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Electrical, Optical, and Elastic Properties of Diamond-Type Crystals

II. Lattice Vibrations with Calculation of Atomic Dipole Moments

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The equations of motion corresponding to the crystal energy, deduced previously in Ref. 1, are considered. The vibration spectrum for long waves is investigated. A qualitative study is being made of the possibility of infrared absorption by the lattice vibrations and of birefringence and interaction between the conductivity electrons and lattice vibrations.

THE SPECTRUM OF ELASTIC VIBRATIONS of the diamond lattice has been investigated by many workers[2,3]. However, a general shortcoming of these investigations is that they do not take into consideration the extent of the internal degrees of freedom of the atoms. In addition, the results are unsatisfactory in their consideration of the propagation and absorption of light, and in many other problems, since they do not use the polarization vector (because of atomic neutrality). On the other hand, it was shown in Ref. 1 that the components of the atomic dipole moments $\mathbf{P}_s^l$ (l is the cell number, s is the atom number in the cell) may be selected as variables describing the internal degrees of freedom of the atoms. An expression for the potential energy U of the crystal as a function of $\mathbf{u}_s^l$ (the displacement of the atoms) and $\mathbf{P}_s^l$ may not be considered negligibly small in comparison with the terms which depend only on $\mathbf{u}_s^l$. In this work we consider the equations of motion derived from U. This allows one to study from one point of view a series of elastic, optical, and electrical properties of the above-mentioned crystals.

1. EQUATIONS OF MOTION

The equations of motion are:

$$m\ddot{\mathbf{u}}_s^l = -\partial U / \partial \mathbf{u}_s^l, \quad 0 = -\partial U / \partial \mathbf{P}_s^l, \tag{1}$$

where m is the atomic mass; we neglect the inertia of the dipole moments.

As usual, the solution of these equations is sought in the form of plane monochromatic waves:

$$\begin{aligned} \mathbf{u}_s^l &= \mathbf{u}_s \exp(-i\omega t + i\mathbf{K}\mathbf{r}_s^l), \\ \mathbf{P}_s^l &= \mathbf{P}_s \exp(-i\omega t + i\mathbf{K}\mathbf{r}_s^l). \end{aligned} \tag{2}$$

For dipole moments of this form the internal field $\mathbf{E}_s^l$ contained in the equations of motion[1], may be calculated by means of a direct summation – the Ewald method[4]. As the result of these calculations, we obtained the following

$$\begin{aligned} \mathbf{E}_s^l &= \mathbf{E}_s \exp(-i\omega t + i\mathbf{K}\mathbf{r}_s^l), \\ \mathbf{E}_1 &= \frac{1}{d^3}\Big[\frac{16\pi}{3}\mathbf{P} - 16\pi\frac{(\mathbf{P}\cdot\mathbf{k})\,\mathbf{k} - \mathbf{P}k_0^2}{k^2 - k_0^2} + \\ &+ Si\,(\mathbf{k} \overset{+}{\times} \mathbf{P}_2) + \mathbf{F}_1(\mathbf{k}; \mathbf{P}_1) + \mathbf{F}_2(\mathbf{k}; \mathbf{P}_2)\Big], \end{aligned} \tag{3}$$

$\mathbf{E}_s^l$ is the intensity at the point $\mathbf{r}_s^l$ of the electric field generated by all of the dipoles, including the one located at that point; d is a lattice constant; $\mathbf{k} = \mathbf{K}d/2$ is a dimensionless wave vector; $k_0 = \omega d/2c$ is a dimensionless frequency; c is the velocity of light in a vacuum;

$$\mathbf{P} = \mathbf{P}_1 + \mathbf{P}_2;$$

$$\begin{aligned} (\mathbf{k} \overset{+}{\times} \mathbf{P}) &= \mathbf{i}\,(k_y P_z + k_z P_y) + \mathbf{j}\,(k_z P_x + k_x P_z) \\ &+ \mathbf{k}\,(k_x P_y + k_y P_x), \end{aligned}$$

where, as everywhere hereinafter, the positions of the coordinate axes, i, j, and k are directed along the edges of the cubic crystal; $S = 20.11$;

$$\mathbf{F}_s(\mathbf{k}; \mathbf{P}) = e_s^{(1)}\mathbf{P}k^2 + e_s^{(2)}\mathbf{k}\,(\mathbf{P}, \mathbf{k}) + e_s^{(3)}(\mathbf{P}; \mathbf{kk}),$$

$$(\mathbf{P}; \mathbf{kk}) = \mathbf{i}P_x k_x^2 + \mathbf{j}P_y k_y^2 + \mathbf{k}P_z k_z^2,$$

$$e_1^{(1)} = -1.845, \quad e_1^{(2)} = 2.348, \quad e_1^{(3)} = 3.708,$$

$$e_2^{(1)} = -2.135, \; e_2^{(2)} = -3.335,$$

$$e_2^{(3)} = 9.772;$$

$\mathbf{E}_2$ results from $\mathbf{E}_1$ by interchanging $\mathbf{P}_1$ and $\mathbf{P}_2$ and substituting i for $-i$. Eq. (3) gives the series expansion of $\mathbf{E}_1$ in powers of $\mathbf{k}$ up to the second inclusive. This is sufficient for long waves ($k \ll 1$), which we shall investigate.

