forces:

$$(8.10) \quad \begin{aligned} C_{11} &= {}^C [xxxx] = \frac{e^2}{v_0 v_0} \left\{ \frac{2}{\pi} \sum_k \bar{\chi}_x(k) - \sum_m m_x^2 (f(m) + g(m) \frac{m_x^2}{m^2}) + \sum_l l_x^2 (f(l) + g(l) \frac{l_x^2}{l^2}) \right\} \\ C_{12} &= {}^C [xxyy] = \frac{e^2}{v_0 v_0} \left\{ \frac{2}{\pi} \sum_k \bar{\chi}_y(k) - \sum_m m_y^2 (f(m) + g(m) \frac{m_y^2}{m^2}) + \sum_l l_y^2 (f(l) + g(l) \frac{l_y^2}{l^2}) \right\} \\ C_{44} &= {}^C [xyxy] = \frac{e^2}{v_0 v_0} \left\{ \frac{1}{\pi} \sum_k \bar{\chi}(k) - \sum_m g(m) \frac{m_x^2 m_y^2}{m^2} + \sum_l g(l) \frac{l_x^2 l_y^2}{l^2} \right\} \end{aligned}$$

That part of the elastic constants which is due to the repulsive forces can be calculated in the same way. From (7.8), (7.10) we find

$$(8.11) \quad \sum_{kk'} {}^R [{}_{xy}^{kk'}]_{(2)} = 2 \left\{ {}^R [{}_{xx}^{11}]_{(2)} + {}^R [{}_{xx}^{12}]_{(2)} \right\} = \frac{e^2}{v_0} \left\{ -A s_x^2 - B (s_y^2 + s_z^2) \right\} \\ \sum_{kk'} {}^R [{}_{xy}^{kk'}]_{(2)} = 0$$

so that

$$(8.12) \quad {}^R C_{11} = \frac{e^2}{v_0 v_0} \frac{A}{2}, \quad {}^R C_{12} = \frac{e^2}{v_0 v_0} \frac{B}{2}, \quad {}^R C_{44} = 0$$

The Cauchy/

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

The numerical calculation gives

$$(8.13) \quad \begin{aligned} c_{11} &= -2.56 \frac{e^2}{2r_0^4} ; & R_{c_{11}} &= 5.09 \frac{e^2}{2r_0^4} ; & C_{11} &= 2.53 \frac{e^2}{2r_0^4} \\ c_{12} &= 1.278 \frac{e^2}{2r_0^4} ; & R_{c_{12}} &= -.583 \frac{e^2}{2r_0^4} ; & C_{12} &= .695 \frac{e^2}{2r_0^4} \\ c_{44} &= .696 \frac{e^2}{2r_0^4} ; & R_{c_{44}} &= 0 ; & C_{44} &= .696 \frac{e^2}{2r_0^4} \end{aligned}$$

The value  $c_{11}$  calculated by Madelung's method has been given by Born (1920); he finds the value  $-2.55 \frac{e^2}{2r_0^4}$ . Since we have confined our numerical calculations to an accuracy of 1% the two values agree with each other.

In the following table we compare our results with the experimental values<sup>1)</sup>. The units are

	theoret.	exp	$\text{cm}^2/\text{dyn } 10^{-11}$
$c_{11}$	4.65	4.95	( $\rho = 4.8 \cdot 10^{-10}$ e.s.u.) ( $r_0 = 2.814 \cdot 10^{-8}$ cm)
$c_{12}$	1.28	1.4	
$c_{44}$	1.28	1.28	

It should be noted that the only experimental parameter entering the calculation of  $c_{44}$  is the lattice constant. Since we obtain good agreement for this value it is not surprising that  $c_{11}$  is also in good agreement; for, in the calculation of  $c_{11}$  we have also used the experimental value for the compressibility.

1) The experimental values have been calculated from the elastic moduli  $\Delta_{ij}$  given in Landolt-Börnstein, 1935, 3. Erg. Bd., vol. I, p. 74.  $\Delta_{12}$  has not been measured within 10% error so that  $c_{12}$  is not very useful for comparison.

