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LONG-WAVE VIBRATIONS IN IONIC CRYSTALS

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Phenomenological equations relating the macroscopic dipole moment, the macroscopic electric field, and the deviation of the ions from their equilibrium position for qa ≪ 1 (q is the wave vector of the vibration and a is the distance between nearest neighbors in the lattice) are formulated and solved. The initial portion of the phonon spectrum in cubic crystals of the ionic type has been determined. The equations of the acoustic and optical vibrations split in the approximation considered here which is quadratic with respect to qa. The dispersion law for longitudinal optical vibrations and transverse optical vibrations differs from the hole spectrum in cubic crystals of the type of germanium in which the splitting is due to spin–orbit interaction. The constants defining the long-wave portion of the phonon spectrum can be expressed in terms of the known characteristics of ionic crystals with weak spatial dispersion. The method proposed here can be applied to calculate the initial spectrum in ionic crystals with a lower tetragonal symmetry.

1. INTRODUCTION

A rather large number of papers has been devoted to the calculation of the phonon spectrum in ionic crystals; among these one can discern three main trends: 1) the determination of the limiting frequencies of the optical vibrations for $\mathbf{q} \to 0$ ($\mathbf{q}$ is the phonon wave number);[1] 2) the calculation of the long-wave portion of the spectrum of acoustic phonons which made it possible to relate the elastic constants of the crystal with its microscopic characteristics (see, for instance, [2]); 3) numerical calculations of the spectrum in the entire range of $\mathbf{q}$[3] by using Ewald's method (see [1], Sec. 30). In this paper we have obtained an analytic expression for the phonon spectrum, both optical and acoustic, in the region qa ≪ 1 (a is the distance between nearest neighbors in the crystal) in a manner similar to that employed in the problem of the electron spectrum in semiconductors.[4] It turns out that the optical phonon spectrum in ionic crystals is not similar to the hole spectrum in germanium,[4] although in both cases for $\mathbf{q} \to 0$ there are three branches of the spectrum—one doubly degenerate and one split. The reason for such a difference lies in the differing nature of the splitting mechanism. Whereas in germanium this splitting is due to the spin–orbit interaction which tends for $\mathbf{q} \to 0$ to a fully determined limit, in ionic crystals the splitting of the phonon branches is due to an electric field which is a nonanalytic function at $\mathbf{q} = 0$ (see below). The method developed below makes it possible to find the form of the invariants quadratic in q in the expansion of the frequencies of optical phonons in a series in qa; in the case of cubic crystals such invariants are not only q^2, but also such as, for example, $(q_x^4 + q_y^4 + q_z^4)/q^2$. In addition this method allows one to express the parameters which determine the long-wave spectrum in terms of other known constants, such as ω_0—the infrared dispersion frequency (the limiting frequency of the transverse optical vibrations), and ϵ_0 and ϵ_∞—the static and high-frequency dielectric permittivity, etc.

It is essential to note that it is precisely the long-wave portion of the spectrum which is important in the study of many interesting phenomena in ionic crystals. Such phenomena are, for example, optical effects, since the proposed method makes it possible to calculate the dielectric tensor under conditions of spatial and time dispersion for qa ≪ 1 but arbitrary refractive index. This makes it possible, first, to extend the limits of applicability of Ginzburg's theory[5] in the region of frequencies close to ω_0, and, secondly, to determine the constants in the phenomenological expansion of the dielectric tensor in a series in $\mathbf{q}$.[5]

In addition, a knowledge of the long-wave portion of the optical phonon spectrum makes it possible to set up the problem of local vibrations in ionic crystals in the presence of a defect with long-range interaction, i.e., in the case when Lifshitz' method[6] of determining the frequencies of local vibrations ceases to be constructive. Such local vibrations can occur in the presence of an F center in the crystal when an electron is localized on a lattice point, as happens in the case of strong electron–phonon interaction,[7, 8] etc.

2. OPTICAL VIBRATION BRANCHES

For simplicity we restrict ourselves in this paper to a consideration of crystals belonging to the symmetry class O_h with two atoms per unit cell, i.e., the theory presented below is in fact applicable to two types of lattices—NaCl and CsCl. In principle, the proposed method is also suitable for lattices of lower tetragonal symmetry.

In the approximation neglecting spatial dispersion the equations of motion of the optical vibration branches of ionic crystals can be written by introducing a macroscopic electric field **E** and a macroscopic dipole moment **P** (see [1], Secs. 7 and 9). Unlike (7.1) and (7.2) in [1], we write them in the $\mathbf{q}$ representation:

$$\omega^2 v_\alpha(\mathbf{q}) = \omega_0{}^2 v_\alpha(\mathbf{q}) - \omega_0\left(\frac{\varepsilon_0 - \varepsilon_\infty}{4\pi}\frac{v_a}{M}\right)^{1/2} E_\alpha(\mathbf{q}), \qquad M = \frac{M_+ M_-}{M_+ + M_-}, \tag{1}$$

$$P_\alpha(\mathbf{q}) = \omega_0\left(\frac{\varepsilon_0 - \varepsilon_\infty}{4\pi}\frac{M}{v_a}\right)^{1/2} v_\alpha(\mathbf{q}) + \frac{\varepsilon_\infty - 1}{4\pi} E_\alpha(\mathbf{q}), \tag{2}$$

$$E_\alpha(\mathbf{q}) = -4\pi \sum_\beta \frac{q_\alpha q_\beta}{q^2} P_\beta(\mathbf{q}). \tag{3}$$

Here v_a is the volume of the unit cell, the Greek subscripts $\alpha = 1, 2, 3$ denote projections on the Cartesian coordinate axes, $\mathbf{v}(\mathbf{q}) = \underset{+}{\mathbf{u}}(\mathbf{q}) - \underset{-}{\mathbf{u}}(\mathbf{q})$ where $\underset{-}{\mathbf{u}}(\mathbf{q})$ is the displacement of an ion of the type ± from its equilibrium position. Equation (3) is the electrostatic Maxwell–Lorentz equation in the $\mathbf{q}$ representation. The purpose of this work is to obtain correction terms due to dispersion for the right-hand sides of (1) and (2). However, we find it convenient first to obtain a solution of Eqs. (1)–(3), because the steps of this calculation will be repeated in solving a similar system of equations in the presence of dispersion. Let us substitute $P_\alpha(\mathbf{q})$ from (2) and (3), and assuming

$$E_\alpha(\mathbf{q}) = q_\alpha \chi(\mathbf{q}), \tag{4}$$

we obtain

$$E_\alpha(\mathbf{q}) = -\frac{\omega_0}{\varepsilon_\infty}\left[\frac{4\pi M(\varepsilon_0 - \varepsilon_\infty)}{v_a}\right]^{1/2} \sum_\beta \frac{q_\alpha q_\beta}{q^2} v_\beta(\mathbf{q}). \tag{5}$$

Substituting (5) in (1):

$$\omega^2 v_\alpha(\mathbf{q}) = \omega_0^2 v_\alpha(\mathbf{q}) + \omega_0^2 \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_\infty} \sum_\beta \frac{q_\alpha q_\beta}{q^2} v_\beta(\mathbf{q}). \tag{6}$$

