Lattice Vibrations in Polar Crystals

R. H. LYDDANE, *The Johns Hopkins University, Baltimore, Maryland*

AND

K. F. HERZFELD, *The Catholic University of America, Washington, D. C.*

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This paper investigates the free vibrations of a polar crystal of the sodium chloride type. The main purpose is the calculation of the Coulomb force, which has been done by an extension of the Madelung method. For numerical evaluation, a short range repulsion is assumed, and the van der Waals forces are neglected. The results are: For long waves one finds in the acoustical branch three waves whose frequencies are inversely proportional to the wave-length, in agreement with Born. The optical branch has two transverse waves (Reststrahlen) with a Coulomb force of $4\pi/3$ times the polarization, as Born has calculated, and one longitudinal one with a Coulomb force of $-8\pi/3$ times the polarization. For short waves the vibrations are in general not exactly transverse or longitudinal, but even in the optical branch there remain separate modes of vibration with different frequencies for a given wave-length. In addition, the neutral simple cubic lattice is considered. It is shown that the free vibrations are characterized by $D=0$. The influence of the shape of the crystal is discussed.

I. INTRODUCTION

THE problem of vibrations in crystals is important for many of their properties; for example, the specific heat and the optical behavior. Accordingly, it has been treated by many authors. A group of papers investigates the distribution of the frequencies under the simplifying assumption that each particle is bound only to its neighbors. This treatment was originated by Born and v. Kármán,[1] a simplified procedure introduced by Debye,[2] and much new information gained in recent papers by Blackman.[3] On the other hand, electric forces play a considerable role in many cases, and their range is so great that the above assumption is not a good approximation. The problem of calculating the electric force which is exerted on one particle by all the others during oscillation was attacked by Born[4] for long transverse waves in polar cubic crystals. His result was in agreement with the formula for the so-called Lorentz-Lorenz force, which expresses the interaction of the polarized molecules in the quasi-statical case. Born used his value for all possible modes of vibration in these crystals. Since 1912 Ewald[5] has been working on a method to calculate the propagation of electromagnetic waves in crystals. His interest lies mainly in the dispersion of light and propagation of x-rays, but his method is applicable also to the present problem. He himself has made calculations only on transverse waves. Thompson,[6] however, has developed the general formula for the propagation of arbitrary vibrations. Broch,[7] has recently started an investigation of the proper vibrations of a one-dimensional polar lattice.

This paper is intended to answer the following questions: First of all, no actual calculation of the electric force has been made for waves comparable with the lattice distance. According to the preceding theories, such waves are of prime importance to the specific heat. Secondly, Born's results seem to conflict with the direct calculation made by Herzfeld for another purpose. (See Section V.) Thirdly, the preceding methods leave some questions of principle in doubt. While it seems physically clear that the properties of the crystal (at least, at temperatures somewhat removed from the absolute zero) should be independent of the form, the electro-

[1] M. Born and Th. v. Kármán, Physik. Zeits. **13**, 297 (1912).
[2] P. Debye, Ann. d. Physik **39**, 789 (1912).
[3] M. Blackman, Zeits. f. Physik **86**, 421 (1933); Proc. Roy. Soc. **A148**, 384 (1935); Proc. Roy. Soc. **A159**, 416 (1937).
[4] M. Born, Ann. d. Physik **61**, 87 (1920).
[5] P. P. Ewald, Ann. d. Physik **49**, 1, 117 (1916).
[6] M. Born and J. H. C. Thompson, Proc. Roy. Soc. **A147**, 594 (1934); J. H. C. Thompson, Proc. Roy. Soc. **A149**, 487 (1935).
[7] E. Broch, Proc. Camb. Phil. Soc. **33**, 485 (1937).

static forces converge so badly that it does not seem obvious that the physical result is reconcilable with the assumption of electrostatic forces. It is true that Born[8] has given reasons for this independence of the form, but a more detailed investigation seemed advisable.

II. The Forces and Frequencies in a General Crystal

To calculate the frequencies of a vibrating crystal, one assumes that the crystal is in a definite state of vibration, and calculates the force on one constituent particle due to all the others, under the assumption that the distortion from the equilibrium position is small. This restoring force will be linear in the displacements of the constituent particles (the assumption of small displacements implying that the vibrations will be harmonic), so that one has the usual secular equation for harmonic motion with many degrees of freedom to solve for the frequencies pertaining to the previously fixed state of vibration.

The first question then, is the determination of the state of vibration of the crystal; that is, what function of its position in the crystal is the displacement of a particle. This will be, as in the case of an elastic continuum, largely influenced by the boundary conditions, which in turn depend upon the shape of the crystal, among other things. One knows, however, from the work of Weyl, that the influence of the boundary conditions on the higher frequencies is small if the crystal is large, provided the forces have a short range. This question will not be further investigated here; what is more interesting is the question whether, in a polar lattice, the very slow decrease of the Coulomb force with increasing separation will cause particles at great distances to contribute noticeably to the force on a given particle of the crystal, and thus cause the shape of the crystal to influence the frequency spectrum. In accordance with the above, the boundary conditions to be imposed here are to be those which make the calculations as simple as possible. They will be those characterizing the "periodic lattice" introduced by Born.[8] The assumption here is that one has a crystal block, whose sides are parallel to those of the unit cell, of dimensions $G_1 \times G_2 \times G_3$ cells, which one builds up to an infinite lattice by adding other blocks of the same shape and size. The boundary conditions to be imposed are that the displacements of two particles at corresponding points in any two blocks are the same. It will be shown later that the influence of the other blocks on the forces, and hence the frequencies, is really not great.

One should assume standing waves in the lattice (compatible with the boundary conditions), but since the force at a lattice point is linear in the displacements of the particles causing it, provided that the latter are small, one can, instead, write the standing wave as a linear combination of progressive waves, work with a progressive wave, and take a linear combination of the forces at the end. In the interest of simplicity of calculation, this will be done.

Let us consider first a general lattice, with a unit cell specified by the three vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. The cells are distinguished by the index l which is an abbreviation for the triple of integers l_1, l_2, l_3; the particles in a cell are distinguished by the index k. The equilibrium position of the kth particle in the lth cell is given by $\mathbf{r}(k;l) = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 + \mathbf{r}(k;0)$; $\mathbf{r}(k;0)$ is the equilibrium position of the kth particle in the origin cell. The displacement of the l, kth particle at any time is assumed to be

$$\mathbf{u}(k;l) = \mathbf{U}(k) \exp\{-i\omega t + i(\mathbf{s}\cdot\mathbf{r}(k;l))\}, \quad (1)$$

where $\mathbf{U}(k)$ is a vector giving the characteristic amplitude of the particle of type k. The direction of the vector $\mathbf{s}$ is the direction of propagation of the wave, and its magnitude is 2π divided by the wave-length.

The assumption of a periodic lattice made above now yields the condition that

$$\mathbf{s} = \pi(n_1/G_1)\mathbf{b}_1 + (n_2/G_2)\mathbf{b}_2 + (n_3/G_3)\mathbf{b}_3.$$

The $\mathbf{b}$'s are the lattice vectors inverse to the $\mathbf{a}$'s and n_1, n_2, and n_3 are integers, $-G_i < n_i \leqslant G_i$.

If $\mathbf{K}(k;l)$ is the force on the l, kth particle, the equations of motion are

$$m_k \partial^2\mathbf{u}(k;l)/\partial t^2 = \mathbf{K}(k;l). \quad (2)$$

[8] For this, as indeed for almost all the notation used in this paper, see the article by M. Born and M. Göppert-Mayer, *Handbuch der Physik* XXIV/2, p. 623.

If the potential energy of the interaction between two particles of types k and k', whose difference in position is $\mathbf{r}$, is given by $\phi_{kk'}(|\mathbf{r}|)$, then

$$K_x(k;l)=-\mathop{\mathbf{S}'}_{l'}\sum_{k'}[(\partial/\partial x)\phi_{kk'}(|\mathbf{r}|)]_{\mathbf{r}'}$$

$$\mathbf{r}'=\mathbf{r}(kk';l-l')+\mathbf{u}(k;l)-\mathbf{u}(k';l').$$

The symbol $\mathbf{S}$ indicates the summation over the three indices abbreviated by l'; the prime attached indicates that the l, kth particle is to be omitted. $\mathbf{r}(kk';l-l')$ is defined as $\mathbf{r}(k;l)-\mathbf{r}(k';l')$.

Since the displacements are small, this can be developed in a Taylor series, in which only terms to the first degree in the displacement are preserved:

$$K_x(k;l)=-\mathop{\mathbf{S}'}_{l'}\sum_{k'}[(\partial/\partial x)\varphi_{kk'}(|\mathbf{r}|)]_{\mathbf{r}=\mathbf{r}(kk';\,l-l')}$$

$$-\sum_y\mathop{\mathbf{S}'}_{l'}\sum_{k'}[(\partial^2/\partial x\partial y)\varphi_{kk'}(|\mathbf{r}|)]_{\mathbf{r}=\mathbf{r}(kk';\,l-l')}$$

$$\times(u_y(k;l)-u_y(k';l')).$$

Here the first term represents the force on a particle in the equilibrium lattice, which must vanish. Writing

$$\varphi_{xy}(kk';l-l')=[(\partial^2/\partial x\partial y)\varphi_{kk'}(|\mathbf{r}|)]_{\mathbf{r}=\mathbf{r}(kk';\,l-l')}$$

and substituting for $\mathbf{u}(k;l)$ its value from Eq. (1), we obtain

$$K_x(k;l)=\exp\{-i\omega t+i(\mathbf{s}\cdot\mathbf{r}(k;l))\}$$
$$\times\{\sum_y\mathop{\mathbf{S}'}_{l'}\sum_{k'}U_y(k')\varphi_{xy}(kk';l-l')$$
$$\times\exp[-i(\mathbf{s}\cdot\mathbf{r}(k';l'))]$$
$$-\sum_y U_y(k)\mathop{\mathbf{S}'}_{l'}\sum_{k'}\varphi_{xy}(kk';l-l')\}.$$

The first term here represents the force on the l, kth particle in its equilibrium position due to the displacements of the other particles; the second the force on the displaced l, kth particle due to the undisplaced lattice of the other particles. The possibility of breaking the force into these two terms rests, of course, on the assumption of small displacements. The second term, in a cubic holohedry, is zero, as will be shown later.