## IX. Numerical Results for the Coupling Coefficients.

For the purpose of numerical calculation of the coupling coefficients we have chosen the adjustable parameter  $\epsilon$  in equation (6.10) equal to 1. We neglected all terms smaller than 1% of the largest term in each series. Since the series in question converge rapidly this gives an accuracy of 1%-2%

We have calculated all coefficients independently from each other so that the equations (5.12) could be used to check the results. These equations were satisfied in each case within 1%. The only exceptions are  $p_1(6.6.0)$  and  $p_1(6.6.2)$ . In these cases the final coefficients are the differences between two nearly equal quantities and therefore the error is larger than 1%; but the error in the total coefficients, including the repulsive forces, is again not larger than 1% so that it is not worth while to increase the accuracy of the electric part.

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  $\epsilon$ . Each coefficient has therefore been calculated twice by means of numerically/

numerically different series. The agreement in each case was within 1%.

The results are given in the following table (Table I) which contains that part of the coupling coefficients which is due to the Coulomb force. The values are given in units of  $\frac{e^2}{\bar{v}_a}$  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  $\frac{1}{10} \frac{1}{\bar{v}_a}$ ; the numbers describing the wave vector are identical with the components  $\rho_x, \rho_y, \rho_z$  introduced in (6.19). Table II contains the total coupling coefficients for NaCl, obtained by summing the contributions of the Coulomb force and the repulsive force (cf. (1.21)). The latter contribution, of course, depends on the properties of the Na and Cl ions. The coefficients are given again in units of  $\frac{e^2}{\bar{v}_a}$ .

Since the coefficients  ${}^a [{}_{xy}^{kk'}] = 0, x \neq y$ , cf. (7.8) the bracket symbols  ${}^a [{}_{xy}^{kk'}] = [{}_{xy}^{kk'}]$  are already the total coefficients and therefore Table I and Table II represent the whole set of the coefficients for the equation of motion.

$P_x$	$P_y$	$P_z$		${}^c [KK] \frac{U_a}{\bar{c}^2}$	${}^c [KK] \frac{U_a}{\bar{c}^2}$	${}^c [KK] \frac{U_a}{\bar{c}^2}$	${}^c [KK'] \frac{U_a}{\bar{c}^2}$	$[KK'] \frac{U_a}{\bar{c}^2}$	$[KK'] \frac{U_a}{\bar{c}^2}$
10	5	0	1.)	-2.785	+1.594	+1.785	+10.981	0	-10.981
10	4	0		-1.812	+1.640	+1.181	+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		- .714	+1.453	- .714	+10.530	0	-10.530
9	3	3		-1.583	+ .795	+ .795	+11.513	-5.758	-5.758
9	3	1		-2.699	+1.663	+ .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		+ .059	+1.195	-1.298	+8.549	+3.003	-11.548
8	4	2		-1.471	+1.142	+ .339	+10.375	-2.375	-8.003
8	4	0		-1.975	+1.450	+ .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	7	1		+ .795	+ .795	-1.582	+5.758	+5.758	-11.513
7	5	3		- .286	+ .571	- .286	+6.838	0	-6.838
7	5	1		- .894	+ .846	+ .062	+8.148	+1.342	-9.479
7	3	3		-1.859	+ .932	+ .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		+ .140	+ .140	- .274	+4.312	+4.312	-8.615
6	6	0		+ .017	+ .017	- .022	+5.004	+5.004	-9.997
6	4	4		- .552	+ .279	+ .279	+4.933	-2.470	-2.470
6	4	2		-1.594	+ .621	+ .976	+7.120	- .548	-6.566
6	4	0		-2.090	+ .684	+1.428	+8.025	+ .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		- .228	- .228	+ .450	+2.379	+2.379	-4.761
5	5	1		- .600	- .600	+1.214	+3.929	+3.929	-7.845
5	3	3		-1.659	+ .836	+ .836	+5.252	-2.628	-2.628
5	3	1		-3.050	+ .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		- .751	- .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		-	-	-	-	-	-

1) The vector 10.5.0 is really not a vector within our choice. We have, however, considered it since it is one of the corner points of our phase space.