The equations of motion can be solved by the usual Born method, expanding the frequency k_0 and the amplitudes $\mathbf{u}_s$ and $\mathbf{P}_s$ in powers of k. We, however, shall use a somewhat different method. We introduce the dimensionless variables:

$$\mathbf{v}_s = \mathbf{u}_s / d, \quad \mathbf{w}_s = \mathbf{P}_s / ed, \quad M = 4mc^2 d / e^2,$$
$$Mk_0^2 = \Omega^2, \quad n = \frac{k}{k_0} = \frac{2\pi c}{\lambda\omega}, \quad n\Omega = \varkappa, \quad M^{-1/2} = \mu,$$
$$A = d^3 / \alpha, \quad B = 4b_p d^3 / e, \quad C = c_p d^5 / 4e,$$
$$D = d_p d^5 / 2e^2, \quad G = g_p d^3 / e^2,$$
$$F = B + C, \quad L = D + 8G$$

(α, b_p, c_p, d_p, g_p are parameters from the expression for U in Ref. 1, e is the charge on an electron, λ is the wave length.) Then from (1) to (3) we obtain equations for the amplitudes in the following form:

$$-\Omega^2 \mathbf{v}_1 + L(\mathbf{v}_1 - \mathbf{v}_2) + F(\mathbf{w}_1 - \mathbf{w}_2)$$
$$= i\mu\varkappa \left[\frac{D}{2}(\mathbf{s} \overset{+}{\times} \mathbf{v}_2) + \frac{C}{2}(\mathbf{s} \overset{+}{\times} \mathbf{w}_2)\right] - \mu^2\varkappa^2 \boldsymbol{\varphi}(\mathbf{v}_2; \mathbf{w}_2),$$
$$A\mathbf{w}_1 + F(\mathbf{v}_1 - \mathbf{v}_2) - \frac{16\pi}{3}\mathbf{w} + 16\pi \frac{\varkappa^2 (\mathbf{w}, \mathbf{s})\, \mathbf{s} - \Omega^2 \mathbf{w}}{\varkappa^2 - \Omega^2}$$
$$= i\mu\varkappa \left[\frac{C}{2}(\mathbf{s} \overset{+}{\times} \mathbf{v}_2) + S(\mathbf{s} \overset{+}{\times} \mathbf{w}_2)\right] + \mu^2\varkappa^2 \mathbf{f}(\mathbf{v}_2; \mathbf{w}_1; \mathbf{w}_2), \tag{4}$$

the two remaining equations here and in what follows are obtained by exchanging the subscripts 1 and 2 of the amplitudes and substituting i for $-i$; $\mathbf{w} = \mathbf{w}_1 + \mathbf{w}_2$; $\mathbf{s}$ is the position of the wave vector;

$$\boldsymbol{\varphi}(\mathbf{v}, \mathbf{w}) = \frac{L}{8}\mathbf{v} + \frac{D}{4}\mathbf{s}(\mathbf{s}, \mathbf{v}) - \frac{D}{4}(\mathbf{v}; \mathbf{ss}) + \frac{F}{8}\mathbf{w}$$
$$+ \frac{C}{4}\mathbf{s}(\mathbf{w}, \mathbf{s}) - \frac{C}{4}(\mathbf{w}; \mathbf{ss}), \tag{4a}$$
$$\mathbf{f}(\mathbf{v}; \mathbf{w}_1; \mathbf{w}_2) = -\frac{F}{8}\mathbf{v} - \frac{C}{4}\mathbf{s}(\mathbf{s}, \mathbf{v}) + \frac{C}{4}(\mathbf{v}; \mathbf{ss})$$
$$+ \mathbf{F}_1(\mathbf{s}; \mathbf{w}_1) + \mathbf{F}_2(\mathbf{s}; \mathbf{w}_2).$$

Equation (4) contains κ and Ω. It is clear that these equations can be presented in such a form that they would include any two of the three variables κ, Ω, or n. For a solution of the equations by the method of successive approximations, we shall compute one of these two variables by means of an independent parameter, but the other, together with the amplitudes $\mathbf{v}_s$ and $\mathbf{w}_s$ will be sought in the form of an expansion in powers of μ. The inclusion of a small parameter of fixed value μ in place of the variables k allows one to carry out the solution more rigorously; in particular, this makes it possible to take into account the large numerical value of $M(\sim 10^{10})$. In those cases where it does not result in inconsistencies, the independent parameter κ, Ω, or n, should be considered to be of order of magnitude $\mu^0 = 1$.