Since in a polar lattice the interaction between two particles (ions) is the sum of their Coulomb interaction and other terms, (van der Waals and repulsive) and since only the Coulomb part presents any difficulty in evaluation, one breaks the force $\mathbf{K}(k;l)$ into the sum of two terms

$$[e_k(\mathbf{F}(k)+\mathbf{G}(k))+\mathbf{R}(k)]\exp\{-i\omega t+i(\mathbf{s}\cdot\mathbf{r}(k;l))\}$$

where $\mathbf{F}(k)+\mathbf{G}(k)$ represents (except for the phase factor) the electric field of the contribution of the Coulomb interaction to the force, and $\mathbf{R}(k)$ the part of the force due to all other interactions. $\mathbf{F}(k)$ is that term in the field due to the displacements of other particles; $\mathbf{G}(k)$ that due to the displacement of the particle l, k. If the Coulomb interaction is denoted by $\psi_{kk'}(|\mathbf{r}|)=(e_ke_{k'})/|\mathbf{r}|$ and the coefficients $(kk';xy)$ and $[kk';xy]$ defined by

$$(kk';\,xy)=\mathop{\mathbf{S}'}_{l'}\psi_{xy}(kk';l-l')$$
$$\times\exp[-i(\mathbf{s}\cdot\mathbf{r}(kk';l-l'))],\quad(4)$$
$$[kk';xy]=\mathop{\mathbf{S}'}_{l'}\psi_{xy}(kk';l-l'),$$

then the Coulomb field, from Eq. (3), is

$$F_x(k)=(1/e_k)\sum_y\sum_{k'}(kk';xy)U_y(k'),$$
$$G_x(k)=-(1/e_k)\sum_y\sum_{k'}[kk';xy]U_y(k).$$

One observes that $[kk';xy]$ is the value that $(kk';xy)$ assumes when $\mathbf{s}=\mathbf{0}$, i.e., for infinitely long waves. $(\mathbf{s}\cdot\mathbf{r}(kk';l-l'))$ is simply the phase difference between the l, kth and l', kth particles.

If $(kk';xy)_a$ and $[kk';xy]_a$ are defined as the corresponding quantities for the repulsive interaction, so that

$$R_x(k)=\sum_y\sum_{k'}\{(kk';xy)_aU_y(k')$$
$$-[kk';xy]_aU_y(k)\},$$

and substitutions in Eq. (2) are made for $\mathbf{u}(k;l)$ and $\mathbf{K}(k;l)$, the equations of motion assume the form:

$$-m_k\omega^2U_x(k)=\sum_y\sum_{k'}\{[(kk';xy)+(kk';xy)_a]U_y(k')$$
$$-[[kk';xy]+[kk';xy]_a]U_y(k)\}.\quad(5)$$

These form a set of $3k$ linear homogeneous equations in $3k$ unknowns; the condition that the determinant of the coefficients vanish gives the usual secular equation for the frequencies.

The problem now is to calculate the coefficients $(kk';xy)$ for a general value of s. First, $\psi_{xy}(kk';l-l')$ may be written as

$$[(\partial^2/\partial x\partial y)\psi_{kk'}(|\mathbf{r}-\mathbf{r}(k';l')|)]_{\mathbf{r}=\mathbf{r}(k;\,l)},$$

so that

$$\begin{aligned}(kk';xy)=&\sum_{l}{}'[(\partial^2/\partial x\partial y)\psi_{kk'}(|\mathbf{r}-\mathbf{r}(k';l')|)]_{\mathbf{r}=\mathbf{r}(k;\,l)}\\&\times\exp[-i(\mathbf{s}\cdot\mathbf{r}(kk';l-l'))]\\=&[\sum_{l}{}'(\partial^2/\partial x\partial y)\exp[-i(\mathbf{s}\cdot\mathbf{r}(kk';l-l'))]\\&\times\psi_{kk'}(|\mathbf{r}-\mathbf{r}(k';l')|)]_{\mathbf{r}=\mathbf{r}(k;\,l)},\end{aligned}$$

or if the convergence of the series is sufficiently good,

$$\begin{aligned}(kk';xy)=&[(\partial^2/\partial x\partial y)\sum_{l}{}'\exp[-i(\mathbf{s}\cdot\mathbf{r}(kk';l-l'))]\\&\times\psi_{kk'}(|\mathbf{r}-\mathbf{r}(k';l')|)]_{\mathbf{r}=\mathbf{r}(k;\,l)}.\end{aligned}$$

While this may seem a slightly dubious procedure in the case of the poorly convergent Coulomb interaction, we will proceed with it, and show that it is justified by the results.

Putting in $(e_ke_{k'})/|\mathbf{r}|$ for $\psi_{kk'}(|\mathbf{r}|)$, one may write

$$F_x(k)\exp[-i\omega t+i(\mathbf{s}\cdot\mathbf{r}(k;l))]$$

as

$$\begin{aligned}-\exp(-i\omega t)\sum_{y}\sum_{k'}&e_{k'}U_y(k')[(\partial^2/\partial x\partial y)\sum_{l'}{}'\\&\times\exp[i(\mathbf{s}\cdot\mathbf{r}(k';l'))](|\mathbf{r}-\mathbf{r}(k';l')|)^{-1}]_{\mathbf{r}=\mathbf{r}(k;\,l)}\end{aligned}$$

or in a somewhat different form,

$$\begin{aligned}[-\partial/\partial x\sum_{y}\partial/\partial y\sum_{l'}{}'\sum_{k'}&e_{k'}U_y(k')\\&\times\exp\{-i\omega t+i(\mathbf{s}\cdot\mathbf{r}(k';l'))\}\\&\times(|\mathbf{r}-\mathbf{r}(k';l')|)^{-1}]_{\mathbf{r}=\mathbf{r}(k;\,l)}.\end{aligned}$$

The interpretation of this expression is the following. The sum over l' and k' gives the electric potential at an arbitrary point $\mathbf{r}$ due to a set of charges $e_{k'}U_y(k')\exp[-i\omega t+i(\mathbf{s}\cdot\mathbf{r}(k';l'))]$ at the lattice points. Differentiation with respect to y gives the potential of a set of dipoles at the lattice points; the moments of the dipoles are in the y direction, and the magnitude of the moment of the l', k'th dipole is

$$e_{k'}U_y(k')\exp[-i\omega t+i(\mathbf{s}\cdot\mathbf{r}(k';l'))].$$

The summation over y adds in the potentials of corresponding sets of dipoles in the x and z directions, the differentiation with respect to x gives the x component of the field, and the evaluation gives the field at the l, kth lattice point. This expression then, as is physically obvious, also could be obtained by replacing each displaced charge in the lattice by an undisplaced charge plus a dipole plus a quadrupole plus and so on. Neglecting the higher poles, and observing that the force due to the undisplaced charges is zero, we obtain the above result for the field, since the dipole put in the l', k'th position must have a vector moment equal to the product of the charge and the displacement, or

$$e_{k'}\mathbf{U}(k')\exp[-i\omega t+i(\mathbf{s}\cdot\mathbf{r}(k';l'))].$$

The coefficient $(kk';xy)$ therefore, except for a factor represents the field in the x direction due to a polarization in the y direction of the simple lattice k', whose magnitude varies periodically in space.

The procedure to be followed to calculate the Coulomb force may, then, be summarized as follows: one sets at each point l' of the simple lattice k' a charge $\exp[-i(\mathbf{s}\cdot\mathbf{r}(kk';l-l'))]$, finds the potential due to this "auxiliary lattice" of charges at an arbitrary point, differentiates twice, with respect to x and to y, and evaluates at the point l, k. The result multiplied by $e_ke_{k'}$ is the value of $(kk';xy)$, which is to be substituted in Eq. (5). It must be noted that $(kk';xy)$ is symmetric with respect to interchange of x and y, from its definition. Furthermore, the following relation holds:

$$(kk';xx)+(kk';yy)+(kk';zz)=0.$$

This, of course, is simply the Laplace equation, as appears from the definition of the coefficients, because one is calculating the exciting field; that is, the field at the position of a dipole after the removal of that dipole; and after the removal of the dipole there is no charge at the lattice point. Born writes instead on the right side

$-(4\pi e)/\Delta$ because he considers a uniform compensating charge extending over the crystal. If the crystal is polarized and the charges are displaced, this uniform compensating charge also has to be displaced, and gives under certain conditions a surface charge, which just compensates the effect of the right side and is responsible for the difference of force between transverse and longitudinal waves of great wave-length.

We are using the static potential for the electric field, neglecting any retardation. It is obvious that this is permissible if the wave-length of the particle wave is short compared with the wave-length of the light wave with the same frequency, that is, if $\omega/c \ll |\mathbf{s}|$. This is, for a polar lattice, always fulfilled for the acoustical branch and the short waves of the optical branch, but one might doubt its validity for the long waves of the optical branch. However, the direct calculation of Ewald[5] gives for the long transverse waves of the optical branch (Reststrahlen) the same result as the static calculation,[9] and therefore we feel justified in applying it also to the long longitudinal ones.