$p_x$	$p_y$	$p_z$	$[KK]_{xx} \frac{U_a}{e^2}$	$[KK]_{yy} \frac{U_a}{e^2}$	$[KK]_{zz} \frac{U_a}{e^2}$	$[KK']_{xx} \frac{U_a}{e^2}$	$[KK']_{yy} \frac{U_a}{e^2}$	$[KK']_{zz} \frac{U_a}{e^2}$
10	5	0	--8.635	-6.256	-8.635	- .364	0	+ .364
10	4	0	- 9.662	-6.210	-7.669	+ .461	+ .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	- .260	0	+ .260
9	3	3	- 9.433	-7.055	-7.055	+ .461	+ .649	+ .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	- .492	- .366	- .066
8	4	2	- 9.321	-6.708	-7.511	+ .837	+ .771	+ .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	7	1	- 7.055	-7.055	-9.432	- .649	- .649	- .461
7	5	3	- 8.136	-7.279	-8.136	+ .169	0	- .169
7	5	1	- 8.744	-7.004	-7.788	+1.056	+ .919	+ .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	+ .583	+ .583	+ .341
6	6	0	- 7.833	-7.833	-7.872	+1.053	+1.053	+ .903
6	4	4	- 8.402	-7.571	-7.571	+1.067	+ .676	+ .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	-	-	-	-	-	-





### X. Evaluation of the Frequencies.

In the case of NaCl ( $s=2$ ) the equations of motion for any given wave vector  $\underline{k}$  constitute a system of 6 homogeneous equations for the amplitudes  $u_{\underline{k}}$  of the vibration. For a nontrivial solution the determinant of the system must vanish. This gives us the secular equation for the frequencies:

$$(9.0) \quad \begin{vmatrix} \{x x\} - \lambda & \{x x\} & \{x y\} & \{x y\} & \{x z\} & \{x z\} \\ \{x x\} & \{x x\} - \lambda & \{x y\} & \{x y\} & \{x z\} & \{x z\} \\ \{y x\} & \{y x\} & \{y y\} - \lambda & \{y y\} & \{y z\} & \{y z\} \\ \{y x\} & \{y x\} & \{y y\} & \{y y\} - \lambda & \{y z\} & \{y z\} \\ \{z x\} & \{z x\} & \{z y\} & \{z y\} & \{z z\} - \lambda & \{z z\} \\ \{z x\} & \{z x\} & \{z y\} & \{z y\} & \{z z\} & \{z z\} - \lambda \end{vmatrix} = 0$$

Here we have normalized the matrix in such a way that

$$(9.1) \quad \{ \begin{matrix} k & k' \\ x & y \end{matrix} \} = - \frac{1}{\sqrt{m_k} \sqrt{m_{k'}}} [ \begin{matrix} k & k' \\ x & y \end{matrix} ]$$

and/

and

$$(9.2) \quad \lambda = \omega^2$$

The matrix belonging to the determinant (9.0) is symmetric since

$$\begin{Bmatrix} \kappa\kappa' \\ xy \end{Bmatrix} = \begin{Bmatrix} \kappa'\kappa \\ yx \end{Bmatrix}$$

as follows from (6.1), (6.2).

In a large number of cases the determinant (9.0) can easily be split up into a product of three determinants. We shall now consider these cases.

1.)  $\underline{q} = (q_x, 0, 0)$ . In this case we have (cf. (6.12) (6.11))

$$\begin{Bmatrix} \kappa\kappa' \\ yy \end{Bmatrix} = \begin{Bmatrix} \kappa\kappa' \\ zz \end{Bmatrix}, \quad \begin{Bmatrix} \kappa\kappa' \\ xy \end{Bmatrix} = \begin{Bmatrix} \kappa\kappa' \\ yz \end{Bmatrix} = \begin{Bmatrix} \kappa\kappa' \\ zx \end{Bmatrix} = 0$$

We introduce for abbreviation the notation

$$a = \begin{Bmatrix} 11 \\ xx \end{Bmatrix}, \quad b = \begin{Bmatrix} 22 \\ xx \end{Bmatrix}, \quad c = \begin{Bmatrix} 12 \\ xx \end{Bmatrix}$$