Diagonalizing the system of Eqs. (6) by means of the transformation

$$\tilde{v}_\alpha(\mathbf{q}) = \sum_\beta U_{\alpha\beta}(\mathbf{q}) v_\beta(\mathbf{q}), \tag{7}$$

$$U = \begin{pmatrix} -\dfrac{1}{q_1^2 + q_2^2}\left(\dfrac{q_1^2 q_3}{q} + q_2^2\right) & \dfrac{q_1 q_2}{q_1^2 + q_2^2}\left(1 - \dfrac{q_3}{q}\right) & \dfrac{q_1}{q} \\ \dfrac{q_1 q_2}{q_1^2 + q_2^2}\left(1 - \dfrac{q_3}{q}\right) & -\dfrac{1}{q_1^2 + q_2^2}\left(\dfrac{q_2^2 q_3}{q} + q_1^2\right) & \dfrac{q_2}{q} \\ \dfrac{q_1}{q} & \dfrac{q_2}{q} & \dfrac{q_3}{q} \end{pmatrix} = U^{-1}. \tag{8}$$

Then

$$(\omega^2 - \omega_\alpha^2)\tilde{v}_\alpha(\mathbf{q}) = 0, \tag{9}$$

$$\omega_{1,2}^2 = \omega_0^2, \qquad \omega_3^2 = \omega_0^2 \varepsilon_0 / \varepsilon_\infty, \tag{10}$$

which coincides with (7.16) and (7.17) from [1].

In the presence of spatial dispersion the coefficients of the right-hand sides of Eqs. (1) and (2) and of $E_\alpha(\mathbf{q})$ and $v_\alpha(\mathbf{q})$ depend on $\mathbf{q}$. For weak dispersion one can expand these coefficients in a series in q (the dimensionless expansion parameter will be qa). Such an expansion will have no odd terms because of the center of inversion in the lattice, and zero-order terms in qa will coincide with the right-hand parts of (1) and (2). We shall retain only the quadratic terms of such an expansion. The resulting equations can be written as follows

$$\omega^2 v_\alpha(\mathbf{q}) = \omega_0^2 v_\alpha(\mathbf{q}) - \omega_0\left(\frac{\varepsilon_0 - \varepsilon_\infty}{4\pi}\frac{v_a}{M}\right)^{1/2} E_\alpha(\mathbf{q}) - \sum_\beta \Pi_{\alpha\beta}(\mathbf{q}) v_\beta(\mathbf{q}) - \frac{v_a}{M}\sum_\beta G_{\alpha\beta}(\mathbf{q}) E_\beta(\mathbf{q}) \tag{11}$$

$$P_\alpha(\mathbf{q}) = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{4\pi}\frac{M}{v_a}\right)^{1/2} \omega_0 v_\alpha(\mathbf{q}) + \frac{\varepsilon_\infty - 1}{4\pi} E_\alpha(\mathbf{q}) + \sum_\beta G_{\alpha\beta}(\mathbf{q}) v_\beta(\mathbf{q}) + \sum_\beta F_{\alpha\beta}(\mathbf{q}) E_\beta(\mathbf{q}). \tag{12}$$

Here $\Pi_{\alpha\beta}(\mathbf{q})$, $G_{\alpha\beta}(\mathbf{q})$, and $F_{\alpha\beta}(\mathbf{q})$ are matrices quadratic in $\mathbf{q}$. From group theory considerations they can be written in the form

$$\Pi_{\alpha\beta}(\mathbf{q}) = \omega_0^2 a^2 \{r q_\alpha q_\beta + \delta_{\alpha\beta}[(l - {}^1\!/_2 s) q^2 + s q_\alpha^2]\}, \tag{13}$$

where r, l, and s are numbers of the order of unity. The matrices $G_{\alpha\beta}(\mathbf{q})$ and $F_{\alpha\beta}(\mathbf{q})$ can be similarly written. Let us emphasize that the latter two matrices describe the corrections due to the deformations of the ions and vanish in the rigid-ion approximation (see [1], Sec. 44).

Equations (11) and (12) along with (3) describe the dynamics of long-wave optical vibration branches. Eliminating with the aid of (11) $\mathbf{v}(\mathbf{q})$ from Eq. (12), one can obtain the dielectric tensor $\epsilon_{\alpha\beta}(\mathbf{q}, \omega)$:

$$\varepsilon_{\alpha\beta}(\mathbf{q}, \omega) = \varepsilon_\infty \delta_{\alpha\beta} - \omega_0^2 \frac{\varepsilon_0 - \varepsilon_\infty}{\Delta(\mathbf{q}, \omega)} A_{\alpha\beta}(\mathbf{q}, \omega) + 4\pi F_{\alpha\beta}(\mathbf{q}) - \left[\frac{4\pi v_a}{M}(\varepsilon_0 - \varepsilon_\infty)\right]^{1/2} \frac{1}{\Delta(\mathbf{q}, \omega)} \sum_\gamma [A_{\alpha\gamma}(\mathbf{q}, \omega) G_{\gamma\beta}(\mathbf{q}) + G_{\alpha\gamma}(\mathbf{q}) A_{\gamma\beta}(q, \omega)]. \tag{14}$$

Here

$$\Delta(\mathbf{q}, \omega) = \mathrm{Det}[(\omega^2 - \omega_0^2)\delta_{\alpha\beta} + \Pi_{\alpha\beta}(\mathbf{q})], \tag{15}$$

and $A_{\alpha\beta}(\mathbf{q}, \omega)$ are the algebraic complements of this determinant constructed on the row α and column β ($A_{\alpha\beta} \equiv A_{\beta\alpha}$). In the rigid-ion approximation only the first two terms remain on the right-hand side of (14).

It will be shown in the Appendix that from $\epsilon_{\alpha\beta}(\mathbf{q}, \omega)$ one can find the optical phonon spectrum. However, in the main text of the article it will be more convenient for us to seek the spectrum in accordance with the calculation scheme presented above, bearing in mind that this scheme can be used to find the frequency spectrum of local vibrations in the presence of a defect with long-range interaction.1) We shall turn to this problem in our following article.

Eliminating the field $\mathbf{E}(\mathbf{q})$ from (11) with the aid of (12) and (3), we obtain

$$(\omega^2 - \omega_0^2) v_\alpha(\mathbf{q}) - \omega_0^2 \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon} \sum_\beta \frac{q_\alpha q_\beta}{a^2} v_\beta(\mathbf{q}) - \int_\beta H_{\alpha\beta}(\mathbf{q}) v_\beta(\mathbf{q}) = 0, \tag{16}$$

where

$$H_{\alpha\beta}(\mathbf{q}) = -\Pi_{\alpha\beta}(\mathbf{q}) - 4\pi \frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_\infty^2} \sum_{\gamma, \nu} \frac{q_\alpha q_\beta q_\gamma q_\nu}{q^4} F_{\gamma\nu}(\mathbf{q}) + \frac{\omega_0}{\varepsilon_\infty}\left[\frac{4\pi v_a(\varepsilon_0 - \varepsilon_\infty)}{M}\right]^{1/2} \sum_\gamma \frac{q_\gamma}{q^2}[q_\alpha G_{\gamma\beta}(\mathbf{q}) + G_{\alpha\gamma}(\mathbf{q}) q_\beta]. \tag{17}$$

The splitting of the longitudinal and transverse modes is due to the second term in (16) which appears because of the presence of an electric field. We note that (16) differs from its analog for the hole spectrum in germanium.[4] First, the form of the $H_{\alpha\beta}(\mathbf{q})$ matrix in our case is more complex than in [4], and secondly the "splitting" perturbation is here, unlike in the case of germanium, nonanalytic at the point $\mathbf{q} = 0$. We note that in the rigid-ion model ($F_{\alpha\beta} = G_{\alpha\beta} = 0$) the form of the matrix $H_{\alpha\beta}(\mathbf{q})$ becomes characteristic for the hole

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1) An integral term with a symmetric kernel $K_{\alpha\beta}(\mathbf{q}, \mathbf{q}')$ which plays the role of the "potential" energy will appear in the right-hand part of Eq. (11) in the presence of such a defect. This equation can then be transformed into a differential one, its eigenvalues ω_j^2 giving the spectrum of local vibrations.

spectrum of germanium [see (13)], but the difference in the "splitting" terms remains.