It is appropriate to consider here the effect of the other blocks which have been added to the crystal to make an infinite lattice. If the wave-length is finite in all three coordinate directions, the first nonvanishing moment of a block is one of the fourth order, which is proportional to the wave-length times the size of the block, cubed. The field at a distance is therefore that of a fifth-order pole, and the ratio of the effect of all the other blocks to the effect of the infinite crystal will be of the order of magnitude of the wave-length divided by the size of the block, cubed. Now, in a macroscopic crystal the number of vibrations with a wave-length comparable to the size of the crystal is extremely small, and it is precisely these vibrations which are strongly influenced by the boundary conditions, even for short-range interactions. Hence, the effect of the other blocks is, for all practical purposes, negligible.

[9] J. H. C. Thompson, reference 6, discusses the problem of retardation in general according to the Ewald method and finds for long waves one term in which it has to be taken into account. But this term represents that wave which in the infinite crystal compensates the primary light wave.

III. Polar Cubic Crystals

The present calculation for polar lattices will be concerned exclusively with the lattice of the sodium chloride type. In order to discuss the solutions of the secular equation, we must make some assumption about the form of the short range interaction. For simplicity we assume that this interaction acts only between nearest neighbors and that the potential energy of interaction is of the form $f(r)$. Letting $(\partial^2 f/\partial r^2)_{r=a} = 4\pi e^2 c_1/a^3$ and $(\partial f/r\partial r)_{r=a} = 4\pi e^2 c_2/a^3$ where a is the distance between nearest neighbors, one can immediately write down the coefficients of the repulsive force. They are all zero with the exception of $(12; xx)_a$ and $[12; xx]_a$ in which x assumes the values x, y, and z:

$$(12; xx)_a = (4\pi e^2/a^3)[c_1 \cos as_x + c_2(\cos as_y + \cos as_3)], \quad (6)$$

$$[12; xx]_a = (4\pi e^2/a^3)(c_1 + c_2).$$

The lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are orthogonal for the NaCl lattice, and may be taken in the directions of the three coordinate axes. Then for this lattice $\mathbf{s} = (\pi/a)(n_1/G_1, n_2/G_2, n_3/G_3)$. It will be convenient to define a vector $\boldsymbol{\tau}$ by $\mathbf{s} = (2\pi/a)\boldsymbol{\tau}$. It will be much simpler not to divide the lattice up into cells, but to consider it as comprised of two simple lattices, that of the positive ions, and that of the negative. Then k assumes only two values, of which 1 will be taken to refer to the positive ions, and 2 to the negative ions. Since every positive ion is surrounded by positive ions in precisely the same way that every negative ion is surrounded by negative ions, $(11; xy) = (22; xy)$. Similarly $(12; xy)$ must be $= (21; xy)$.

Let us consider the range of possible values of $\boldsymbol{\tau}$. Since, as stated in Section II, $|n_i| \leqslant G_i$, and $\tau_i = n_i/2G_i$, $|\tau_i| \leqslant \frac{1}{2}$. The discussion, however, can be limited to positive values of all three components of $\boldsymbol{\tau}$ since changing the sign of one of them changes no physical feature of the wave. Furthermore, if τ_1, τ_2, τ_3 are replaced by $\frac{1}{2}-\tau_1$, $\frac{1}{2}-\tau_2$, $\frac{1}{2}-\tau_3$, respectively, one has the same wave as before, since this is equivalent to replacing $\mathbf{U}(2)$ by its negative. One will obtain the same frequencies, and the same relation between the amplitudes except for this change in sign. Finally, any permutation of τ_1, τ_2, τ_3 gives again

a wave with the same frequencies and amplitude ratios.[10] This does not appear from the form of the coefficients for the Coulomb force given below, but calculation of their values shows it to be true, as it must be. Thus one can restrict oneself to values of τ given by $0<\tau_1<\frac{1}{2}$, $0<\tau_2<\frac{1}{4}$, $0<\tau_3<\frac{1}{4}$.

One of the simple lattices, the lattice of positive ions, for example, in this crystal forms a face-centered cubic array. The "auxiliary lattice" will be for simplicity considered to be simple cubic. The points are identified only by the values of l' and the charge at the point l' is $\exp[-2\pi i(\tau\cdot 1-1')]f(l_1'+l_2'+l_3')$ where $f(n)=0$ if n is odd, and 1 if n is even (obviously $f(n+2)=f(n)$), and 1′ is a vector defined as (l_1', l_2', l_3'). A point of this lattice where the charge is zero is a point of the lattice of negative ions; one where the charge is different from zero is a point of the lattice of positive ions. Then to find $(11; xy)$ or $(21; xy)$ by the procedure stated above, the calculation is exactly the same up to the final evaluation at the point l. This is to be made at a point for which the charge of the auxiliary lattice is not zero ($l_1+l_2+l_3$ is even) to get $(11; xy)$; at a point for which the charge is zero ($l_1+l_2+l_3$ odd) to get $(21; xy)$.

The potential of the auxiliary lattice will be found here by an extension of the Madelung method.[11] The simple cubic lattice is broken up into lines and planes of points in the usual manner of this method. The lines are taken parallel to the x axis and the planes normal to the z axis. The lattice sums are divided into three parts: (0) the sum over the line containing the point l; (1) the sum over the other lines in the same plane; and (2) the sum over the other planes. 0, 1, and 2 will be used as indices to distinguish the parts of the coefficients coming from each of these three partial sums, so that

$$(kk'; xy)=(kk'; xy)_0+(kk'; xy)_1+(kk'; xy)_2.$$

The separate evaluation of the three parts of each coefficient follows.

0. The evaluation of $(kk'; xy)_0$ may be carried out most easily by directly differentiating term by term the sum giving the potential due to the points in the line containing the point l. If the general point in the lattice be denoted by l', the points in this sum are those for which $l_1'=l_1+\mu$, $l_2'=l_2$, and $l_3'=l_3$, where μ is a non-zero integer. Hence $\mathbf{r}(l-l')=(\mu a, 0, 0)$. As a sample, $(11; xx)_0$ will be calculated explicitly; only the results for the others will be given. The charge at a point,

$$f(l_1'+l_2'+l_3')\exp[-2\pi i(\tau\cdot 1-1')]$$
$$=f(l_1+\mu+l_2+l_3)\exp(2\pi i\tau_x\mu).$$

Since for $(11; xx)_0$, $l_1+l_2+l_3$ is to be taken as even, this becomes $f(\mu)\exp(2\pi i\tau_x\mu)$. Furthermore

$$[\partial^2/\partial x^2(|\mathbf{r}-\mathbf{r}(l')|)^{-1}]_{\mathbf{r}=\mathbf{r}(l)}$$
$$=[3(x(l-l'))^2-(r(l-l'))^2]/(r(l-l'))^5=2/|\mu a|^3.$$

Combining these, we obtain

$$(11; xx)_0=e^2\sum_{\mu=-\infty}^{+\infty}{}' f(\mu)\exp(2\pi i\tau_x\mu)(2/|\mu a|^3)$$
$$=(4e^2/a^3)\sum_{\mu=1}^{\infty}(f(\mu)\cos 2\pi\tau_x\mu)/\mu^3$$
$$=(4e^2/a^3)\sum_{\nu=1}^{\infty}(\cos 2\pi\tau_x(2\nu))/(2\nu)^3$$

from the definition of f. Similarly $(11; yy)_0=(11; zz)_0=-(\frac{1}{2})(11; xx)_0$,

$$(12; xx)_0=-2(12; yy)_0=-2(12; zz)_0$$
$$=-(4e^2/a^3)\sum_{\nu=1}^{\infty}(\cos 2\pi\tau_x(2\nu+1))/(2\nu+1)^3.$$

All the other coefficients with the subscript zero vanish.

1. One calculates first the potential at an arbitrary point due to the line of charges designated by $1'=(l_1', l_2+\mu, l_3)$, (μ fixed, $\neq 0$) proceeds with the differentiation and evaluation at l, and then sums over all the lines (that is, over μ). If $p=l_1'-l_1$, then $\mathbf{r}(l-l')=(pa, \mu a, 0)$. Again $(11; xx)_1$ will be evaluated for example. If there be given, in a Cartesian coordinate system (ξ, η, ζ) a set of charges e_p at the points $(\xi_p, 0, 0)$ and if the charges be periodic along

[10] This assumes that the G_i's are so large that there is a value of $n_1/2G_1$ very close to every value of $n_2/2G_2$ and so forth. The G_i's are $\sim 10^8$ for a macroscopic crystal.