(9.3)

$$a' = \begin{Bmatrix} 11 \\ yy \end{Bmatrix} = \begin{Bmatrix} 11 \\ zz \end{Bmatrix}, \quad b' = \begin{Bmatrix} 22 \\ yy \end{Bmatrix} = \begin{Bmatrix} 22 \\ zz \end{Bmatrix}, \quad c' = \begin{Bmatrix} 12 \\ yy \end{Bmatrix} = \begin{Bmatrix} 12 \\ zz \end{Bmatrix}$$

The determinant can then be written as the product

$$(9.4) \quad \begin{vmatrix} a-\lambda & c \\ c & b-\lambda \end{vmatrix} \begin{vmatrix} a'-\lambda & c' \\ c' & b'-\lambda \end{vmatrix}^2 = 0$$

and/

and we get the solutions

$$\lambda_{1,2}^e = (\omega_{1,2}^e)^2 = \frac{e^2}{v_a} \left[ \frac{a+b}{2} \pm \sqrt{\left(\frac{a+b}{2}\right)^2 - (ab-c^2)} \right]$$

$$(9.5)_{tr} \lambda_{1,2}^{tr} = (\omega_{1,2}^{tr})^2 = \frac{e^2}{v_a} \left[ \frac{a'+b'}{2} \pm \sqrt{\left(\frac{a'+b'}{2}\right)^2 - (a'b'-c'^2)} \right]$$

By inspection of the equation of motion one finds easily 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.

The numerical results for these wave vectors are contained in Table III. In the first column the wave vectors are given expressed by  $p_x, p_y, p_z$  as in Tables I, II, the frequencies are given in units of  $10^{13} \text{ sec}^{-1}$ . The next two columns give the frequencies of the transverse waves, the last two columns the frequencies of the longitudinal waves. The first of these pairs represents always the 'optical' frequency (+sign of the root), the other one those of the 'elastic' branch (-sign).

2.) For a wave vector  $(10, 9y, 0)$  we find, also because of (6.12), that the determinant splits up into three. The numerical values of the frequencies for this case are given in Table IV. The vibrations are in the  $x, y$  and  $z$  direction.

Table III/

Table III.

$P_x$	$P_y$	$P_z$	$\omega_1^l$	$\omega_2^l$	$\omega_1^{tr}$	$\omega_2^{tr}$	$\cdot 10^{-13} \text{ sec}$
2	0	0	5.87	1.02	2.88	.54	
4	0	0	5.44	1.90	2.94	1.03	
6	0	0	4.87	2.59	3.01	1.42	
8	0	0	4.38	2.99	3.07	1.69	
10	0	0	4.20	3.10	3.09	1.78	

Table IV.

$P_x$	$P_y$	$P_z$	$\omega_1^x$	$\omega_2^x$	$\omega_1^y$	$\omega_2^y$	$\omega_1^z$	$\omega_2^z$	$\cdot 10^{-13} \text{ sec}$
10	2	0	4.03	3.06	3.05	1.96	3.13	2.01	
10	4	0	3.63	2.90	2.95	2.28	3.28	2.52	
10	5	0	3.43	2.75	2.91	2.35			

In the case  $(10, 9, 0)$  we have <sup>in general</sup> three different determinants.

Only in the case  $(10, 5, 0)$  we have because of the symmetry

$$[K K']_{10,5,0} = [Z Z']_{10,5,0} \quad (\text{cf. Table II})$$

only two different determinants, but the frequencies are to be counted twice.

The/

The frequencies for the cases (10.5.0), (10.0.0), (5.5.5) [and (0.0.0)] have already been calculated by Herzfeld and Lyddane. Their values for the electric part of the coefficients agree with ours, but there is a difference in the constants  $A$  and  $B$  which are due to the repulsive forces. The authors obtain for  $A : 10.606, B : 1.073$ . cf. (7.4). This is due to the fact that they use the repulsive potential of Born and Mayer's (1932) for the calculation of these constants, thus neglecting the London forces.