The determinant of (16) is a cubic equation with respect to ω^2 and determines the optical phonon spectrum. In this case too, the transformation (7) makes it possible to decouple the equations for longitudinal and transverse vibrations in the parameter $(qa)^2\epsilon_0/(\epsilon_0-\epsilon_\infty)$, as is done in the calculation of electron spectra.[4] Making use of (8), we have

$$\mathrm{Det}[(\omega^2-\omega_\alpha^2)\delta_{\alpha\beta}-\tilde{H}_{\alpha\beta}(\mathbf{q})]=0,\qquad \tilde{H}=UHU^{-1}\equiv UHU. \tag{18}$$

It is readily seen that for $(qa)^2\epsilon_0/(\epsilon_0-\epsilon_\infty)\ll 1$ the determinant in (18) separates into a product of two determinants of the first and second order. One can then readily find the frequency of the longitudinal branch:

$$\omega_3^2=\frac{\varepsilon_0}{\varepsilon_\infty}\omega_0^2+\tilde{H}_{33}(\mathbf{q})=\frac{\varepsilon_0}{\varepsilon_\infty}\omega_0^2+\sum_{\alpha,\beta}\frac{q_\alpha q_\beta}{q^2}H_{\alpha\beta}(\mathbf{q}). \tag{19}$$

Substituting in (19) expression (17) for $H_{\alpha\beta}(\mathbf{q})$, we obtain

$$\omega_3^2=\frac{\varepsilon_0}{\varepsilon_\infty}\omega_0^2+\sum_{\alpha,\beta}\frac{q_\alpha q_\beta}{q^2}\Phi_{\alpha\beta}(\mathbf{q}), \tag{19a}$$

where

$$\Phi_{\alpha\beta}(\mathbf{q})=-\Pi_{\alpha\beta}(\mathbf{q})+\left[\frac{16\pi\omega_0^2 v_a(\varepsilon_0-\varepsilon_\infty)}{M\varepsilon_\infty^2}\right]^{1/2}G_{\alpha\beta}(\mathbf{q})$$
$$-4\pi\omega_0^2\frac{\varepsilon_0-\varepsilon_\infty}{\varepsilon_\infty^2}F_{\alpha\beta}(\mathbf{q}). \tag{20}$$

Analogously with the expression for transverse frequencies, one finds from the second-order determinant:

$$\mathrm{Det}[(\omega^2-\omega_0^2)\delta_{ij}-\tilde{H}_{ij}(\mathbf{q})]=0,\qquad i,j=1,2. \tag{21}$$

After straightforward algebraic transformations, we obtain

$$\omega_{1,2}^2=\omega_0^2+\frac{1}{2}\sum_{\alpha,\beta}\left(\frac{q_\alpha q_\beta}{q^2}-\delta_{\alpha\beta}\right)\Pi_{\alpha\beta}(\mathbf{q})\pm\Bigg\{\frac{1}{2}\sum_{\alpha,\beta}[\Pi_{\alpha\beta}(\mathbf{q})]^2$$
$$-\left[\frac{1}{2}\sum_{\alpha}\Pi_{\alpha\alpha}(\mathbf{q})\right]^2+\left[\frac{1}{2}\sum_{\alpha,\beta}\frac{q_\alpha q_\beta}{q^2}\Pi_{\alpha\beta}(\mathbf{q})\right]^2$$
$$+\frac{1}{2}\sum_{\alpha,\beta,\gamma}\frac{q_\alpha q_\beta}{q^2}\Pi_{\alpha\beta}(\mathbf{q})\Pi_{\gamma\gamma}(\mathbf{q})-\sum_{\alpha,\beta,\gamma}\frac{q_\alpha q_\beta}{q^2}\Pi_{\alpha\gamma}(\mathbf{q})\Pi_{\gamma\beta}(\mathbf{q})\Bigg\}^{1/2}. \tag{22}$$

The expressions for ω^2 can be further simplified if the matrix elements $\Pi_{\alpha\beta}(\mathbf{q})$ and $\Phi_{\alpha\beta}(\mathbf{q})$ are represented in the form (13)

$$\Phi_{\alpha\beta}(\mathbf{q})=\frac{\varepsilon_0}{\varepsilon_\infty}\omega_0^2a^2\{pq_\alpha q_\beta+\delta_{\alpha\beta}[(m-p)q^2+nq_\alpha^2]\}, \tag{13a}$$

where p, m, and n are numbers of the order of unity. Then

$$\omega_3^2=\frac{\varepsilon_0}{\varepsilon_\infty}\omega_0^2\left\{1+mq^2a^2+na^2\sum_\alpha\frac{q_\alpha^4}{q^2}\right\}, \tag{23}$$

$$\omega_{1,2}^2=\omega_0^2\Bigg\{1-lq^2a^2+\frac{1}{2}sa^2\sum_\alpha\frac{q_\alpha^4}{q^2}$$
$$\pm\frac{sa^2}{q^2}[q_1^4q_2^4+q_1^4q_3^4+q_2^4q_3^4-q^2q_1^2q_3^2]^{1/2}\Bigg\}. \tag{24}$$

According to (24) the transverse frequencies do not split along the crystallographic [100] and [111] axes in the approximation quadratic in q. The determination of the values of m, n, *l*, and s entering in the expressions for the frequencies is a problem of the microscopic theory which we shall present in the following Section.

3. EQUATIONS OF MOTION OF THE ION LATTICE

The purpose of this section is to obtain Eqs. (11), (12), and (3) from microscopic considerations. To this end it is essential to consider the equations of motion of the ion lattice.

An arbitrary ion of the lattice is acted upon by short-range nonelectrical forces, as well as by long-range Coulomb forces. In considering the short-range part of the interaction we restrict ourselves to the model of pair and central forces. The dynamical matrix of short-range forces is then written in the form (see [1], Sec. 29)

$$C_{\alpha\beta}\begin{pmatrix}\mathbf{q}\\ kk'\end{pmatrix}=-\sum_l{}'\Bigg\{2\delta_{\alpha\beta}\varphi'_{kk'}\left[r^2\begin{pmatrix}l\\ kk'\end{pmatrix}\right]$$
$$+4r_\alpha\begin{pmatrix}l\\ kk'\end{pmatrix}r_\beta\begin{pmatrix}l\\ kk'\end{pmatrix}\varphi''_{kk'}\left[r^2\begin{pmatrix}l\\ kk'\end{pmatrix}\right]\Bigg\}\cos\left[\mathbf{qr}\begin{pmatrix}l\\ kk'\end{pmatrix}\right]. \tag{25}$$