[11] E. Madelung, Physik. Zeits. **19**, 524 (1918).

the axis with a period a', then the potential at any point is given by

$$\varphi(\xi,\rho)=(2/a')\sum_{n=-\infty}^{+\infty}{}'\sum_p e_p K_0(2\pi|n|\rho/a')\times\exp[2\pi i n(\xi-\xi_p)/a']-(2/a')\ln\rho\sum_p e_p,$$

where $\rho^2=\xi^2+\eta^2$ and K_0 is the Hankel function of zero order. The summation over n is to omit $n=0$, and that over p is over one complete period of the charge distribution. In the present case $\xi_p=pa$,

$$e_p=f(l_1+p+l_2+\mu+l_3)\exp[2\pi i(\tau_x p+\tau_y\mu)]=f(p+\mu)\exp[2\pi i(\tau_x p+\tau_y\mu)],$$

since again $l_1+l_2+l_3$ is even. Thus since $\tau_x=n_1/2G_1$, the period $a'=2G_1 a$, and in the summation p runs from 0 to $2G_1-1$. Substituting, we obtain

$$\varphi(\xi,\rho)=(1/G_1 a)\exp(2\pi i\tau_y\mu)\times\sum_n{}'K_0(\pi|n|\rho/G_1 a)\exp(\pi i n\xi/G_1 a)\sum_{p=0}^{2G_1-1}f(\rho+u)\times\exp[-\pi i(n-n_1)p/G_1]-(1/G_1 a)\ln\rho\sum_p e_p.$$

The last term is retained here because of the possibility that τ_x may be $=0$, in which case $\Sigma e_p=G_1\exp(2\pi i\tau_y\mu)$. Let us consider separately the summation over p. This is equal to

$$\{f(\mu)+\exp[-(\pi i/G_1)(n-n_1)]f(\mu+1)\}\times\sum_{p=0}^{G_1-1}\exp[-(2\pi i/G_1)(n-n_1)p].$$

This last sum is a geometrical series whose sum is zero unless

$$n=n_1+\kappa G_1=G_1(\kappa+2\tau_x),$$

κ any integer or zero, and is equal to G_1 in the latter case. If $n_1=0$ or G_1, zero or -1 is not a possible value for κ. Hence

$$\varphi(\xi,\rho)=(1/a)\exp(2\pi i\tau_y\mu)\sum_{\kappa=-\infty}^{+\infty}K_0(\pi\rho|\kappa+2\tau_x|/a)\times\exp[\pi i\xi(\kappa+2\tau_x)/a]\{f(\mu)+\exp(\pi i\kappa)f(\mu+1)\}-(1/G_1 a)\ln\rho\sum_p e_p.$$

By differentiation, we have

$$(\partial^2/\partial\xi^2)\varphi(\xi,\rho)=-(\pi^2/a^3)\exp(2\pi i\tau_y\mu)\times\sum_\kappa(\kappa+2\tau_x)^2K_0(\pi|\mu||\kappa+2\tau_x|)\times\exp[\pi i\xi(\kappa+2\tau_x)/a]\{f(\mu)+(-1)^\kappa f(\mu+1)\}.$$

The evaluation of this is to be made at the point $(\xi,\eta,\zeta)=(0,\mu a,0)$ so that

$$(11;xx)_1=-(\pi^2e^2/a^3)\sum_{\mu=-\infty}^{+\infty}{}'\exp(2\pi i\tau_y\mu)\times\sum_\kappa(\kappa+2\tau_x)^2K_0(\pi|\mu||\kappa+2\tau_x|)\times\{f(\mu)+(-1)^\kappa f(\mu+1)\}$$

$$=-(2\pi^2e^2/a^3)\sum_{\mu=1}^{\infty}\cos 2\pi\tau_y\mu\sum_\kappa(-1)^{\kappa\mu}\times(\kappa+2\tau_x)^2K_0(\pi\mu|\kappa+2\tau_x|).$$

Proceeding in exactly the same way, one finds

$$(11;yy)_1=(2\pi^2e^2/a^3)\sum_{\mu=1}^{\infty}\cos 2\pi\tau_y\mu\times\{\sum_\kappa(-1)^{\kappa\mu}(\kappa+2\tau_x)^2K_0''(\pi\mu|\kappa+2\tau_x|)+[(-1)^{2\tau_x\mu}/\pi^2\mu^2G_1]\sum_p\exp(4\pi i\tau_x p)\},$$

$$(11;zz)_1=-(2\pi^2e^2/a^3)\sum_{\mu=1}^{\infty}\cos 2\pi\tau_y\mu\{\sum_\kappa(-1)^{\kappa\mu}\times(|\kappa+2\tau_x|/\pi\mu)K_1(\pi\mu|\kappa+2\tau_x|)+[(-1)^{2\tau_x\mu}/\pi^2\mu^2G_1]\sum_p\exp(4\pi i\tau_x p)\},$$

$$(11;xy)_1=-(2\pi^2e^2/a^3)\sum_{\mu=1}^{\infty}\sin 2\pi\tau_y\mu\sum_\kappa(-1)^{\kappa\mu}\times(\kappa+2\tau_x)|\kappa+2\tau_x|K_1(\pi\mu|\kappa+2\tau_x|),$$

$$(11;xz)_1=(11;yz)_1=0.$$

The coefficients $(12;xy)_1$ are of the same form as the coefficients $(11;xy)_1$, but each of the former contains an additional factor of $(-1)^{\kappa-1}$ within the summation sign ($(-1)^{2\tau_x-1}$ for the $1/\mu^2$ term).

2. Here one proceeds in a fashion analogous to that under (1). One calculates first the potential of that one of the planes designated by $\mathfrak{l}'=(l_1', l_2', l_3+\mu)$, differentiates, evaluates, and sums over μ. If $p=l_1'-l_1$ and $q=l_2'-l_2$, then $\mathfrak{r}(l-l')=(pa, qa, \mu a)$. The same coordinate system (ξ, η, ζ) is chosen, and the potential of the (ξ, η)-plane bearing a periodic distribution of charges is written down:

$$\psi(\xi,\eta,\zeta)=(2\pi/a'b')\{\sum_{n,\,m=-\infty}^{+\infty}\sum_{p,\,q}e_{pq}\times(\exp(-k_{nm}|\zeta|)/k_{nm})\exp[2\pi in(\xi-\xi_p)/a']\times\exp[2\pi im(\eta-\eta_q)/b']-|\zeta|\sum_{p,\,q}e_{pq}\}.$$

Here e_{pq} is the charge at $(\xi_p, \eta_q, 0)$ and

$$k_{nm}^2=4\pi^2((n^2/a'^2)+(m^2/b'^2)).$$

The term with $n=m=0$ is to be omitted in the summation, and p and q run over one complete period. For the present calculation, $\xi_p=pa$, $\eta_q=qa$, and

$$e_{pq}=f(l_1+p+l_2+q+l_3+\mu)\times\exp[2\pi i(\tau_x p+\tau_y q+\tau_z\mu)]=f(p+q+\mu)\times\exp[2\pi i(\tau_x p+\tau_y q+\tau_z\mu)].$$

Since $\tau_x=n_1/2G_1$ and $\tau_y=n_2/2G_2$, $a'=2G_1a$, $b'=2G_2a$, and p runs from 0 to $2G_1-1$, q from 0 to $2G_2-1$. Substituting, and carrying out the summation over p and q as in the case of the line, one obtains

$$\psi(\xi,\eta,\zeta)=(\pi/2a)\exp(2\pi i\tau_z\mu)\sum_{s,\,t=-\infty}^{+\infty}\times(\exp(-g_{st}|\zeta|/a)/g_{st})\exp[\pi i\xi(s+2\tau_x)/a]\times\exp[\pi i\eta(t+2\tau_y)/a][1+(-1)^{s+t}]\times\{f(\mu)+(-1)^t f(\mu+1)\}-(\pi/2G_1G_2a^2)|\zeta|\sum_{p,\,q}e_{pq},$$

where $g_{st}^2=\pi^2[(s+2\tau_x)^2+(t+2\tau_y)^2]$. Here again, if $\tau_x=\tau_y=0$ or $\frac{1}{2}$, $s=t=-2\tau_x$ is to be omitted. Differentiating, and observing that the quantity in curled brackets is equal to $(-1)^{\mu t}$, we find

$$(\partial^2/\partial\xi^2)\psi(\xi,\eta,\zeta)=-(\pi^3/2a^3)\exp(2\pi i\tau_z\mu)\times\sum_{s,\,t}(-1)^{\mu t}[1+(-1)^{s+t}](\exp(-g_{st}|\zeta|/a)/g_{st})\times(s+2\tau_x)^2\exp[\pi i\xi(s+2\tau_x)/a]\times\exp[\pi i\eta(t+2\tau_y)/a].$$

The evaluation is to be made at the point $(\xi, \eta, \zeta)=(0, 0, \mu a)$, so that finally

$$(11;xx)_2=-(\pi^3e^2/a^3)\sum_{\mu=1}^{\infty}\cos 2\pi\tau_z u\sum_{s,\,t}(-1)^{\mu t}\times[1+(-1)^{s+t}](\exp(-g_{st}\mu)/g_{st})(s+2\tau_x)^2.$$

The remaining coefficients are:

$$(11;yy)_2=-(\pi^3e^2/a^3)\sum_{\mu}\cos 2\pi\tau_z\mu\sum_{s,\,t}(-1)^{\mu t}\times[1+(-1)^{s+t}](\exp(-g_{st}\mu)/g_{st})(t+2\tau_y)^2,$$

$$(11;zz)_2=(\pi e^2/a^3)\sum_{\mu}\cos 2\pi\tau_z\mu\sum_{s,\,t}(-1)^{\mu t}\times[1+(-1)^{s+t}]\exp(-g_{st}\mu)g_{st},$$

$$(11;xy)_2=-(\pi^3e^2/a^3)\sum_{\mu}\cos 2\pi\tau_z\mu\sum_{s,\,t}(-1)^{\mu t}\times[1+(-1)^{s+t}](\exp(-g_{st}\mu)/g_{st})\times(s+2\tau_x)(t+2\tau_y),$$

$$(11;xz)_2=-(\pi^2e^2/a^3)\sum_{\mu}\sin 2\pi\tau_z\mu\sum_{s,\,t}(-1)^{\mu t}\times[1+(-1)^{s+t}]\exp(-g_{st}\mu)(s+2\tau_x),$$

$$(11;yz)_2=-(\pi^2e^2/a^3)\sum_{\mu}\sin 2\pi\tau_z\mu\sum_{s,\,t}(-1)^{\mu t}\times[1+(-1)^{s+t}]\exp(-g_{st}\mu)(t+2\tau_y).$$

Again, the coefficients $(12;xy)_2$ can be obtained from the coefficients $(11;xy)_2$ by multiplying each by a factor $(-1)^{t-1}$ inside the summation sign.