2. ACOUSTICAL VIBRATIONS

Let us consider κ as an independent parameter and Ω^2 as a dependent one which is taken to be

$$\Omega^2 = \Omega_0^2 + \mu\Omega_1^2 + \mu^2\Omega_2^2 + \ldots, \tag{5}$$

$$\mathbf{v}_s = \mathbf{v}_s^0 + \mu\mathbf{v}_s' + \mu^2\mathbf{v}_s'' + \ldots,$$
$$\mathbf{w}_s = \mathbf{w}_s^0 + \mu\mathbf{w}_s' + \mu^2\mathbf{w}_s'' + \ldots. \tag{6}$$

Substituting (5) and (6) in (4) and retaining only the terms $\sim\mu^0$, we have zero-approximation equations:

$$-\Omega_0^2\mathbf{v}_1^0 + L(\mathbf{v}_1^0 - \mathbf{v}_2^0) + F(\mathbf{w}_1^0 - \mathbf{w}_2^0) = 0,$$
$$A\mathbf{w}_1^0 + F(\mathbf{v}_1^0 - \mathbf{v}_2^0) - \frac{16\pi}{3}\mathbf{w}^0$$
$$+ 16\pi \frac{\varkappa^2 (\mathbf{w}^0 \cdot \mathbf{s})\, \mathbf{s} - \Omega_0^2 \mathbf{w}^0}{\varkappa^2 - \Omega_0^2} = 0. \tag{7}$$

The system (7) has the following obvious solution:

$$\Omega_0^2 = 0, \quad \mathbf{v}_2^0 = \mathbf{v}_1^0, \quad \mathbf{w}_2^0 = \mathbf{w}_1^0 = 0. \tag{8}$$

It obviously has the nature of acoustic vibrations: in the zero approximation the frequency is zero, the dipole moment is absent, and the displacements of the two atoms of the cell are identical.

After investigating the terms of order μ in (4) we find the first approximation equations, from which we obtain

$$\Omega_1^2 = 0, \tag{9}$$

$$\mathbf{v}_1' - \mathbf{v}_2' = \frac{AD - 2FC}{2(AL - 2F^2)}\, i\varkappa(\mathbf{s} \overset{+}{\times} \mathbf{v}_1^0),$$
$$-\mathbf{w}_2' = \mathbf{w}_1' = \frac{LC - FD}{2(AL - 2F^2)}\, i\varkappa(\mathbf{s} \overset{+}{\times} \mathbf{v}_1^0). \tag{10}$$

The second-approximation equations result in

$$2\Omega_2^2\mathbf{v}_1^0 - i\varkappa\frac{D}{2}(\mathbf{s} \overset{+}{\times} \mathbf{v}_1' - \mathbf{v}_2') - i\varkappa\frac{C}{2}(\mathbf{s} \overset{+}{\times} \mathbf{w}_1' - \mathbf{w}_2')$$
$$-2\varkappa^2\boldsymbol{\varphi}(\mathbf{v}_1^0; \bar{0}) = 0, \tag{11}$$

which after inserting (1) gives an equation for the firection of $\mathbf{v}_1^0$:

$$\Omega_2^2\mathbf{v}_1^0 + \frac{AD^2 + 2LC^2 - 4FCD}{8(AL - 2F^2)}\varkappa^2 (\mathbf{s} \overset{+}{\times} (\mathbf{s} \overset{+}{\times} \mathbf{v}_1^0)) - \varkappa^2 \boldsymbol{\varphi}(\mathbf{v}_1^0; 0) = 0. \tag{12}$$

Having set the determinant of this system equal to zero, we have a cubic equation for Ω_2^2 and, accordingly, three branches of acoustic vibrations. If we introduce the symbols

$$b_1 = \frac{(AD^2 + 2LC^2 - 4FCD)\,e^2}{4(AL - 2F^2)\,d^4}, \quad b_2 = \frac{Le^2}{4d^4}, \quad b_3 = \frac{De^2}{2d^4} \tag{13}$$

and make some simple transformations, the first of the three scalar equations (12) takes the form

$$v_{1x}^0 [-\rho v^2 + b_2 s_x^2 + (b_2 - b_1)(s_y^2 + s_z^2)] + v_{1y}^0 (b_3 - b_1) s_x s_y + v_{1z}^0 (b_3 - b_1) s_x s_z = 0, \tag{14}$$

in which ρ is the density and v is the velocity of sound in the crystal. Comparing (14) with the analogous equation of the theory of elasticity

$$u_x [-\rho v^2 + c_{11} s_x^2 + c_{44}(s_y^2 + s_z^2)] + u_y (c_{12} + c_{44}) s_x s_y + u_z (c_{12} + c_{44}) s_x s_z = 0 \tag{15}$$

(c_{ik} is the modulus of elasticity), we have

$$b_1 = c_{11} - c_{44}, \quad b_2 = c_{11}, \quad b_3 = c_{11} + c_{12}. \tag{16}$$

These three relations can be used for determining the parameters of the theory.