3.)  $q_x = q_y = q_z$  . We have the following identities:

$$(9.7) \quad \begin{aligned} a &= \left\{ \begin{matrix} 11 \\ xx \end{matrix} \right\} = \left\{ \begin{matrix} 11 \\ yy \end{matrix} \right\} = \left\{ \begin{matrix} 11 \\ zz \end{matrix} \right\}, & d &= \left\{ \begin{matrix} 11 \\ xy \end{matrix} \right\} = \left\{ \begin{matrix} 11 \\ yz \end{matrix} \right\} = \left\{ \begin{matrix} 11 \\ zx \end{matrix} \right\} \\ b &= \left\{ \begin{matrix} 22 \\ xx \end{matrix} \right\} = \left\{ \begin{matrix} 22 \\ yy \end{matrix} \right\} = \left\{ \begin{matrix} 22 \\ zz \end{matrix} \right\}, & f &= \left\{ \begin{matrix} 22 \\ xy \end{matrix} \right\} = \left\{ \begin{matrix} 22 \\ yz \end{matrix} \right\} = \left\{ \begin{matrix} 22 \\ zx \end{matrix} \right\} \\ c &= \left\{ \begin{matrix} 12 \\ xx \end{matrix} \right\} = \left\{ \begin{matrix} 12 \\ yy \end{matrix} \right\} = \left\{ \begin{matrix} 12 \\ zz \end{matrix} \right\}, & e &= \left\{ \begin{matrix} 12 \\ xy \end{matrix} \right\} = \left\{ \begin{matrix} 12 \\ yz \end{matrix} \right\} = \left\{ \begin{matrix} 12 \\ zx \end{matrix} \right\} \end{aligned}$$

The secular determinant gives

$$(9.8) \quad \begin{vmatrix} a+2d-1 & c+2e \\ c+2e & b+2f-1 \end{vmatrix} \begin{vmatrix} a-d-1 & c-e \\ c-e & b-f-1 \end{vmatrix} = 0.$$

We obtain again two longitudinal and twice two transversal waves with the frequencies:

$$(9.9) \quad \begin{aligned} \lambda_{1,2}^L &= (\omega_{1,2}^L)^2 = \frac{e^2}{v_a^2} \left[ \frac{\alpha+\beta}{2} \pm \sqrt{\left(\frac{\alpha+\beta}{2}\right)^2 - (\alpha\beta - \gamma^2)} \right] \\ \lambda_{1,2}^{tr} &= (\omega_{1,2}^{tr})^2 = \frac{e^2}{v_a^2} \left[ \frac{\alpha'+\beta'}{2} \pm \sqrt{\left(\frac{\alpha'+\beta'}{2}\right)^2 - (\alpha'\beta' - \gamma'^2)} \right] \end{aligned}$$

The/

$$\begin{aligned} \alpha &= a+2d & \alpha' &= a-d \\ \beta &= b+2f & \beta' &= b-f \\ \gamma &= c+2e & \gamma' &= c-e \end{aligned}$$

The numerical results are given in Table V.

4.)  $q_x = q_y, q_z = 0$ . We have the identities:

$$(9.10) \quad \begin{aligned} a &= \left\{ \begin{matrix} 'x' \\ 'x' \end{matrix} \right\} = \left\{ \begin{matrix} 'y' \\ 'y' \end{matrix} \right\} & \bar{a} &= \left\{ \begin{matrix} 'z' \\ 'z' \end{matrix} \right\} \\ b &= \left\{ \begin{matrix} 'z' \\ 'z' \end{matrix} \right\} = \left\{ \begin{matrix} 'y' \\ 'y' \end{matrix} \right\} & \bar{b} &= \left\{ \begin{matrix} 'z' \\ 'z' \end{matrix} \right\} \\ c &= \left\{ \begin{matrix} 'z' \\ 'x' \end{matrix} \right\} = \left\{ \begin{matrix} 'z' \\ 'y' \end{matrix} \right\} & \bar{c} &= \left\{ \begin{matrix} 'z' \\ 'z' \end{matrix} \right\} \\ d &= \left\{ \begin{matrix} 'x' \\ 'y' \end{matrix} \right\}, f = \left\{ \begin{matrix} 'z' \\ 'x' \end{matrix} \right\}, e = \left\{ \begin{matrix} 'z' \\ 'y' \end{matrix} \right\} \end{aligned}$$