IV. The Influence of Polarizibility

The effect of the fact that the ions are not really rigid charges, but are polarizible, is important for all waves in the crystal. One may write in general the result of the calculation of the Coulomb force as

$$F_i(1)=(4\pi e_1/a^3)(\gamma_{i\alpha}(1)U_\alpha(1)+\gamma_{i\alpha}(2)U_\alpha(2)),$$

$$F_i(2)=(4\pi e_2/a^3)(\gamma_{i\alpha}(2)U_\alpha(1)+\gamma_{i\alpha}(1)U_\alpha(2)),$$

where the components of the vectors are now numbered from 1 to 3 instead of being labeled with x, y, and z, and where the appearance of a Greek letter suffix indicates summation over that suffix. The effect of the polarizibility is that one must replace the dipole moment due to the displacement of the ion. $e_iU_i(j)$, by $e_jU_i(j)$

$+p_i(j)$, where $p_i(j)=\alpha_j F_i(j)$, and α_j is the polarizibility of the ion of type j. Hence

$$(\delta_{i\alpha}-(4\pi\alpha_1/a^3)\gamma_{i\alpha}(1))F_\alpha(1)$$
$$+(4\pi\alpha_i/a^3)\gamma_{i\alpha}(2)F_\alpha(2)$$
$$=(4\pi e/a^3)(\gamma_{i\alpha}(1)U_\alpha(1)+\gamma_{i\alpha}(2)U_\alpha(2)),$$
$$(4\pi\alpha_1/a^3)\gamma_{i\alpha}(2)F_\alpha(1)$$
$$+(\delta_{i\alpha}-(4\pi\alpha_2/a^3)\gamma_{i\alpha}(1))F_\alpha(2)$$
$$=-(4\pi e/a^3)(\gamma_{i\alpha}(2)U_\alpha(1)+\gamma_{i\alpha}(1)U_\alpha(2)),$$

where $(\delta_{i\alpha})$ is the unit matrix.

Since for NaCl $(4\pi\alpha_1/a^3)=0.111$ and $(4\pi\alpha_2/a^3)=2.00$,[12] one can simplify by neglecting terms containing α_1. One has then, letting $k=(4\pi\alpha_2/a^3)$

$$F_i(1)+k\gamma_{i\alpha}(2)F_\alpha(2)$$
$$=(4\pi e/a^3)(\gamma_{i\alpha}(1)U_\alpha(1)+\gamma_{i\alpha}(2)U_\alpha(2),$$
$$(\delta_{i\alpha}-k\gamma_{i\alpha}(1))F_\alpha(2)$$
$$=-(4\pi e/a^3)(\gamma_{i\alpha}(2)U_\alpha(1)+\gamma_{i\alpha}(1)U_\alpha(2).$$

These equations are to be solved for $F_i(1)$ and $F_i(2)$; the result is the corrected Coulomb field which is to be substituted in the equations of motion.

V. The Coulomb Field for Waves Long Compared to the Crystal

In the particularly interesting case of long waves, the components of τ may be regarded as small quantities, and the coefficients may be expanded in terms of them about $\tau=0$. The results give for the field (up to and including terms linear in the components of τ)

$$F_1(1)=-(4\pi e/a^3)[-(\tfrac{1}{6})(U_1(1)-U_1(2))$$
$$+(\tau_1/2\tau^2)(\tau\cdot\mathbf{U}(1)-\mathbf{U}(2)],$$
$$F_2(1)=-(4\pi e/a^3)[-(\tfrac{1}{6})(U_2(1)-U_2(2))$$
$$+(\tau_2/2\tau^2)(\tau\cdot\mathbf{U}(1)-\mathbf{U}(2)],$$
$$F_3(1)=-(4\pi e/a^3)[(\tfrac{1}{3})(U_3(1)-U_3(2))$$
$$-((\tau_1^2+\tau_2^2)/2\tau^2)(U_3(1)-U_3(2))$$
$$+(\tau_3/2\tau^2)\{\tau_1(U_1(1)-U_1(2))$$
$$+\tau_2(U_2(1)-U_2(2))\}]$$

and $\mathbf{F}(2)=\mathbf{F}(1)$.

[12] The values of α_1 and α_2 are taken from K. Fajans and G. Joos, Zeits. f. Physik **23**, 1 (1924).

Special consideration given to the case $\tau=0$ (infinitely long waves) shows that then all terms in τ_1, τ_2 and τ_3 in these equations are to be dropped. One sees from these equations what the value of $\mathbf{G}(k)$ must be. By its definition $\mathbf{G}(k)$ may be obtained from $\mathbf{F}(k)$ by replacing $\mathbf{U}(k')$ by $\mathbf{U}(k)$ in the expression for $\mathbf{F}(k)$ and then letting τ approach zero. For the present case, then, $\mathbf{G}(1)=\mathbf{G}(2)=\mathbf{0}$.

In the event that the wave-length is infinite, one may put the average electric moment per unit volume $(e/2a^3)(\mathbf{U}(1)-\mathbf{U}(2))$, equal to the (uniform) polarization $\mathbf{P}$. If the polarization is in the x direction, $\mathbf{F}=(4\pi/3)\mathbf{P}$; if it is in the z direction, $\mathbf{F}=-(8\pi/3)\mathbf{P}$. These two cases are apparently physically identical; how then is one to account for the difference in the result?

The reason for the difference, mathematically at least, is apparent. One has summed a conditionally convergent series in two different orders, and should not be surprised at obtaining two different results. It is pertinent to inquire as to what the physical meaning of this difference is. For the sake of the discussion of this meaning, a third method of carrying out the summation will be considered. If one calculates the field at a point due to a cubic lattice of constant dipoles by grouping together all those at a given distance from the point, and then adding the results of the groups, the field turns out to be zero.

It is apparent that the physical analog of the conditional convergence of the series is the fact that the shape of the crystal exerts a distinguishing influence upon the field at a point in it, so that the value of the field in a strictly infinite crystal is quite undefined. For in the case of the method of summation last mentioned, one adds the contributions from the points within a spherical shell and then adds shell upon shell, so that the final result is the summation over a very large sphere. In the Madelung method, one adds together the contributions of planes, so that here the final result is the summation over a slab which is infinite in two directions and large in the third. The polarization is, for this method, either normal to or along the favored direction. One has, then, for a sphere the field $\mathbf{F}=\mathbf{0}$; for a slab with the polarization normal $\mathbf{F}=-(8\pi/3)\mathbf{P}$; for a slab with the

polarization parallel $\mathbf{F}=(4\pi/3)\mathbf{P}$. Let us compare these results with those of continuum theory.

In the continuum theory one calculates (for homogeneous polarization) the exciting field as due to three contributions: the influence of the true external charges, which gives the electric displacement $\mathbf{D}$; the influence of the induced charges on the surface of a spherical cavity surrounding the point at which the field is to be calculated, which gives the Lorentz-Lorenz force $(4\pi/3)\mathbf{P}$; and the influence of the surface charges on the outer surface of the dielectric. For a sphere, the latter gives $-(4\pi/3)\mathbf{P}$. Therefore the exciting field in the center of a sphere is $\mathbf{D}+(4\pi/3)\mathbf{P}-(4\pi/3)\mathbf{P}=\mathbf{D}$. In our calculations with no external charges $\mathbf{D}=\mathbf{0}$. If the dielectric is a slab with the field normal, the charges on the faces of the slab give $-4\pi\mathbf{P}$, reducing $\mathbf{D}$ to $\mathbf{E}=\mathbf{D}-4\pi\mathbf{P}$. The exciting field is $\mathbf{D}+(4\pi/3)\mathbf{P}-4\pi\mathbf{P}=\mathbf{D}-(8\pi/3)\mathbf{P}$. In our case ($\mathbf{D}=\mathbf{0}$) we have in fact found $-(8\pi/3)\mathbf{P}$. If the dielectric is a slab with the field parallel, the external surface charges are induced at the ends of the slab, which are so remote, in comparison to their size that they do not contribute appreciably. Therefore $\mathbf{D}+(4\pi/3)\mathbf{P}$ is the exciting field. For this case we calculate by direct summation $(4\pi/3)\mathbf{P}$.[13]

VI. Waves Long Compared to the Lattice Distance but Short Compared to the Size of the Crystal

The importance of the preceding discussion for our purpose lies in the fact that conditions with regard to the convergence difficulty are completely different if the wave-length is long but not infinite. For here the equations for $\mathbf{F}(k)$ become:

$$\mathbf{F}(1)=\mathbf{F}(2)=-(4\pi e/a^3)[-(\tfrac{1}{6})(\mathbf{U}(1)-\mathbf{U}(2))+(\boldsymbol{\tau}/2\tau^2)(\boldsymbol{\tau}\cdot\mathbf{U}(1)-\mathbf{U}(2))],$$

which expressions are completely symmetrical in x, y, and z, and are independent of the manner in which the planes in the crystal have been chosen. (The same result, as would be expected, is observed for such of the shorter waves as have been calculated). One concludes, therefore, that the field in an infinite crystal in a real state of vibration with a finite wave-length does have meaning, and that the phase difference in space between the polarizations at the various lattice points has removed the conditionality of the convergence, as Born[8] has pointed out. Since this is true, the exchange of the order of summation and differentiation made at the beginning of the calculation is justified by the results.