According to (8) and (10) the dipole moment of the cell is equal to zero in the first approximation (it is possible to show that $\mathbf{w}' \neq 0$). However, a calculation of the dipole moments is essential for investigation of the acoustic vibrations. According to (13), the parameters F, C, and A, which appear on account of the dipole moments, enter into (14).

3. OPTICAL VIBRATIONS

We now take n as the independent parameter, and Ω as the dependent one:

$$\Omega = \Omega_0 + \mu\Omega_1 + \mu^2\Omega_2 + \ldots. \tag{17}$$

Substituting (6) and (17) in (4), we obtain for the zero approximation:

$$\begin{gathered} -\Omega_0^2\mathbf{v}_1^0 + L(\mathbf{v}_1^0 - \mathbf{v}_2^0) + F(\mathbf{w}_1^0 - \mathbf{w}_2^0) = 0, \\ A\mathbf{w}_1^0 + F(\mathbf{v}_1^0 - \mathbf{v}_2^0) - \frac{16\pi}{3}\mathbf{w}^{0\prime} \\ + 16\pi\frac{n^2\mathbf{s}(\mathbf{w}^0, \mathbf{s}) - \mathbf{w}^0}{n^2 - 1} = 0. \end{gathered} \tag{18}$$

[It is apparent that (18) is the same as (7)]. Let us examine the solution for the case when

$$\Omega_0 \neq 0, \quad n^2 \neq 1,$$

$$n^2 \neq n_0^2 = (A + 64\pi/3)/(A - 32\pi/3).$$

The solution takes the following form:

$$\Omega_0^2 = (2LA - 4F^2)/A = \Omega_{\mathrm{lim}}^2, \quad \mathbf{v}_2^0 = -\mathbf{v}_1^0, \quad -\mathbf{w}_2^0 = \mathbf{w}_1^0 = -(2F/A)\mathbf{v}_1^0, \tag{19}$$

i.e., it has the nature of optical vibrations: the limiting frequency differs from zero and the displacements of the two atoms of the cell are opposite in the zero approximation.

From the condition for solvability of the first-approximation equations, it is possible to ascertain that $\Omega_1 = 0$. Using this, from the first-approximation equations we obtain

$$\begin{gathered} \mathbf{v}_1' + \mathbf{v}_2' = \Omega_{\mathrm{lim}}^{-1}(D - 2FC/A)\,i\,(\mathbf{s} \overset{+}{\times} \mathbf{v}_1^0), \\ \mathbf{w}' = \frac{\Omega_{\mathrm{lim}} n (n_0^2 - 1)(C - 4FS/A)}{32\pi (n^2 - n_0^2)}\,i \left[\frac{n^2}{n_0^2}(n_0^2 - 1)((\mathbf{s} \overset{+}{\times} \mathbf{v}_1^0), \mathbf{s})\mathbf{s} - (n^2 - 1)(\mathbf{s} \overset{+}{\times} \mathbf{v}_1^0)\right]. \end{gathered} \tag{20}$$

Examining the condition of solvability of the second-approximation equations and using (20), it is easy to obtain an equation for the direction of $\mathbf{v}_1^0$:

$$\begin{gathered} 2\Omega_{\mathrm{lim}}\Omega_2\mathbf{v}_1^0 - (D/2 - FC/A)^2 n (\mathbf{s} \overset{+}{\times} (\mathbf{s} \overset{+}{\times} \mathbf{v}_1^0) + {}^1/_4 n\Omega_{\mathrm{lim}}(C - 4FS/A)\,i\mathbf{w}' \\ + n^2\Omega_{\mathrm{lim}}^2[\boldsymbol{\varphi}(\mathbf{v}_1^0; \mathbf{w}_1^0) - \mathbf{f}(\mathbf{v}_1^0; \mathbf{w}_2^0; \mathbf{w}_1^0)] = 0, \end{gathered} \tag{21}$$

in which $\mathbf{w}'$, $\mathbf{w}_1^0$, and $\mathbf{w}_2^0$ are substituted from (20) and (19). This equation gives, as is apparent, three modes of optical vibrations with one and the same limiting frequency Ω_{lim}. Therefore, there is only one line in the first-order Raman spectrum. Optical vibrations with limiting frequency Ω_{lim} are active in the Raman effect since the polarizability of the crystal in opposite senses is dissimilar.[5] This theoretical result was reported long ago and confirmed experimentally.[6]

From (20) it follows that our solution cannot be used to find the values of n close to n_0. For $|n - n_0| \sim \mu$, the terms of first order become comparable with the terms of zero order and the series for solutions do not converge. Thus $n = n_0$ is a singular point of this solution.