Here $\mathbf{r}\binom{l}{kk'}$ is the vector joining the equilibrium positions of an ion of the type k′ in the zeroth unit cell (in the case under consideration k′ takes on two values: + and −) and of an ion of the k-th type in the *l*-th unit cell, $\varphi_{kk'}(x)$ is the energy of the pair interaction which decreases rapidly with increasing x (the primes of $\varphi_{kk'}$ indicate differentiation with respect to the argument), the subscripts α and β denote projections on the axes of a Cartesian coordinate system which we shall orient along the crystallographic axes. The prime in the summation sign signifies the exclusion from it of the term with $l = 0$ and $k = k'$. We shall restrict ourselves to terms quadratic in qa. Expanding (25) in qa and using the symmetry relations, we obtain

$$C_{\alpha\beta}\begin{pmatrix}\mathbf{q}\\ kk'\end{pmatrix}\approx C^{(0)}_{\alpha\beta}\begin{pmatrix}\mathbf{q}\\ kk'\end{pmatrix}+C^{(2)}_{\alpha\beta}\begin{pmatrix}\mathbf{q}\\ kk'\end{pmatrix}+\ldots,$$
$$C^{(0)}_{\alpha\beta}\begin{pmatrix}\mathbf{q}\\ kk'\end{pmatrix}=-\delta_{\alpha\beta}\,\xi(kk'),$$
$$C^{(2)}_{\alpha\beta}\begin{pmatrix}\mathbf{q}\\ kk'\end{pmatrix}=\xi_1(kk')q_\alpha q_\beta+\delta_{\alpha\beta}[\xi_2(kk')q^2+\xi_3(kk')q_\alpha^2], \tag{26}$$

where

$$\xi(kk')=\sum_l{}'\left\{2\varphi'_{kk'}\left[r^2\begin{pmatrix}l\\ kk'\end{pmatrix}\right]+\frac{4}{3}r^2\begin{pmatrix}l\\ kk'\end{pmatrix}\varphi''_{kk'}\left[r^2\begin{pmatrix}l\\ kk'\end{pmatrix}\right]\right\},$$
$$\xi_1(kk')=\sum_l{}'\left[\frac{2}{3}r^4\begin{pmatrix}l\\ kk'\end{pmatrix}-2r_\alpha^4\begin{pmatrix}l\\ kk'\end{pmatrix}\right]\varphi''_{kk'}\left[r^2\begin{pmatrix}l\\ kk'\end{pmatrix}\right],$$
$$\xi_2(kk')=\frac{1}{2}\xi_1(kk')+\sum_l{}'\frac{1}{3}r^2\begin{pmatrix}l\\ kk'\end{pmatrix}\varphi'_{kk'}\left[r^2\begin{pmatrix}l\\ kk'\end{pmatrix}\right],$$
$$\xi_3(kk')=\sum_l{}'\left[5r_\alpha^4\begin{pmatrix}l\\ kk'\end{pmatrix}-r^4\begin{pmatrix}l\\ kk'\end{pmatrix}\right]\varphi''_{kk'}\left[r^2\begin{pmatrix}l\\ kk'\end{pmatrix}\right]$$
$$\xi_i(kk')=\xi_i(k'k). \tag{27}$$

In the case when in considering short-range interaction one can restrict oneself to the interaction of nearest neighbors (we shall refer to such a model as the short-range interaction model), (27) takes on the form

$$\xi=2\nu\varphi'+\frac{4}{3}a^2\nu\varphi',\qquad \xi_1=\frac{2}{3}\varphi''\left(\nu a^4-3\sum_{\mathbf{a}}a_\alpha^4\right), \tag{27a}$$

$$\xi_2=\frac{1}{2}\xi_1+\frac{1}{3}\nu a^2\varphi'',\quad \xi_3=-\varphi''\Big(\nu a^4-5\sum_{\mathbf{a}}a_\alpha{}^4\Big),$$

$$\xi_i\equiv\xi_i(+-),\quad \xi_i(kk)=0;\quad \varphi'\equiv\varphi_{+-}{}'(a^2),\quad \varphi''\equiv\varphi_{+-}{}''(a^2).$$

Here ν is the number of nearest neighbors, and $\mathbf{a}$ is a vector drawn to the site of the nearest neighbor. Below the constants φ' and φ'' will be expressed in terms of experimentally observed quantities.

Let us now turn to the Coulomb interaction. According to [1], Sec. 30, the effective electric field acting upon an ion of type k can in the $\mathbf{q}$ representation be written in the form

$$\tilde{E}_\alpha\binom{\mathbf{q}}{k}=E_\alpha(\mathbf{q})+\sum_{k',\beta}Q_{\alpha\beta}\binom{\mathbf{q}}{kk'}p_\beta\binom{\mathbf{q}}{k'},\tag{28}$$

where $\mathbf{p}\binom{\mathbf{q}}{k}$ is the dipole moment of the ion of the type k resulting from the deviation of the ion from the equilibrium position as well as from its polarization by the field, and $\mathbf{E}(\mathbf{q})$ is the macroscopic field defined in (3); $Q_{\alpha\beta}$ is a widely known matrix [see, for example, (30.31) in [1]]. Expanding $Q_{\alpha\beta}$ in a series in qa and using the symmetry relations, we obtain after cumbersome but not complicated calculations

$$Q_{\alpha\beta}\binom{\mathbf{q}}{kk'}\approx Q^{(0)}_{\alpha\beta}\binom{\mathbf{q}}{kk'}+Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{kk'}+\ldots,\quad Q^{(0)}_{\alpha\beta}\binom{\mathbf{q}}{kk'}=\frac{4\pi}{3v_a}\delta_{\alpha\beta},$$

$$Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{kk'}=-\frac{1}{a}\Big\{A_2(kk')q_\alpha q_\beta+\delta_{\alpha\beta}\Big(\Big[\frac{3}{2}A_1(kk')-A_2(kk')\Big]q_\alpha{}^2$$

$$-\frac{1}{2}A_1(kk')q^2\Big)\Big\};\ A_i(+-)=A_i(-+)$$

$$=A_i{}^-;\ A_i(++)=A_i(--)=A_i{}^+;\tag{29}$$

$$Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{+-}=Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{-+}=Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{-},$$

$$Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{++}=Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{--}=Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{+},$$

where A_1 and A_2 are numbers of the order of unity which depend only on the symmetry of the lattice. They can be calculated by using the following expressions:

$$A_1(kk')=\frac{4a}{\sqrt{\pi}}\sum_l{}'\int_H^\infty ds\exp\Big[-s^2r^2\binom{l}{kk'}\Big]\Big[s^4r_\alpha{}^4\binom{l}{kk'}$$

$$-\frac{1}{6}s^2r^2\binom{l}{kk'}\Big]-\frac{\pi a}{v_a H^2}+\frac{4\pi a}{v_a}\sum_{h\neq 0}\exp\Big[-ig(h)\mathbf{r}\binom{0}{kk'}-\frac{g^2(h)}{4H^2}\Big]$$

$$\times\Big\{g_\alpha{}^4(h)\Big[\frac{4}{g^6(h)}+\frac{1}{H^2g^4(h)}+\frac{1}{8H^4g^2(h)}\Big]-\frac{2}{3g^2(h)}-\frac{5}{12H^2}\Big\}$$

$$A_2(kk')=\frac{4a}{\sqrt{\pi}}\sum_l{}'\int_H^\infty ds\exp\Big[-s^2r^2\binom{l}{kk'}\Big]\Big[\frac{1}{3}r^4\binom{l}{kk'}-r_\alpha{}^4\binom{l}{kk'}\Big]s^4$$

$$-\frac{\pi a}{v_aH^2}+\frac{4\pi a}{v_a}\sum_{h\neq 0}\exp\Big[-ig(h)\mathbf{r}\binom{0}{kk'}-\frac{g^2(h)}{4H^2}\Big]$$

$$\times\Big\{\Big[\frac{1}{3}g^4(h)-g_\alpha{}^4(h)\Big]\Big[\frac{4}{g^6(h)}+\frac{1}{H^2g^4(h)}+\frac{1}{8H^4g^2(h)}\Big]-\frac{1}{3g^2(h)}-\frac{1}{3H^2}\Big\},\tag{30}$$

where $\mathbf{g}(h)$ is a reciprocal lattice vector, h is the number of the reciprocal lattice point, H is a parameter which has the dimension of a reciprocal length and which insures the rapid convergence of both series in (30) [see [1], Sec. 30]. The quantities A_1 and A_2 do not depend on H, since by differentiating them with respect to H and taking into account certain relations between sums over the real and reciprocal lattice we find that these derivatives vanish.