Upon including the correction for polarizability, one has for the Coulomb force

$$e_1\mathbf{F}(1)=-e_2\mathbf{F}(2)=(4\pi e^2/a^3)\times(1+k/3)^{-1}(1-k/6)^{-1}[(\tfrac{1}{6})(1+k/3)\times(\mathbf{U}(1)-\mathbf{U}(2))-(\boldsymbol{\tau}/2\tau^2)(\boldsymbol{\tau}\cdot\mathbf{U}(1)-\mathbf{U}(2))].$$

The repulsive force is

$$\mathbf{R}(1)=-\mathbf{R}(2)=-(4\pi e^2/a^3)(c_1+2c_2)(\mathbf{U}(1)-\mathbf{U}(2)).$$

The secular equation to be satisfied is that resulting from the set of equations

$$-m_k\omega^2\mathbf{U}(k)=e_k\mathbf{F}(k)+\mathbf{R}(k).$$

The result is that if μ is the reduced mass, then

$$\omega^6[\mu\omega^2-(4\pi e^2/a^3)(c_1+2c_2-(\tfrac{1}{6})(1-k/6)^{-1})]^2\times[\mu\omega^2-(4\pi e^2/a^3)(c_1+2c_2+(\tfrac{1}{3})(1+k/3)^{-1}]=0,$$

which gives the following results:

(a) There are three possible vibrations (with a given wave vector $\boldsymbol{\tau}$) whose frequency is zero. These are characterized by $\mathbf{U}(1)=\mathbf{U}(2)$, so that the displacements of neighboring particles are but very little different. In other words, these are the three frequencies belonging to the acoustical branch. They are zero only because we have neglected the contribution to the forces of terms proportional to squares of the components of $\boldsymbol{\tau}$. Inclusion of these would give $\omega^2\sim\tau^2$, or $\omega\sim\tau$, as it should be in the acoustical branch. Without this inclusion we can say no more about the characteristics of these vibrations beyond the statement that the amplitudes of the two kinds of particles are equal, and that hence the electric field vanishes in this approximation.

(b) There are two vibrations for which

$$\omega^2=(4\pi e^2/\mu a^3)(c_1+2c_2-(\tfrac{1}{6})(1-k/6)^{-1}).$$

[13] This calculation for infinite waves is identical with that carried out by K. F. Herzfeld, J. Opt. Soc. Am. **17**, 26 (1928).

These are characterized by $m_1\mathbf{U}(1)+m_2\mathbf{U}(2)=\mathbf{0}$ and $(\boldsymbol{\tau}\cdot\mathbf{U}(1)-\mathbf{U}(2))=0$. The former condition implies that the two kinds of particles are vibrating exactly out of phase and with an amplitude ratio inversely proportional to that of the masses; the latter condition that the direction of vibration of a particle is normal to the direction of motion of the wave; that is, that these waves are transverse. The fact that this frequency appears twice in the secular equation corresponds to the existence of two possible independent modes of vibration normal to the wave vector. The electric field for these vibrations is given by

$$\mathbf{F}(1)=\mathbf{F}(2)=(4\pi e/a^3)(\tfrac{1}{6})[1-(k/6)]^{-1}\times(\mathbf{U}(1)-\mathbf{U}(2))=(4\pi/3)\mathbf{P},$$

in which we have introduced again the polarization vector $\mathbf{P}$.[14]

(c) The remaining vibration has

$$\omega^2=(4\pi e^2/\mu a^3)\{c_1+c_2+(\tfrac{1}{3})[1+(k/3)]^{-1}\}.$$

The amplitudes are characterized by $m_1\mathbf{U}(1)+m_2\mathbf{U}(2)=\mathbf{0}$ and $[\boldsymbol{\tau}\cdot\mathbf{U}(1)-\mathbf{U}(2)]=\mathbf{0}$. This, then, is a vibration like the preceding two, with the exception that it is longitudinal. The electric field here is $\mathbf{F}(1)=\mathbf{F}(2)=-(8\pi/3)\mathbf{P}$.

The results both for the acoustical branch and for the transverse waves in the optical branch agree with what has been known,[8] but the result for the longitudinal waves is a new one.

One must be careful to recognize that the reappearance here of $(4\pi/3)\mathbf{P}$ and $-(8\pi/3)\mathbf{P}$ for the electric field is not for the same formal reason as in Section V. There it was a question of the dependence of the convergence of the sum over the lattice on the shape of the crystal, whereas there is no such difficulty here. Here it is a question of the difference between longitudinal and transverse waves; that is, whether the displacement is in the direction in which it varies in space, or perpendicular to it. The result is independent of the shape of the crystal and of the manner in which it is broken up into planes to calculate the electric field.

It is not surprising, however, that in the transition from very long to infinitely long waves, the transverse waves give the same result as uniform polarization along an infinite slab, the longitudinal waves the same as uniform polarization normal to the slab. Consider for a moment forced vibrations, for example a plane light wave falling on the slab. Then plane waves (transverse) with the polarization along the slab are possible. If, on the other hand, a light wave should fall on the (narrow) sides of the slab, there would be diffraction effects, so that no plane wave, polarized normal to the slab and progressing along it, is possible (the thickness of the slab is now considered small compared to the wave-length). The converse is true for longitudinal waves. Such waves, progressing along a slab, would be subject to edge effects, which we call diffraction for the transverse waves.

It must be pointed out that the polarizability correction to the Coulomb force and the repulsive force (provided it acts only on nearest neighbors) do not change the solutions of the secular equation as far as the types of waves (that is, the conditions on the amplitudes) are concerned, but only alter the numerical values of the frequencies. This is true for all the waves that we consider here, and for reasons to be given in section VIII, we will give only the uncorrected values of the Coulomb force for the other waves to be discussed.

VII. Short Waves

Case I

$\boldsymbol{\tau}=(\frac{1}{4},\frac{1}{4},\frac{1}{4})$. This represents the vibration in which one of the simple lattices (composed of all the particles of one kind) remains at rest; the other vibrating so that all particles in a given plane normal to the line $x=y=z$ (the direction of propagation of the wave, which is the diagonal of the cube) are in phase, and successive planes are exactly out of phase. (One remembers that the phase difference between the particles 1 and 1′ is $\exp[2\pi i(\boldsymbol{\tau}\cdot 1-1')]$. The Coulomb force, uncorrected, is

$$e_1F_i(1)=-(4\pi e^2/a^3)(0.1438)(U_j(1)+U_k(1)),$$

$$e_2F_i(2)=-(4\pi e^2/a^3)(0.1438)(U_j(2)+U_k(2))\qquad(i\neq j\neq k).$$

[14] This result is in agreement with that of Heckmann, Zeits. f. Krist. **61**, 250 (1925).

The repulsive force is

$$\mathbf{R}(1) = -(4\pi e^2/a^3)(c_1+2c_2)\mathbf{U}(1),$$
$$\mathbf{R}(2) = -(4\pi e^2/a^3)(c_1+2c_2)\mathbf{U}(2).$$

The solution of the secular determinant shows that there are two sets of three vibrations each, one set for the vibration of the Na lattice and one for that of the Cl lattice. Of each of these two sets, two vibrations are transverse, with the same frequency, and one is longitudinal. The transverse frequencies are given by

$$\omega^2 = (4\pi e^2/m_i a^3)(c_1+2c_2-0.1438);$$

the longitudinal by

$$\omega^2 = (4\pi e^2/m_i a^3)(c_1+2c_2+0.2876).$$

As τ changes from (0, 0, 0) to $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, the frequencies in the acoustical branch rise greatly, and those in the optical branch drop slightly, until when τ arrives at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ both branches have frequencies of the same order of magnitude; in fact, they are in the ratio of the square roots of the masses.[15] This is one of the points of similarity which these vibrations have to the shortest waves of the acoustical and optical branches in the Born-v. Kármán linear lattice. In this case only one type of particle takes part in a vibration, and the two branches are closest together, since the optical branch frequencies are a minimum and the acoustical are a maximum. The frequencies of the two branches are in the inverse ratio of the square roots of the masses. In the three-dimensional lattice, however, there is at least one other direction in which the two branches are as close together for the shortest waves as this one, and another direction in which the longitudinal wave in the optical branch has a lower frequency.

Case II

$\tau = (\frac{1}{2}, 0, 0)$. Here the direction of propagation is along the x axis, and particles in any plane normal to the x axis are in phase, since successive lattice planes are exactly out of phase. The Coulomb force is calculated to be:

$$e_1F_1(1) = (4\pi e^2/a^3)(-0.1724U_1(1)+0.5984U_1(2)),$$
$$e_1F_2(1) = (4\pi e^2/a^3)(0.0862U_2(1)-0.2992U_2(2)),$$
$$e_1F_3(1) = (4\pi e^2/a^3)(0.0862U_3(1)-0.2992U_3(2)),$$

the repulsive force:

$$R_1(1) = -(4\pi e^2/a^3)[(c_1+2c_2)U_1(1) + (c_1-2c_2)U_1(2)],$$
$$R_2(1) = -(4\pi e^2/a^3)[(c_1+2c_2)U_2(1) - c_1U_2(2)],$$
$$R_3(1) = -(4\pi e^2/a^3)[(c_1+2c_2)U_3(1) - c_1U_3(2)].$$

The value of $e_2\mathbf{F}(2)$ can be obtained from that of $e_1\mathbf{F}(1)$, and that of $\mathbf{R}(2)$ from that of $\mathbf{R}(1)$, by interchanging $\mathbf{U}(1)$ and $\mathbf{U}(2)$ in the above expressions.