4. RADIATION VIBRATIONS

We now make Ω as the independent parameter and n dependent:

$$n = n_0 + \mu n_1 + \mu^2 n_2 + \ldots \tag{22}$$

When $\Omega \neq \Omega_{\text{lim}}$ and $n_0 \neq 1$, the zero-approximation equations yield the following solution:

$$\begin{gathered} \mathbf{v}_2^0 = \mathbf{v}_1^0 = 0, \quad \mathbf{w}_2^0 = \mathbf{w}_1^0, \\ n_0^2 = (A + 64\pi/3)/(A - 32\pi/3), \end{gathered} \tag{23}$$

$$(\mathbf{w}_1^0 \cdot \mathbf{s}) = 0. \tag{23a}$$

It describes the propagation of electromagnetic waves in the crystal, while the index of refraction n_0 corresponds with the longest wavelength. Let us call these vibrations radiation vibrations. They differ from the usual optical vibrations for which, according to (19), $\mathbf{w}^0 = 0$, $\mathbf{v}_s^0 \neq 0$.

The conditions of solvability of the first-approximation equations give $n_{11} = 0$. Taking this into account, we obtain from the first-approximation equation

$$\begin{gathered} -\mathbf{v}_2' = \mathbf{v}_1' = \frac{n_0 \Omega (AC - 4FS)}{2A(\Omega_{\text{lim}}^2 - \Omega^2)} i (\mathbf{s} \overset{+}{\times} \mathbf{w}_1^0), \quad (\mathbf{w}' \cdot \mathbf{s}) = 0, \\ \mathbf{w}_1' - \mathbf{w}_2' = \frac{n_0 \Omega [(2L - \Omega^2) 2S - 2FC]}{A(\Omega_{\text{lim}}^2 - \Omega^2)} i (\mathbf{s} \overset{+}{\times} \mathbf{w}_1^0). \end{gathered} \tag{24}$$

Eq. (24) indicates that the solution under consideration is not applicable for $|\Omega - \Omega_{\text{lim}}| \sim \mu$.

The condition of solvability of the second-approximation equations, taking (24) into account, gives

$$\begin{gathered} \Big\{ -n_2 \mathbf{w}_1^0 + q\Omega^2 \Big[\mathbf{f}(0; \mathbf{w}_1^0; \mathbf{w}_1^0) + \frac{S^2}{A} (\mathbf{s} \overset{+}{\times} (\mathbf{s} \overset{+}{\times} \mathbf{w}_1^0)) \Big] \\ + Q \frac{\Omega^2}{\Omega_{\text{lim}}^2 - \Omega^2} (\mathbf{s} \overset{+}{\times} (\mathbf{s} \overset{+}{\times} \mathbf{w}_1^0)) \Big\} \times \mathbf{s} = 0, \end{gathered} \tag{25}$$

$$q = n_0 (n_0^2 - 1)^2 / 64\pi, \quad Q = q(C/2 - 2FS/A)^2.$$

(25) and (23a) represent a system of equations for n_2 and the direction of $\mathbf{w}_1^0$. It is clear that only three of these equations arè linearly independent. The corresponding characteristic equation is:

$$\begin{gathered} n_2^2 - n_2 \Omega^2 \{2N + H[1 - (s_x^4 + s_y^4 + s_z^4)]\} \\ + \Omega^4 \{N^2 + NH[1 - (s_x^4 + s_y^4 + s_z^4)] \\ + 3H^2 s_x^2 s_y^2 s_z^2\} = 0, \end{gathered} \tag{26}$$

$$\begin{gathered} N = q(e_1^{(1)} + e_2^{(1)} + S^2/A) + Q/(\Omega_{\text{lim}}^2 - \Omega^2), \\ H = q(e_1^{(3)} + e_2^{(3)} - 2S^2/A) - 2Q/(\Omega_{\text{lim}}^2 - \Omega^2). \end{gathered}$$

It gives two modes of the radiation vibrations. Thus double refraction must take place, reaching a maximum in the vicinity of Ω_{lim}.

At the point $\Omega = \Omega_{\text{lim}}$ we have $n_2 = \pm\infty$, and the $\mathbf{v}_s$ are similarly infinitely large. This indicates absorption of light in the vicinity of this point. The latter absorption represents an effect of first-order in $\mu \sim d/\lambda$ (and not zero order as occurs in ionic crystals), since $\mathbf{v}_s^0 = 0$ and only the $\mathbf{v}_s'$ increase without limit. Therefore, the absorption must be considerably weaker than in ionic crystals; this is confirmed experimentally[6].