Let us consider the model of isotropically polarizable ions. One can then find the magnitude of the induced dipole $\mathbf{p}$ from the relation (see Secs. 9 and 35 in [1]):

$$\tilde{p}_\alpha\binom{\mathbf{q}}{k}=\alpha_k\tilde{E}_\alpha\binom{\mathbf{q}}{k},\tag{31}$$

where α_k is the polarizability of the ion of type k (in the rigid-ion approximation $\alpha_k = 0$). The equation for determining $\mathbf{p}$ can be written in the form

$$p_\alpha\binom{\mathbf{q}}{k}=\alpha_kE_\alpha(\mathbf{q})+e_ku_\alpha\binom{\mathbf{q}}{k}+\alpha_k\sum_{\beta,k'}Q_{\alpha\beta}\binom{\mathbf{q}}{kk'}p_\beta\binom{\mathbf{q}}{k'},\tag{32}$$

where we have used (28), (31), and the relation

$$\mathbf{p}\binom{\mathbf{q}}{k}=\tilde{\mathbf{p}}\binom{\mathbf{q}}{k}+e_k\mathbf{u}\binom{\mathbf{q}}{k}.$$

Here $\mathbf{u}\binom{\mathbf{q}}{k}$ is the deviation of the ion of type k from its equilibrium position, and e_k is the effective charge of the ion of type k.

The solution of Eq. (32) can be written in the form

$$p_\alpha\binom{\mathbf{q}}{k}=\sum_{\beta,k'}\Lambda^{-1}_{\alpha\beta}\binom{\mathbf{q}}{kk'}\Big\{\alpha_{k'}E_\beta(\mathbf{q})+e_{k'}u_\beta\binom{\mathbf{q}}{k'}\Big\},\tag{33}$$

$$\Lambda_{\alpha\beta}\binom{\mathbf{q}}{kk'}=\delta_{\alpha\beta}\delta_{kk'}-\alpha_{k'}Q_{\alpha\beta}\binom{\mathbf{q}}{kk'};$$

$$\sum_{\gamma,k''}\Lambda^{-1}_{\alpha\gamma}\binom{\mathbf{q}}{k'k''}\Lambda_{\gamma\beta}\binom{\mathbf{q}}{k''k}=\delta_{\alpha\beta}\delta_{k'k}.$$

Using (33) one can write an expression for the macroscopic dipole moment:

$$P_\alpha(\mathbf{q})=\frac{1}{v_a}\sum_k p_\alpha\binom{\mathbf{q}}{k}=\frac{1}{v_a}\sum_{\beta,k'}\Gamma_{\alpha\beta}\binom{\mathbf{q}}{k'}\Big\{\alpha_{k'}E_\beta(\mathbf{q})+e_{k'}u_\beta\binom{\mathbf{q}}{k'}\Big\}$$

$$\Gamma_{\alpha\beta}\binom{\mathbf{q}}{k'}=\sum_k\Lambda^{-1}_{\alpha\beta}\binom{\mathbf{q}}{kk'}.\tag{34}$$

An equation for $\Gamma_{\alpha\beta}$ can be obtained from (33):

$$\sum_{\gamma,k'}\Gamma_{\alpha\gamma}\binom{\mathbf{q}}{k'}\Lambda_{\gamma\beta}\binom{\mathbf{q}}{k'k}=\delta_{\alpha\beta}.\tag{35}$$

Substituting in (35) the expression for $\Lambda_{\alpha\beta}$ from (33) and expanding in a series $Q_{\alpha\beta}$ accurate up to terms $\sim q^2$, we obtain a closed expression for $\Gamma_{\alpha\beta}$:

$$\Gamma_{\alpha\beta}\binom{\mathbf{q}}{+}=\lambda\delta_{\alpha\beta}+\lambda^2\sum_{k'}\alpha_{k'}$$

$$\times\Big\{Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{k'+}\Big(1-\frac{4\pi}{3v_a}\alpha_-\Big)+Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{k'-}\frac{4\pi}{3v_a}\alpha_-\Big\},\tag{36}$$

$$\lambda=(1-\varkappa_1)^{-1},\ \varkappa_1=\frac{4\pi}{3v_a}(\alpha_++\alpha_-).$$

The expression for $\Gamma_{\alpha\beta}\binom{\mathbf{q}}{-}$ is obtained from (36) by a replacement of subscripts $+\rightleftarrows-$.

Let us introduce coordinates connected with the center of gravity of the unit cell:

$$\mathbf{v}(\mathbf{q})=\mathbf{u}\binom{\mathbf{q}}{+}-\mathbf{u}\binom{\mathbf{q}}{-},\ \mathbf{w}(\mathbf{q})=\frac{M_+\mathbf{u}\binom{\mathbf{q}}{+}+M_-\mathbf{u}\binom{\mathbf{q}}{-}}{M_++M_-}.\tag{37}$$

Substituting (36) and (37) in (34), we obtain an expression for $P_\alpha(\mathbf{q})$:

$$P_\alpha(\mathbf{q}) = \frac{e\lambda}{v_a} v_\alpha(\mathbf{q}) + \frac{3}{4\pi}\lambda\varkappa_1 E_\alpha(\mathbf{q}) + \sum_\beta G_{\alpha\beta}(\mathbf{q}) v_\beta(\mathbf{q})$$

$$+ \sum_\beta F_{\alpha\beta}(\mathbf{q}) E_\beta(\mathbf{q}) + \frac{3}{8\pi} e\lambda(\alpha_+ - \alpha_-)\left(\frac{M_+ + M_-}{M_+ - M_-}\right)^2 \sum_\beta Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{2} w_\beta(\mathbf{q}), \qquad (38)$$

where

$$G_{\alpha\beta}(\mathbf{q}) = \frac{3}{4\pi} e\lambda^2 \Big\{ Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{1}\varkappa_1 + Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{2}\varkappa\Big(\varkappa - \frac{1}{2} + \frac{1}{2}\varkappa_1\Big)\Big\},$$

$$F_{\alpha\beta}(\mathbf{q}) = \left(\frac{3\lambda}{4\pi}\right)^2 v_a \Big\{ Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{1}\varkappa_1^2 + Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{2}\varkappa(\varkappa - \varkappa_1)\Big\},$$

$$Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{1} = \frac{M_+ M_-}{(M_+ + M_-)^2}\Big\{ Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{+}\frac{M_+^2 + M_-^2}{M_+ M_-} + 2Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{-}\Big\},$$

$$Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{2} = 2\left(\frac{M_+ - M_-}{M_+ + M_-}\right)^2 \Big\{ Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{+} - Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{-}\Big\}, \qquad (39)$$

$$\varkappa = \frac{4\pi}{3v_a}\frac{\alpha_+ M_+ - \alpha_- M_-}{M_+ - M_-}, \quad e \equiv e_+.$$