It appears by inspection that the waves can be divided again into longitudinal and transverse, the former are a vibration in the x direction, and the latter a vibration in the y or z direction. The secular determinant breaks into three; each is of the form

$$\begin{vmatrix} A-(m_1a^3/4\pi e^2)\omega^2 & B \\ B & A-(m_2a^3/4\pi e^2)\omega^2 \end{vmatrix} = 0,$$

the solution of which is

$$\omega^2 = (4\pi e^2/a^3)\{(A/2\mu) \pm [(A/2\mu)^2-(A^2-B^2)/m_1m_2]^{\frac{1}{2}}\}.$$

For the two longitudinal waves, $A = 0.1724+c_1+2c_2$, $B = 0.5984-c_1+2c_2$. For the four transverse waves, $A = -0.0862+c_1+2c_2$, $B = -0.2992+c_1$. For the acoustical branch (lower frequency of a pair), the displacements of the two types of particles are in the same direction; for the optical branch, in the opposite direction.

Case III

$\tau = (\frac{1}{2}, \frac{1}{4}, 0)$. This is the shortest wave possible in the crystal, provided that of the equivalent pair of wave vectors (τ_1, τ_2, τ_3) and $(|\frac{1}{2}-\tau_1|, |\frac{1}{2}-\tau_2|, |\frac{1}{2}-\tau_3|)$ one always chooses the one of longer wave-length. The direction of propagation is in the (x, y) plane, at an angle of about 60° with the x axis. The Coulomb force here is:

$$e_1F_1(1) = (4\pi e^2/a^3)(-0.03135U_1(1) + 0.4371U_1(2)),$$
$$e_1F_2(1) = (4\pi e^2/a^3)0.06270U_2(1),$$
$$e_1F_3(1) = (4\pi e^2/a^3)(-0.03135U_3(1) - 0.04371U_3(2)),$$

and the repulsive force:

$$R_1(1) = -(4\pi e^2/a^3)[(c_1+2c_2)U_1(1) + (c_1-c_2)U_1(2)],$$
$$R_2(1) = -(4\pi e^2/a^3)(c_1+2c_2)U_2(1),$$
$$R_3(1) = -(4\pi e^2/a^3)[(c_1+2c_2)U_3(1) - (c_1-c_2)U_3(2)].$$

[15] This statement is true for the transverse and longitudinal vibrations separately.

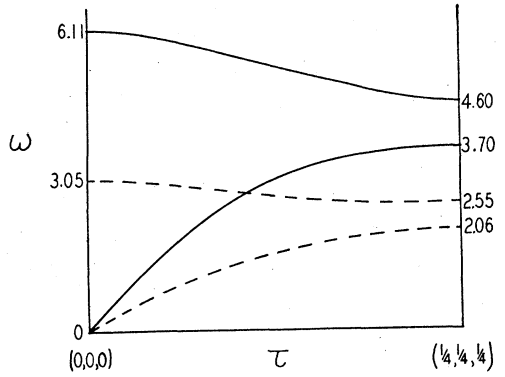

FIG. 1. This graph represents the frequencies in a sodium chloride crystal (in units of 10^{13} sec.$^{-1}$) as functions of the magnitude of $\boldsymbol{\tau}$, as $\boldsymbol{\tau}$ changes from (0, 0, 0) to $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$; that is, for waves of all possible lengths traveling along the cube diagonal. The terminal points of each curve have been calculated, and the curves in between are merely sketched, taking advantage of the knowledge that, for example, the highest curve must be horizontal at both ends. The curves for longitudinal waves are drawn solid, for transverse broken (each of the transverse curves represents two frequencies). In each case the upper curve represents the optical branch, the lower the acoustical branch.

The normal vibrations are along the x, the y, or the z direction again, but they cannot be divided into longitudinal and transverse. The secular determinant breaks into three, of the same type as for $\boldsymbol{\tau}=(\frac{1}{2}, 0, 0)$. The same frequencies are given by the vibrations along the x or the z direction, for which A is equal to $0.03135+c_1+2c_2$ and B is equal to $\pm(0.4371-c_1+c_2)$. The vibration along the x direction is neither longitudinal nor transverse; that along the z direction is transverse. The two frequencies of the vibration along the y direction, which is neither longitudinal nor transverse, are given by

$$\omega^2=(4\pi e^2/m_i a^3)(-0.06270+c_1+2c_2).$$

But here the distinction between longitudinal and transverse waves means but little, since for the x and z vibrations not only the frequencies, but the displacements themselves are indistinguishable, as solution of the secular equation for the amplitudes shows.

VIII. Numerical Values of the Frequencies

To obtain numerical values of these frequencies, one must make an estimate of the size of the repulsive forces. For this purpose, we assume that the function $f(r)$ which gives the repulsive interaction between nearest neighbors is of the form $be^{-r/\rho}$ and evaluate the constants b and ρ by the method of Born and Mayer.[16] If we remember that the van der Waals interaction is to be neglected, this gives for the two constants appearing in the frequencies $c_1=0.4220$ and $c_2=-0.0427$. The numerical results for the frequencies follow. (The frequencies are stated in multiples of 10^{13} sec.$^{-1}$.)

Long waves, optical branch:

Transverse: 3.051; Longitudinal: 6.113 (The transverse frequency calculated from the Reststrahlen frequency is $\omega=3.06$. Such good agreement is to be regarded as fortuitous.)

$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$:

Transverse, Na lattice vibrating: 2.553; Transverse, Cl lattice vibrating: 2.057; Longitudinal, Na lattice vibrating: 4.595; Longitudinal, Cl lattice vibrating: 3.701.

$(\frac{1}{2}, 0, 0)$:

Transverse: 3.263, 1.862; Longitudinal: 4.255, 3.205.

$(\frac{1}{2}, \frac{1}{4}, 0)$:

Vibration along x or z direction: 3.545, 2.820; Vibration along y direction: 3.044, 2.452.

If one calculates these frequencies with the polarizibility correction to the Coulomb force included, the results are bad. The transverse frequency for the long waves drops to about two-thirds of its present value; the transverse frequencies for $(\frac{1}{2}, 0, 0)$ and the frequencies for the vibrations in the x or z directions for $(\frac{1}{2}, \frac{1}{4}, 0)$ become imaginary. As Heckmann has pointed out (reference 14) for the long waves, such a

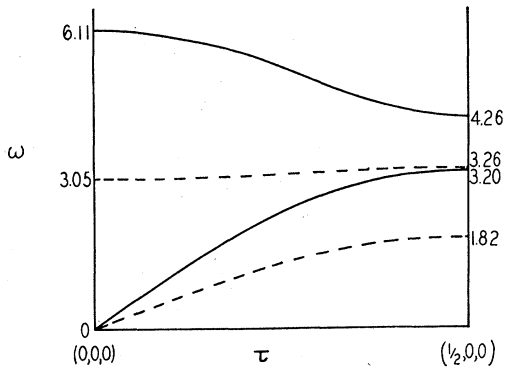

FIG. 2. This represents the frequencies of all possible waves traveling along the edge of the cube. Again the waves are divisible into longitudinal and transverse and again the curves are sketched.

[16] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

result is probably due to the fact that the ions in the immediate vicinity of a given ion cannot be considered to be point charges, the deviation of their behavior from that of point charges affecting strongly the polarizing electric field. In other words, the repulsive forces would appear to influence the polarization of the ion.[17]

IX. The Neutral System

There is another possible application of the preceding calculation. Suppose that one has a simple cubic lattice, lattice distance a, composed of identical particles kept in place by some elastic, isotropic binding. Let the lattice be a block of dimensions $G_1 \times G_2 \times G_3$ particles, and let it be built up to an infinite periodic lattice as before. Let the displacement of the lth particle be denoted by $\mathbf{x}(l) = (x_1(l), x_2(l), x_3(l))$, and let there be a dipole moment $e\mathbf{x}(l)$ associated with the displacement $\mathbf{x}(l)$. An arbitrary displacement of the particles of the lattice may be analyzed into a Fourier series:

$$\mathbf{x}(l) = \sum_{\tau} \mathbf{g}(\tau) \exp\left[2\pi i(\boldsymbol{\tau} \cdot l)\right],$$

where $\boldsymbol{\tau} = (l_1'/G_1,\ l_2'/G_2,\ l_3'/G_3)$ and the sum over τ indicates the triple sum over all integers $|l_1'| \leqslant G_1$, $|l_2'| \leqslant G_2$, $|l_3'| \leqslant G_3$. $\mathbf{g}(\tau)$ is a function of the time t. One can calculate the force on one particle due to the dipole moments of all the other particles for one of these Fourier components by the calculation above for the Coulomb force, provided that one makes the two kinds of particles identical; that is, sets $\mathbf{U}(1) = \mathbf{U}(2) = \mathbf{g}(\tau)$ and $e_1 = e_2 = e$.