5. μ-REGION OF SINGULAR POINT

The remarks made in connection with (20) and (24) indicate that the μ-region of the point $\Omega = \Omega_{\text{lim}}$, $n = n_0$, (which we shall call the singular point) requires special investigation since the solutions obtained (the optical as well as the radiation vibrations) do not hold in this region. In order to investigate this region, we assume

$$\begin{gathered} \varkappa = \varkappa_0 + \mu\varkappa_1, \quad \varkappa_0 = n_0 \Omega_{\text{lim}}, \\ \Omega^2 = \Omega_{\text{lim}}^2 + \mu\Omega_1^2 + \mu^2\Omega_2^2 + \ldots \end{gathered} \tag{27}$$

and we consider κ_1 as an independent parameter of order unity. Substituting (27) and (6) in (4), we obtain to a zero approximation

$$\begin{gathered} -\Omega_{\text{lim}}^2 \mathbf{v}_1^0 + L(\mathbf{v}_1^0 - \mathbf{v}_2^0) + F(\mathbf{w}_1^0 - \mathbf{w}_2^0) = 0, \\ A\mathbf{w}_1^0 + F(\mathbf{v}_1^0 - \mathbf{v}_2^0) - 16\pi \mathbf{w}^0/3 \\ + 16\pi [\varkappa_0^2 \mathbf{s}(\mathbf{w}^0, \mathbf{s}) - \Omega_{\text{lim}}^2 \mathbf{w}^0] / (\varkappa_0^2 - \Omega_{\text{lim}}^2) = 0. \end{gathered} \tag{28}$$

The most general solution of this system is

$$-\mathbf{v}_2^0 = \mathbf{v}_1^0, \quad \mathbf{w}_1^0 = \mathbf{w}^0/2 - (2F/A)\,\mathbf{v}_1^0, \quad \mathbf{w}_2^0 = \mathbf{w}^0/2 + (2F/A)\,\mathbf{v}_1^0, \tag{29}$$

$$(\mathbf{w}^0 \cdot \mathbf{s}) = 0. \tag{29a}$$

It represents a superposition of optical and radiation vibrations, which is not surprising, for in the zero approximation the singular point is a point of intersection of the optical and radiation modes.

The conditions of solvability of the first approximation equation lead to the following results:

$$\Omega_1^2 \mathbf{v}_1^0 + Q_1 i\,(\mathbf{s} \overset{+}{\times} \mathbf{w}^0) = 0, \tag{30}$$

$$[{}^1/_2\,(n_0^2\Omega_1^2 - 2\varkappa_0\varkappa_1)\,\mathbf{w}^0 + iR_1\,(\mathbf{s} \overset{+}{\times} \mathbf{v}_1^0)] \times \mathbf{s} = 0,$$

$$Q_1 = {}^1/_4\varkappa_0\,(C - 4FS/A), \tag{30a}$$

$$R_1 = \varkappa_0\,(4FS/A - C)\,(\varkappa_0^2 - \Omega_{\text{lim}}^2)\,/\,(A - 32\pi/3).$$

The system of equations (30), (30a), and (29a) determines the directions of the vectors $\mathbf{v}_1^0$ and $\mathbf{w}^0$, giving a solution in the vicinity of the singular point. In this system there are six linearly independent equations, since in (30a) one of the three scalar equations is a consequence of the other two. Setting the determinant equal to zero, we obtain an equation of fifth degree in Ω_1^2. Thus in the vicinity of the singular point we get five modes, which correspond to three optical and two radiation modes far from the singular point.

We give the name "singular" to the direction of s, parallel to the diagonals of the faces of a lattice cube. It can be shown that for non-singular directions of s, there are one optical and four mixed modes (Fig. 1), but the singular directions of s correspond to two optical, one radiation, and two modes (Fig. 2); the vector $\mathbf{w}^0$ of the radiation mode lies in the plane of the same face of the cube as does s.

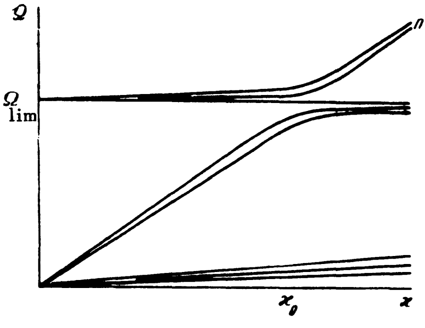

FIG. 1. Vibration spectra for non-singular directions of s. $\varkappa_0$ and Ω_{lim} are the coordinates of the singular point.

Let us note that system (4) allows one more solution, for which $\Omega^2 = \kappa^2$, $(n = 1)$, $\mathbf{w}^0 \parallel \mathbf{s}$. We shall not examine this solution. Although this method was already pointed out by Born for ionic crystals, doubt arises concerning the applicability in this case of the Ewald method[4] for finding $\mathbf{E}_s^1$ (the Fourier expansion will contain an infinitely large zero term). This problem requires a separate investigation.