All other coefficients vanish. The secular equation is

$$(9.11) \quad \left| \begin{array}{cc|cc|cc} a+d-\lambda & c+e & a-d-\lambda & c-e & \bar{a}-\lambda & \bar{c} \\ c+e & b+f-\lambda & c-e & b-f-\lambda & \bar{c} & \bar{b}-\lambda \end{array} \right| = 0$$

We obtain two longitudinal and four transverse waves with the frequencies

$$(9.12) \quad \begin{aligned} \lambda_{1,2}^l &= (\omega_{1,2}^l)^2 = \frac{c^2}{v_a^2} \left[ \frac{\alpha+\beta}{2} \pm \sqrt{\left(\frac{\alpha+\beta}{2}\right)^2 - (\alpha\beta - \gamma^2)} \right] & \alpha &= a+d, \gamma = c+e \\ & & \beta &= b+f, \delta = c-e \\ \lambda_{1,2}^{tr} &= (\omega_{1,2}^{tr})^2 = \frac{c^2}{v_a^2} \left[ \frac{\alpha'+\beta'}{2} \pm \sqrt{\left(\frac{\alpha'+\beta'}{2}\right)^2 - (\alpha'\beta' - \delta'^2)} \right] & \alpha' &= a-d, \delta' = c-e \\ & & \beta' &= b-f, \delta' = c-e \\ \lambda_{3,4}^{tr} &= (\omega_{3,4}^{tr})^2 = \frac{c^2}{v_a^2} \left[ \frac{\bar{a}+\bar{b}}{2} \pm \sqrt{\left(\frac{\bar{a}+\bar{b}}{2}\right)^2 - (\bar{a}\bar{b} - \bar{c}^2)} \right] \end{aligned}$$

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

The numerical results are collected in Table VI.

Table V/

Table V.

$p_x$	$p_y$	$p_z$	$\omega_1^l$	$\omega_2^l$	$\omega_1^{tv}$	$\omega_2^{tv}$	$\cdot 10^{-13} \text{ sec}^{-1}$
1	1	1	5.94	.84	2.84	.51	
2	2	2	5.71	1.67	2.77	.99	
3	3	3	5.33	2.48	2.65	1.42	
4	4	4	4.86	3.22	2.50	1.77	
5	5	5	4.52	3.64	2.40	1.93	

Table VI.