The equations of motion, if $\mathbf{F}(\tau) \exp\left[2\pi i(\boldsymbol{\tau} \cdot l)\right]$ is the force of the interaction, are $m(\partial^2/\partial t^2)\mathbf{g}(\tau) = -k\mathbf{g}(\tau) + \mathbf{F}(\tau)$, in which k is the constant of the elastic restoring force. Now, from the results of the preceding calculation, $\mathbf{F}(\tau)$ will contain $g_1(\tau)$, $g_2(\tau)$, $g_3(\tau)$ and none of the other Fourier components of the displacements. Hence for each value of $\boldsymbol{\tau}$ there will be three normal vibrations of the system, the coordinates for which will be

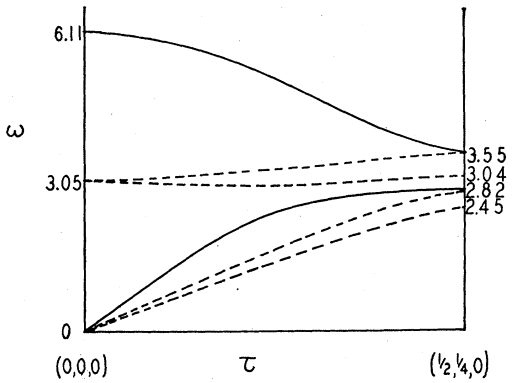

FIG. 3. Here are represented the frequencies as $\boldsymbol{\tau}$ changes from (0, 0, 0) to $(\frac{1}{2}, \frac{1}{4}, 0)$. To aid in drawing the curves the point in the center, $(\frac{1}{4}, \frac{1}{8}, 0)$, has also been calculated. The two broken curves ending on the right at 3.55 and 1.61 represent transverse waves; the others are in general neither, but are drawn broken or solid in accordance with their behavior at large wave-length.

linear combinations of the three coefficients $g_1(\tau) g_2(\tau)$ and $g_3(\tau)$. One can then write $\partial^2\mathbf{g}(\tau)/\partial t^2 = -\omega^2\mathbf{g}(\tau)$, and has the secular equation to solve resulting from $(-m\omega^2 + k)\mathbf{g}(\tau) - \mathbf{F}(\tau) = 0$. The results for this calculation follow.

(1) Long waves ($\boldsymbol{\tau} \ll 1$)

$$\mathbf{F}(\tau) = (4\pi e^2/a^3)\left[(\tfrac{1}{3})\mathbf{g}(\tau) - (\boldsymbol{\tau}/\tau^2)(\boldsymbol{\tau} \cdot \mathbf{g}(\tau))\right].$$

There are two transverse vibrations with $m\omega^2 - k = -(4\pi e^2/a^3)(\frac{1}{3})$ and one longitudinal with $m\omega^2 - k = (4\pi e^2/a^3)(\frac{2}{3})$. Transverse and longitudinal mean here, of course, that $\boldsymbol{\tau}$ and $\mathbf{g}(\tau)$ are normal and collinear, respectively.

(2) $\boldsymbol{\tau} = (\frac{1}{2}, 0, 0)$

$$F_1(\tau) = (4\pi e^2/a^3)(-0.770) g_1(\tau),$$
$$F_2(\tau) = (4\pi e^2/a^3) 0.385 g_2(\tau),$$
$$F_3(\tau) = (4\pi e^2/a^3) 0.385 g_3(\tau).$$

These are the vibrations for which all particles in a plane normal to the x axis vibrate in phase, and successive lattice planes are exactly out of phase. There are two transverse waves with $m\omega^2 - k = -0.385(4\pi e^2/a^3)$ and one longitudinal with $m\omega^2 - k = 0.770(4\pi e^2/a^3)$. The results for this wave are very similar to those for the long waves (0.385 instead of 0.333) since one has the same polarization, except that every alternate plane has the sign of its polarization reversed. Since the effect, for long waves, of planes other than the one containing the lattice point is small, the result is understandable.

[17] These results make it probable that a better calculation of the specific heats in the Debye approximations might be accomplished by taking separately N longitudinal and $2N$ transverse vibrations in part fulfillment of the suggestion of Born and Göppert-Mayer (reference 8, p. 651).

(3) $\tau=(\frac{1}{2},\frac{1}{2},0)$

$$F_1(\tau)=(4\pi e^2/a^3)(-0.213)g_1(\tau),$$
$$F_2(\tau)=(4\pi e^2/a^3)(-0.213)g_2(\tau),$$
$$F_3(\tau)=(4\pi e^2/a^3)0.426g_3(\tau).$$

This wave progresses along the diagonal of the face of the cube, since alternate lattice planes have opposite phase. Here the normal vibrations again can be divided into longitudinal and transverse. There is one transverse vibration in the z direction with $m\omega^2-k=-0.426(4\pi e^2/a^3)$ and one in the direction $(\frac{1}{2},-\frac{1}{2},0)$ with $m\omega^2-k=0.213(4\pi e^2/a^3)$. The longitudinal wave has $m\omega^2-k=0.213(4\pi e^2/a^3)$. This wave presents the feature hitherto not met with of having different frequencies for the two transverse waves.

(4) $\tau=(\frac{1}{2},\frac{1}{2},\frac{1}{4})$

$$F_1(\tau)=(4\pi e^2/a^3)(-0.104)g_1(\tau),$$
$$F_2(\tau)=(4\pi e^2/a^3)(-0.104)g_2(\tau),$$
$$F_3(\tau)=(4\pi e^2/a^3)(0.208)g_3(\tau).$$

The normal vibrations for this wave can be taken along the x, y, and z directions, and cannot be separated into longitudinal and transverse. The frequency for vibrations in the x and y directions is $m\omega^2-k=0.104(4\pi e^2/a^3)$; for vibrations in the z direction, $m\omega^2-k=-0.208\times(4\pi e^2/a^3)$.

(5) $\tau=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$

This is the wave in which nearest neighbors are always exactly out of phase; it is the shortest wave possible in the lattice. The force due to the interaction vanishes, so that all three frequencies are given by $m\omega^2-k=0$. All three vibrations are here geometrically identical.

X. The Field Vectors

The quantity calculated in the preceding sections is the actual microscopic electric force at the place of a particle, the so-called exciting field. Macroscopically one has to distinguish between the electric field $\mathbf{E}$ and the electric displacement $\mathbf{D}$ which are connected by $\mathbf{D}=\mathbf{E}+4\pi\mathbf{P}$. $\mathbf{P}$ is, of course, the total dipole moment per unit volume. The formal definition of $\mathbf{E}$ and $\mathbf{D}$ requires the measurement of the force on a macroscopic probe, situated in an appropriately arranged slit. It is obvious from this definition that $\mathbf{E}$ and $\mathbf{D}$ in this macroscopic sense have meaning only if the wave-length of our vibrations is large in all directions compared with the lattice distance, because otherwise averaging over many lattice distances means also averaging over several wave-lengths and gives, therefore, zero for $\mathbf{D}$, $\mathbf{E}$ and $\mathbf{P}$.

We have to restrict ourselves, therefore, to the above case, in which it is possible to distinguish sharply between transverse and longitudinal waves. As is well known, one defines $\mathbf{D}$ as the force exerted on a probe in a slit at right angles to the field, while $\mathbf{E}$ is measured in a channel parallel to the field. One sees easily that in the latter case one also can substitute a slit which has one long dimension in the direction of the field. While all the dimensions of the slits ought to contain many lattice distances, we are going to build the slits up of narrow slits with a short dimension, small compared with a. We designate the field vectors so defined by primes. We first start with longitudinal waves.

Consider a narrow slit between lattice planes: Due to the factors $\exp(2\pi is\xi/a)$, $\exp(2\pi it\eta/a)$, the average value of the field and therefore $\mathbf{D}'=\mathbf{0}$. Consider next a slit in the lattice plane, with the dipoles of that plane removed. The same argument holds. Therefore $\mathbf{D}$ is zero as it must be so that the condition of transversality for $\mathbf{D}$ is fulfilled.

Consider next the average field in a horizontal slit *with* the dipoles. The field in the slits between lattice planes is zero as above. Next take a narrow slit, cutting the dipoles of a lattice plane. The average value of the field is equal to the charge per unit surface times -4π. (Consider a flat shell, one surface in the slit, the other between lattice planes, and apply Gauss' theorem.) This slit extends over a distance equal to the dipole displacement, so that the average value is $-4\pi\mathbf{P}$. That is $\mathbf{E}$,[18] and $\mathbf{D}=-4\pi\mathbf{P}+4\pi\mathbf{P}=\mathbf{0}$.

That this is $\mathbf{E}$ according to the usual definition (measuring the force in a channel parallel to the field) can be seen because the dipoles that have to be removed to make the channel do not contribute appreciably. One sees, however, that the same argument holds also for transverse waves, as the result is independent of the order of sum-

[18] See H. A. Lorentz, *Theory of Electrons* (Leipzig, 1909), p. 134, last formula.

mation. Therefore the free vibrations considered here are described by

$$\mathbf{D}=0, \quad \mathbf{E}=-4\pi\mathbf{P},$$

which is in agreement with the interpretation of $\mathbf{D}$ as the field due to external sources.

According to electromagnetic theory, the refractive index n is related to the dielectric constant ϵ by $n^2=\epsilon$. The refractive index itself is determined by the frequency of the long transverse waves of the optical branch. On the other hand, the dielectric polarization of a slab between two condenser plates corresponds to the *longitudinal* deformation. Nevertheless, everything comes out correctly. Consider again the neutral simple cubic lattice. Then the optical transverse frequency is given by

$$m\omega^2-k=-(4\pi e^2)/3a^3.$$

On the other hand, the external force polarizing the slab in $\mathbf{D}$; everything else has been included in our summation. Therefore

$$(k+(8\pi e^2)/3a^3)\mathbf{z}=e\mathbf{D}. \tag{7}$$

$\mathbf{z}$ is the amplitude of the displacement; $k+(8\pi e^2)/3a^3$ is $m\omega^2_{\text{long}}$. But as

$$\epsilon-1=(4\pi\mathbf{P})/\mathbf{E}=(4\pi e\mathbf{z})/a^3\mathbf{E},$$

one calculates, by subtracting $(4\pi e^2/a^3)\mathbf{z}$ on both sides of (7),

$$(k-(4\pi e^2)/3a^3)\mathbf{z}=e\mathbf{E},$$

and gets the required connection.

We express our thanks to Dr. Maria Göppert-Mayer for many helpful discussions.