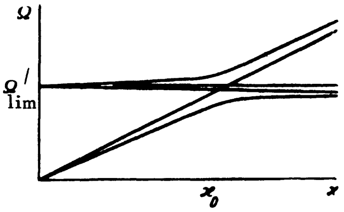

FIG. 2. Optical and radiation modes for singular directions of s.

6. INVESTIGATION OF THE GENERAL EQUATIONS OF MOTION

We shall show here that the limitations used in Ref. 1 in the derivation of the expression for U do not disturb the generality of the qualitative results already derived. With this goal, we investigate the most general equations for long-wave harmonic oscillations. Substituting (2) in (1), assuming U to be an arbitrary quadratic form in $\mathbf{u}_s^1$ and $\mathbf{P}_s^1$, separating explicitly the amplitude of the internal field $\mathbf{E}_s$, and expanding in powers of $\mathbf{k}$, we obtain

$$m\omega^2 T_{x'}^{is}\delta_{i1} + \sum_{s'i'x''}\Big(A_{x'x''}^{(0)ii'ss'}\,T_{x''}^{i's'} + \sum_{y'} A_{x'x''y'}^{(1)ii'ss'}\,T_{x''}^{i's'}\,k_{y'} + \sum_{y'z'} A_{x'x''y'z'}^{(2)ii'ss'}\,T_{x''}^{i's'}\,k_{y'}k_{z'}\Big) + E_{sx'}\delta_{i2} = 0, \tag{31}$$

$$T_{x'}^{is} = \begin{cases} u_{sx'}, & i = 1 \\ P_{sx'}, & i = 2 \end{cases} \qquad x' = x, y, z. \tag{32}$$

We require that the following obvious conditions be fulfilled: I) The system of equations (31) must be self-conjugate. II) The forces contained in (31) must vanish upon translation of the lattice as a whole. III) The coefficients $A^{(0)}$ and $A^{(2)}$ must be real, and $A^{(1)}$ pure imaginary, which follows from the expansion in powers of k. IV) The system (31) must be invariant relative to symmetry transformations of the crystal. The symmetry elements of a crystal of the diamond type are determined from the conditions that (a) the center of the segment between two neighboring atoms is the center of symmetry and (b) the diamond lattice belongs to the point group T_d^8.

The above conditions lead to a series of relationships between the coefficients $A^{(l)}$, from which it is possible to determine the independent $A^{(l)}$s; these turn out to number twenty-six, namely four $A^{(0)}$s:

$$A_{xx}^{(0)1111} = a_1', \ A_{xx}^{(0)1211} = a_2', \qquad A_{xx}^{(0)2211} = a_3', \ A_{xx}^{(0)2212} = a_4', \tag{33}$$

four $A^{(1)}$s:

$$A_{xyz}^{(1)1112} = ib_1', \ A_{xyz}^{(1)2212} = ib_2', \qquad A_{xyz}^{(1)1212} = ib_3', \ A_{xyz}^{(1)1211} = ib_4' \tag{34}$$

and eighteen $A^{(2)}$s:

$$x'y'x''y'' = xxxx,\ xxyy,\ xyxy; \qquad ii' = 11,\ 22,\ 12;\ ss' = 11,\ 12. \tag{35}$$

Introducing, as in Sec. 1, dimensionless quantities and calculating by means of the independent parameter κ, we obtain in the zero approximation relative to μ

$$\begin{gathered} -\Omega_0^2 \mathbf{v}_1^0 + a_1 (\mathbf{v}_2^0 - \mathbf{v}_1^0) + a_2 (\mathbf{w}_2^0 - \mathbf{w}_1^0) = 0, \\ a_2 (\mathbf{v}_2^0 - \mathbf{v}_1^0) - a_3 \mathbf{w}_1^0 - a_4 \mathbf{w}_2^0 - \frac{16\pi}{3} \mathbf{w}^0 \\ + 16\pi \frac{\varkappa^2 (\mathbf{w}^0, \mathbf{s}) - \Omega_0^2 \mathbf{w}^0}{\varkappa^2 - \Omega_0^2} = 0. \end{gathered} \tag{36}$$

Equations (7) result from (36) if we assume

$$a_1 = -L, \quad a_2 = -F, \quad a_3 = -A, \quad a_4 = 0. \tag{37}$$

Thus the generality of (7) would be invalidated only if a_4 were to vanish. However, examining the solution of the zero-approximation equations, it is easy to establish that the coefficient of $\mathbf{w}^0$, which equals $-16\pi/3$, does not affect the qualitative character of the solutions, and bears only on their quantitative character. Hence follows the qualitative similarity of (7) and (36), *i.e.*, the generality of all the qualitative results of the zero-order approximation considered above.