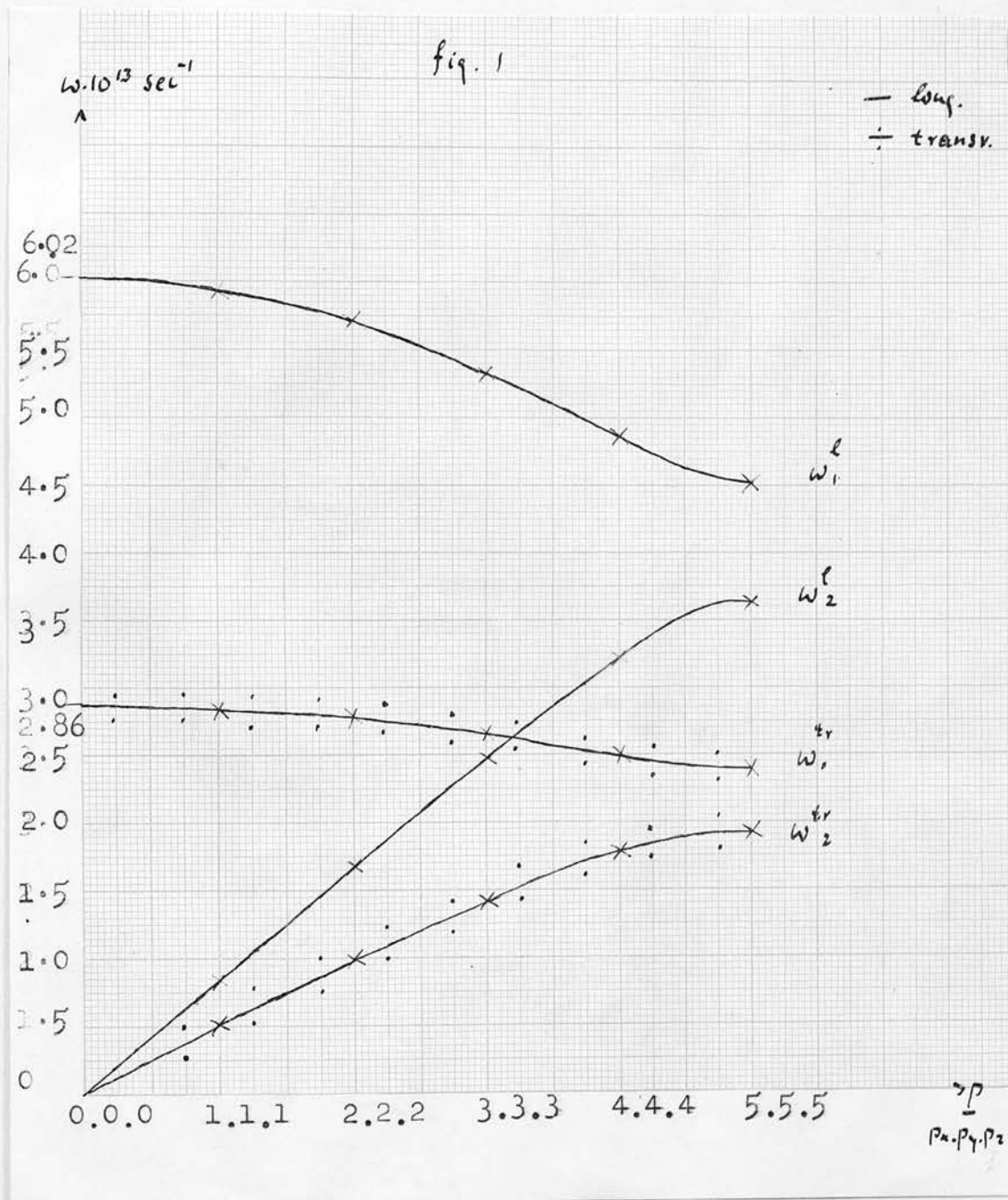
$p_x$	$p_y$	$p_z$	$\omega_1^l$	$\omega_2^l$	$\omega_1^{tv}$	$\omega_2^{tv}$	$\omega_3^{tv}$	$\omega_4^{tv}$	$\cdot 10^{-13} \text{ sec}$
2	2	0	5.78	1.35	2.75	.86	2.91	.79	
4	4	0	5.09	2.39	2.49	1.65	3.03	1.69	
6	6	0	4.05	2.89	2.54	1.96	3.31	2.58	

We have plotted the frequencies for the intervals  $p=(0.0.0) - p=(10.0.0)$ ,  $p=(0.0.0) - p=(5.5.5)$  (Tables VII and VIII). For the limiting case  $(0.0.0)$  we obtain two values, one for longitudinal waves  $10^{13.2}$  given by  $\left[ (A+2B) + \frac{8\pi}{3} \right] \frac{c^2}{v_a} = 6.02 \cdot 10^{13.2} \text{ sec}^{-1}$  and one for transverse waves:  $\left[ (A+2B) - \frac{4\pi}{3} \right] \frac{c^2}{v_a} = 2.86$ . Since the constants  $A$  and  $B$  enter we obtain slightly smaller values of the limiting frequencies than Herzfeld and Lyddane have found (cf. p. 56).

Herzfeld and Lyddane assumed that these limiting frequencies are the frequencies of the residual rays (Reststrahlen) and obtain in this way two different frequencies for longitudinal and transverse waves. We cannot agree with that assumption. One obtains two different values only by taking the electrostatic representation of the coefficients (3.23), (3.27) and proceeding to the limit  $k \rightarrow 0$ . But in this limiting case the effect of the retardation represented by the appearance of the reciprocal wave length in vacuo  $k_0$  in our formula (4.20) can not be neglected.