Let us now go over to setting up the equations of motion:

$$\omega^2 M_k u_\alpha\binom{\mathbf{q}}{k} = \sum_{k',\beta}\Big[C_{\alpha\beta}\binom{\mathbf{q}}{kk'} u_\beta\binom{\mathbf{q}}{k'} - C_{\alpha\beta}\binom{0}{kk'} u_\beta\binom{\mathbf{q}}{k}\Big] - e_k \tilde{E}_\alpha\binom{\mathbf{q}}{k} \qquad (40)$$

By virtue of the electrical neutrality of the unit cell and of the symmetry relations the force exerted on a given dipole by all the remaining stationary ions is zero. Substituting in (40) expression (28) for $\tilde{\mathbf{E}}$, and then expressing $\mathbf{p}$ with the aid of (33), we obtain

$$\omega^2 M_k u_\alpha\binom{\mathbf{q}}{k} = \sum_{k\beta}\Big[C_{\alpha\beta}\binom{\mathbf{q}}{kk'} u_\beta\binom{\mathbf{q}}{k'} - C_{\alpha\beta}\binom{0}{kk'} u_\beta\binom{\mathbf{q}}{k}\Big]$$

$$- e_k E_\alpha(\mathbf{q}) - e_k \sum_{k'\beta} D_{\alpha\beta}\binom{\mathbf{q}}{kk'}\Big\{\alpha_{k'} E_\beta(\mathbf{q}) + e_{k'} u_\beta\binom{\mathbf{q}}{k'}\Big\}, \qquad (41)$$

where $D_{\alpha\beta}$ is determined from the equation

$$\sum_{\gamma, k''} D_{\alpha\gamma}\binom{\mathbf{q}}{kk''}\Lambda_{\gamma\beta}\binom{\mathbf{q}}{k''k'} = Q_{\alpha\beta}\binom{\mathbf{q}}{kk'}. \qquad (42)$$

The solution of Eq. (42) with an accuracy up to terms $\sim q^2$ is found in the same way as used in solving (35). We substitute the obtained value for $D_{\alpha\beta}$ in (41) and expanding all the coefficients in a series in q:

$$\omega^2 w_\alpha(\mathbf{q}) = \sum_\beta L_{\alpha\beta}(\mathbf{q}) w_\beta(\mathbf{q}) + \sum_\beta R_{\alpha\beta}(\mathbf{q}) v_\beta(\mathbf{q}) + \sum_\beta S_{\alpha\beta}(\mathbf{q}) E_\beta(\mathbf{q}), \qquad (43)$$

$$\omega^2 v_\alpha(\mathbf{q}) = \frac{1}{M}\Big[\xi(+-) - \frac{4\pi e^2\lambda}{3v_a}\Big] v_\alpha(\mathbf{q}) - \frac{e\lambda}{M} E_\alpha(\mathbf{q})$$

$$- \sum_\beta \Pi_{\alpha\beta}(\mathbf{q}) v_\beta(\mathbf{q}) - \frac{v_a}{M}\sum_\beta G_{\alpha\beta}(\mathbf{q}) E_\beta(\mathbf{q}) + \sum_\beta K_{\alpha\beta}(\mathbf{q}) w_\beta(\mathbf{q}), \qquad (44)$$

where

$$\Pi_{\alpha\beta}(\mathbf{q}) = \frac{e^2\lambda^2}{M}\Big\{ Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{1} + Q^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{2}\varkappa(\varkappa - 1)\Big\}$$

$$+ \frac{1}{M_+ + M_-}\Big\{ 2C_{\alpha\beta}\binom{\mathbf{q}}{+-} - \frac{M_-}{M_+} C^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{++} - \frac{M_+}{M_-} C^{(2)}_{\alpha\beta}\binom{\mathbf{q}}{--}\Big\}, \qquad (45)$$

$$L_{\alpha\beta}(\mathbf{q}) = \frac{1}{M_+ + M_-}\Big\{ -e^2\left(\frac{M_+ + M_-}{M_+ - M_-}\right)^2 Q_{\alpha\beta}\binom{\mathbf{q}}{2} + \sum_{k,k'} C_{\alpha\beta}\binom{\mathbf{q}}{kk'}\Big\} \qquad (46)$$

The quantities $\xi(+-)$ and $G_{\alpha\beta}(\mathbf{q})$ have been defined in (27) and (39) respectively. The matrices $R_{\alpha\beta}(\mathbf{q})$, $S_{\alpha\beta}(\mathbf{q})$, and $K_{\alpha\beta}(\mathbf{q})$ quadratic in $\mathbf{q}$ will not be required below because taking them into account leads to corrections of higher order than the quadratic approximation in qa which we are employing. We shall therefore not write out these matrices explicitly.

In the approximation quadratic in $\mathbf{q}$ the equations for the optical and acoustic branches are uncoupled. This is readily noted by analyzing Eqs. (43) and (44). Taking into account the fact that the coefficients in the right-hand side of Eq. (43) are $\sim q^2$ and $\omega \sim \omega_0$, one can conclude that in the approximation being considered in the optical vibration branch $\mathbf{w}(\mathbf{q}) = 0$. Then Eqs. (44) and (38) will take on the form of (11) and (12) for

$$\omega_0^2 = \frac{1}{M}\Big[\xi(+-) - \frac{4\pi e^2\lambda}{3v_a}\Big], \quad \varkappa_1 = \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2},$$

$$e^2 = \left(\frac{3\omega_0}{\varepsilon_\infty + 2}\right)^2 M v_a \frac{\varepsilon_0 - \varepsilon_\infty}{4\pi} \qquad (47)$$

which is in agreement with the results of Sec. 9 in [1]. Making use of the expressions obtained for $\Pi_{\alpha\beta}(\mathbf{q})$, $G_{\alpha\beta}(\mathbf{q})$, and $F_{\alpha\beta}(\mathbf{q})$, one can write the quantities m, n, l, and s introduced in the preceding Section in terms of microscopic parameters:

$$m = \Big(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\Big)\frac{v_a}{4\pi a^3}\Big\{\tilde{A}_2 - \frac{1}{2}\tilde{A}_1 + 2\varkappa(2\varkappa + 1)' \tilde{A}_2' - \frac{1}{2}\tilde{A}_1'\Big)\Big\}$$

$$- \frac{\varepsilon_\infty}{\varepsilon_0\omega_0^2(M_+ + M_-)}{}' 2[\xi_1(+-) + \xi_2(+-)] - \frac{M_-}{M_+}[\xi_1(++) + \xi_2(++)]$$

$$- \frac{M_+}{M_-}[\xi_1(--) + \xi_2(--)]\Big\},$$

$$n = \Big(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\Big)\frac{v_a}{4\pi a^3}\Big\{\frac{3}{2}\tilde{A}_1 - \tilde{A}_2 + 2\varkappa(2\varkappa + 1)\Big(\frac{3}{2}\tilde{A}_1' - \tilde{A}_2'\Big)\Big\}$$