The first-approximation equations give significant results only in the vicinity of the singular point. Therefore, we examine only that region. Everything concerning these conclusions results from the conditions of solvability of the first-approximation equations, which after some calculations yield

$$\begin{gathered} 2\,\Omega_1^2 \mathbf{v}_1^0 + i\varkappa_0 \left(b_3 + b_4 - \frac{2\,a_2 b_2}{a_2 - a_4} \right) (\mathbf{s} \overset{+}{\times} \mathbf{w}^0) = 0, \\ \left\{ i\varkappa_0 \left[\frac{4\,a_2}{a_2 - a_4} - 2\,(b_3 + b_4) \right] (\mathbf{s} \overset{+}{\times} \mathbf{v}_1^0) \right. \\ \left. + \frac{a_3 + a_4 + 32\pi/3}{\varkappa_0^2 - \Omega_{\mathrm{lim}}^2} (2\,\varkappa_0 \varkappa_1 - n_0^2 \Omega_1^2)\, \mathbf{w}^0 \right\} \times \mathbf{s} = 0. \end{gathered} \tag{38}$$

Comparing (38) with (30) and (30a), we see that these systems of equations differ only in their constants. Therefore, all the qualitative results of Sec. 5 should be correct in the general case.

Second-approximation equations are essential only for obtaining quantitative results: calculation of the corrections to the frequencies and determination of the directions of $\mathbf{v}_s^0$ and $\mathbf{w}_s^0$. Therefore, examination of their general form is not of interest.

CONCLUSIONS

1. The spectrum of vibrations consists of eight modes (far from the singular point — three acoustic, three optical, and two radiation modes). In the vicinity of the singular point, the transistions occur from the optical modes to the radiation modes and vice versa. For the non-singular directions of s, both of the radiation and two (of the three) optical modes experience discontinuity and mutual transition (Fig. 1). For the singular directions of s only one radiation and one optical mode experience discontinuity and transition (Fig.2).

2. The theory explains qualitatively the absorption of light at a frequency close to Ω_{lim}. Polychromism (the dependence of absorption on the direction of s and the polarization of the light waves) should be observed. A separate work will be devoted to a more detailed and quantitative investigation of the absorption.

3. Double refraction must take place, reaching a maximum in the vicinity of the singular point. A more detailed investigation, to which a separate work will be devoted, shows that the crystal possesses seven optical axes with directions of type (111) and (100).

4. The conduction electrons must interact with both acoustic and optical vibrations, owing to the polarization w which is associated with them. This question will be investigated in a separate work.

5. All the results enumerated above are independent in their qualitative aspects of any special choice of the potential energy U.

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Band Structure of the Polaron Energy Spectrum

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Using the macroscopic treatment of the polaron as the zeroth approximation, the periodic potential of a crystal and the periodic variation of its polarizability with variations in the position of the polaron center of gravity are calculated in the first approximation. We determine the dependence of the energy of a crystal with a polaron on the position of the polaron's center of gravity, and it is found possible to treat polaron motion as the motion of a particle with the polaron mass M in a field with a periodic potential. We determine the widths and spacings of the lowest forbidden and allowed energy bands. A numerical calculation is performed for NaCl, KCl, KBr, and KI.

1. STATUS OF THE PROBLEM

GREAT SUCCESSES in the theory of the electric conductivity of ionic crystals were attained as a result of Pekar's polaron theory[1, 2] in which the interaction between electrons and polar vibrations of the crystal are introduced into the fundamental Hamiltonian of the problem. The periodic potential of the crystal is eliminated with the aid of the effective-mass method[3] (EMM). It is found that electron motion is composed of vibration within a polarization well and wave-like translation of the electron together with the polarization well through the crystal[4]. For a fixed crystal polarization the electron energy spectrum is found to be discrete. At the same time, the problem of electron and ion motion possesses translational degeneracy[2], so that the energy spectrum of the whole crystal is found to be continuous:

$$E = J[\psi] + (\hbar^2 K^2 / 2M) - {}^3/_2\, \hbar\omega + E_{\text{ion}}, \qquad (1)$$

where K and M are the wave vector and effective mass of the polaron[5], $J[\psi]$ is the energy of the crystal with a stationary polaron, and ω is the limiting longitudinal optical crystal vibrations.

The translational degeneracy of the problem of polaron motion led several authors[6, 7] to assert that the electron energy spectrum should have a band-like structure, and that therefore polaron theory is essentially band theory in which the interaction between the electron and the crystal polarizations has been accounted for. This leads only to a formal change of the specific parameters of the current carriers, and according to Tiablikov[7] is of no great consequence, since these parameters are usually obtained experimentally anyway. As was asserted by Tiablikov[8], Eq. (1) gives the energy only in the neighborhood of the lower edge of the first polaron band.

In other works[9-11], Tiablikov suggested a method for calculating the electron energy spectrum by accounting for interactions with the phonon field sim-