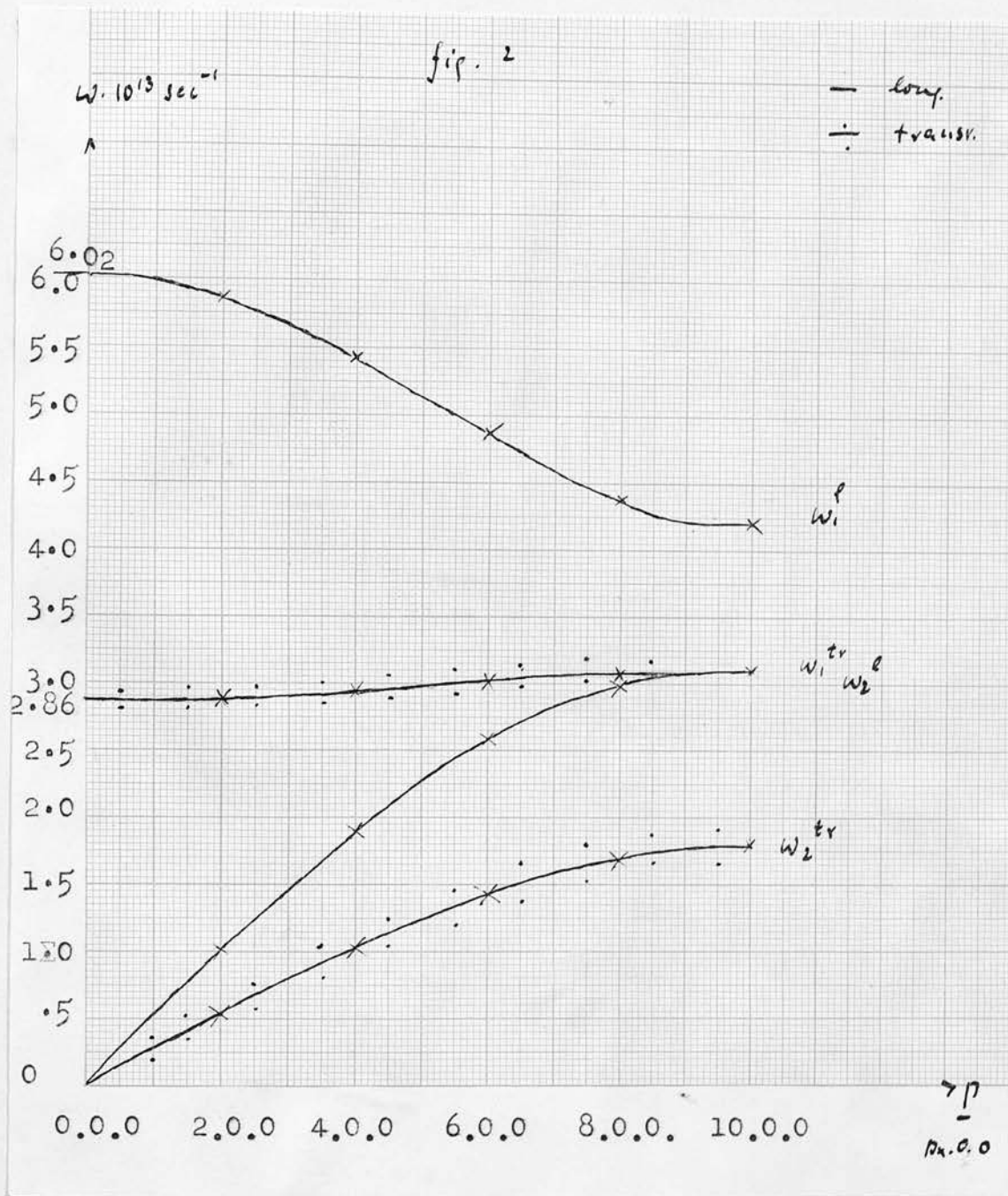
Table VII.



$$\rho_x = \rho_y = \rho_z$$

Table VIII.

I am very much indebted to Professor M. Kern who



p. 0. 0.

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

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