$$- \frac{\varepsilon_\infty}{\varepsilon_0\omega_0^2(M_+ + M_-)}\Big\{2\xi_3(+-) - \frac{M_-}{M_+}\xi_3(++) - \frac{M_+}{M_-}\xi_3(--)\Big\},$$

$$l = (\varepsilon_0 - \varepsilon_\infty)\frac{v_a}{8\pi a^3}\Big\{\tilde{A}_2 - \frac{1}{2}\tilde{A}_1 + \varkappa(\varkappa - 1)\Big(\tilde{A}_2' - \frac{1}{2}\tilde{A}_1'\Big)\Big\}$$

$$+ \frac{1}{\omega_0^2(M_+ + M_-)}\Big\{2\xi_2(+-) + \xi_3(+-) - \frac{M_-}{M_+}\Big[\xi_2(++) + \frac{1}{2}\xi_3(++)\Big]$$

$$- \frac{M_+}{M_-}\Big[\xi_2(--) + \frac{1}{2}\xi_3(--)\Big]\Big\}, \qquad (48)$$

$$s = -(\varepsilon_0 - \varepsilon_\infty)\frac{v_a}{4\pi a^3}\Big\{\frac{3}{2}\tilde{A}_1 - \tilde{A}_2 + \varkappa(\varkappa - 1)\Big(\frac{3}{2}\tilde{A}_1' - \tilde{A}_2'\Big)\Big\}$$

$$+ \frac{1}{\omega_0^2(M_+ + M_-)}\Big\{2\xi_3(+-) - \frac{M_-}{M_+}\xi_3(++) - \frac{M_+}{M_-}\xi_3(--)\Big\},$$

$$\tilde{A}_i = A_i^+\frac{M_+^2 + M_-^2}{(M_+ + M_-)^2} + A_i^-\frac{2M_+M_-}{(M_+ + M_-)^2},$$

$$\tilde{A}_i' = 2\left(\frac{M_+ - M_-}{M_+ + M_-}\right)^2(A_i^+ - A_i^-).$$

In the case in which one can restrict oneself to the short-range interaction model the parameters entering in (48) are expressed in terms of experimentally observed quantities. For this purpose we carry out the minimization of the energy per unit cell:

$$\frac{1}{a}\sum_{l,k,k'} r^2\binom{l}{kk'}\varphi'_{kk'}\Big[r^2\binom{l}{kk'}\Big] + \frac{\alpha' e^2}{a^2} = 0, \qquad (49)$$

where α' is the Madelung constant. In the short-range interaction approximation

$$\varphi' = -\alpha' e^2 / 2\nu a^3. \qquad (50)$$

Using equalities (27a), (47), and (50), we find

$$\varphi'' = \frac{3}{4\nu a^3}\Big\{M\omega_0^2\frac{\varepsilon_0 + 2}{\varepsilon_\infty + 2} + \frac{\alpha' e^2}{a^3}\Big\}. \qquad (51)$$

Substituting (50) and (51) in (27a):

$$\xi_1 = \frac{1}{2}\left(1 - \frac{3}{\nu}\sum_{\mathbf{a}}\frac{a_\alpha{}^4}{a^4}\right)\left(M\omega_0{}^2 a^2\frac{\varepsilon_0+2}{\varepsilon_\infty+2} + \frac{\alpha' e^2}{a}\right),$$

$$\xi_2 = \frac{1}{2}\xi_1 - \frac{\alpha' e^2}{6a},$$

$$\xi_3 = -\frac{3}{4}\left(1 - \frac{5}{\nu}\sum_{\mathbf{a}}\frac{a_\alpha{}^4}{a^4}\right)\left(M\omega_0{}^2 a^2\frac{\varepsilon_0+2}{\varepsilon_\infty+2} + \frac{\alpha' e^2}{a}\right). \tag{52}$$

Thus only one constant κ has remained undetermined in (48). However, according to (39) it is expressed in terms of atomic refractions $4\pi N\alpha_{\pm}/3v_a$ (N is Avogadro's number) which were calculated in [9] and cited in [1].

In concluding the Section we note that formula (24) obtained for the transverse frequencies is not valid in the region of very small q ($q < \omega_0/c$ where c is the speed of light) in view of the fact that we took no account of "retardation" in Maxwell's equations. However, such a generalization presents no difficulty (see [1], Secs. 8 and 44).

4. ACOUSTIC VIBRATION BRANCHES

In considering the acoustic vibration branches it is essential to take into account that the first nonvanishing term of the expansion of ω^2 in a series in $\mathbf{q}$ is proportional to q^2. In the approximation being considered it is then necessary to express from (38), (44), and (3) $\mathbf{E}(\mathbf{q})$ and $\mathbf{v}(\mathbf{q})$ in terms of $\mathbf{w}(\mathbf{q})$ and substitute in (43) in the lowest approximation in $\mathbf{q}$:

$$0 = \omega_0{}^2 v_\alpha(\mathbf{q}) - \omega_0\left(\frac{\varepsilon_0-\varepsilon_\infty}{4\pi}\frac{v_a}{M}\right)^{1/2} E_\alpha(\mathbf{q}), \tag{53}$$

$$P_\alpha(\mathbf{q}) = \omega_0\left(\frac{\varepsilon_0-\varepsilon_\infty}{4\pi}\frac{M}{v_a}\right)^{1/2} v_\alpha(\mathbf{q}) + \frac{\varepsilon_\infty-1}{4\pi}E_\alpha(\mathbf{q}). \tag{54}$$

Expressing from (53) $\mathbf{v}(\mathbf{q})$ in terms of $\mathbf{E}(\mathbf{q})$ and then substituting (54) in (3), we obtain

$$E_\alpha(\mathbf{q}) = (1-\varepsilon_0)\sum_\beta\frac{q_\alpha q_\beta}{q^2}E_\beta(\mathbf{q}). \tag{55}$$

We seek the solution of this equation in the form (4). It is then seen that in view of the fact that $\epsilon_0 \neq 0$ the system (55) has one trivial solution $\mathbf{E}(\mathbf{q}) = 0$. Thus, the equations for describing the acoustic vibration branches are obtained from (43) by setting $\mathbf{v}(\mathbf{q}) = 0$ and $\mathbf{E}(\mathbf{q}) = 0$:

$$\omega^2 w_\alpha(\mathbf{q}) = \sum_\beta{}' L_{\alpha\beta}(\mathbf{q})\, w_\beta(\mathbf{q}). \tag{56}$$

Comparing expression (46) for $L_{\alpha\beta}(\mathbf{q})$ with (26) and (29), it is seen that $L_{\alpha\beta}(\mathbf{q})$ can be written in the form

$$L_{\alpha\beta}(\mathbf{q}) = \chi_1 q_\alpha q_\beta + \delta_{\alpha\beta}(\chi_2 q^2 + \chi_3 q_\alpha{}^2), \tag{57}$$

where

$$\chi_1 = \frac{1}{M_+ + M_-}\sum_{k,k'}\left\{\xi_1(kk') + \frac{e_k e_{k'}}{a}A_2(kk')\right\},$$

$$\chi_2 = \frac{1}{M_+ + M_-}\sum_{k,k'}\left\{\xi_2(kk') - \frac{e_k e_{k'}}{2a}A_1(kk')\right\},$$

$$\chi_3 = \frac{1}{M_+ + M_-}\sum_{k,k'}\left\{\xi_3(kk') + \frac{e_k e_{k'}}{a}\left[\frac{3}{2}A_1(kk') - A_2(kk')\right]\right\}. \tag{58}$$

We note that according to (56)–(58) the polarizability of the ions does not affect the long-wave acoustic vibrations.

A determination of $\omega(\mathbf{q})$ for an arbitrary direction of $\mathbf{q}$ reduces to a cumbersome solution of a cubic equation; we shall therefore restrict ourselves to finding $\omega(\mathbf{q})$ for the propagation of sound along axes of high symmetry which makes it possible to relate χ_1, χ_2, and χ_3 with the elastic constants of the crystal. In the case of the [100] direction we have

$$\omega_1{}^2 = \omega_2{}^2 = \chi_2 q^2, \quad \omega_3{}^2 = (\chi_1 + \chi_2 + \chi_3)q^2. \tag{59}$$

In the case of the [111] direction

$$\omega_1{}^2 = \omega_2{}^2 = (\chi_2 + {}^1/_3\chi_3)q^2, \quad \omega_3{}^2 = (\chi_1 + \chi_2 + {}^1/_3\chi_3)q^2. \tag{60}$$

A direct comparison of (60) and (59) with the equations of the theory of elasticity leads to the following expressions for the elastic constants:

$$c_{11} = \rho(\chi_1 + \chi_2 + \chi_3), \quad c_{12} = \rho(\chi_1 - \chi_2), \quad c_{44} = \rho\chi_2, \tag{61}$$

where ρ is the density of the crystal.

In order to prove the Cauchy relationship, we make use of equality (49). Let us consider the quantity $\chi_1 - 2\chi_2$:

$$\chi_1 - 2\chi_2 = \frac{1}{M_+ + M_-}\left\{\sum_{k,k'}\frac{e_k e_{k'}}{a}[A_1(kk') + A_2(kk')] - \frac{2}{3}\sum_{l,k,k'}{}' r^2\begin{pmatrix} l \\ kk'\end{pmatrix}\varphi'_{kk'}\left[r^2\begin{pmatrix} l \\ kk'\end{pmatrix}\right]\right\}. \tag{62}$$

The first sum of the right-hand side of (62) can be expressed in terms of α' using relations (30). To this end we combine both equalities (30) and then make H approach zero, making use of the fact that the quantities A_1 and A_2 are independent of H. We then obtain[2)]

$$\sum_{k,k'}\frac{e_k e_{k'}}{a}[A_1(kk') + A_2(kk')] = \frac{1}{3}\sum_{l,k,k'}{}' e_k e_{k'}\left|\mathbf{r}\begin{pmatrix} l \\ kk'\end{pmatrix}\right|^{-1} = -\frac{2e^2\alpha'}{3a}. \tag{63}$$

Substituting (49) and (63) in (62), we obtain $\chi_1 = 2\chi_2$, i.e., $c_{12} = c_{44}$.

We note that the sum of the squares of the sound velocities along three mutually perpendicular directions is an invariant with respect to the angle of rotation and is only determined by the short-range interaction:

$$c_{11} + 2c_{44} = \frac{1}{v_a}\sum_{l,k,k'}{}'\left\{r^2\begin{pmatrix} l \\ kk'\end{pmatrix}\varphi'_{kk'}\left[r^2\begin{pmatrix} l \\ kk'\end{pmatrix}\right] + \frac{2}{3}r^4\begin{pmatrix} l \\ kk'\end{pmatrix}\varphi''_{kk'}\left[r^2\begin{pmatrix} l \\ kk'\end{pmatrix}\right]\right\}. \tag{64}$$

If one restricts oneself to the model of short-range interaction, then (64) will take the form

$$c_{11} + 2c_{44} = \xi a^2 / v_a. \tag{65}$$

Comparing (65) with (47), one can obtain an identity relating the elastic constants of a crystal with ω_0:

[2)] We note that making the same assumption one can express in terms of known numbers also another combination of A_1 and A_2:

$$-\sum_{kk'} e_k e_{k'} A_2(kk') = a\sum_{l,k,k'}{}' e_k e_{k'}\left\{\frac{1}{6}\left|\mathbf{r}\begin{pmatrix} l \\ kk'\end{pmatrix}\right|^{-1} - \frac{1}{2}r_\alpha{}^4\begin{pmatrix} l \\ kk'\end{pmatrix}\left|\mathbf{r}\begin{pmatrix} l \\ kk'\end{pmatrix}\right|^{-5}\right\} = 2e^2 z_1{}^{12},$$

where $z_1^{12} = -0.696$ for NaCl type lattices and $z_1^{12} = 1.802$ for CsCl type lattices (see [10], Sec. 16).

$$c_{11}+2c_{44}=M\omega_0{}^2\frac{a^2}{v_a}\frac{\varepsilon_0+2}{\varepsilon_\infty+2}. \tag{66}$$

Only known material constants enter in identity (66); it can therefore be considered as a criterion of the applicability of the short-range interaction model. We note that for the majority of alkali-halide crystals it is fulfilled with an accuracy of ±10%.

APPENDIX

In this Appendix we obtain the optical vibration frequencies with the aid of the dielectric permittivity tensor $\epsilon_{\alpha\beta}(\mathbf{q}, \omega)$ (14). According to the terminology of [5], the case of an irrotational (but nonzero) electric field [see (3)] refers to "fictitious longitudinal waves" (see [5], Sec. 2.2). In this case the dispersion equation takes on the form[5]

$$\sum_{\alpha,\beta}\frac{q_\alpha q_\beta}{q^2}\varepsilon_{\alpha\beta}(\mathbf{q},\omega)=0. \tag{67}$$

If one substitutes in (67) expression (14) for $\epsilon_{\alpha\beta}(\mathbf{q}, \omega)$, then one obtains a cubic equation in ω^2. It is clear from physical considerations that one of the roots of this equation is close to $\omega^2 \sim (\epsilon_0/\epsilon_\infty)\omega_0^2$, and the other two $\omega^2 \sim \omega_0^2$. In seeking the first root the expression for $\epsilon_{\alpha\beta}(\mathbf{q}, \omega)$ can be simplified by expanding it in the parameter $(qa)^2\omega_0^2/(\omega^2 - \omega_0^2)$:

$$\begin{aligned}\varepsilon_{\alpha\beta}(\mathbf{q},\omega)\approx{}&\frac{\varepsilon_\infty\omega^2-\varepsilon_0\omega_0{}^2}{\omega^2-\omega_0{}^2}\delta_{\alpha\beta}+\omega_0{}^2\frac{\varepsilon_0-\varepsilon_\infty}{(\omega^2-\omega_0{}^2)^2}\Pi_{\alpha\beta}(\mathbf{q})\\&-\frac{2}{\omega^2-\omega_0{}^2}\left[\frac{4\pi v_a}{M}(\varepsilon_0-\varepsilon_\infty)\right]^{1/2}G_{\alpha\beta}(\mathbf{q})+4\pi F_{\alpha\beta}(\mathbf{q}),\end{aligned} \tag{68}$$

which coincides with (4.19) of [5] for nongyrotropic crystals.

Substituting (68) in (67), we obtain a value ω_3^2 which coincides with (19a) in the approximation quadratic in $\mathbf{q}$ which is being considered.

In the case when $\omega^2 \sim \omega_0^2$ the largest contribution to $\epsilon_{\alpha\beta}(\mathbf{q}, \omega)$ is due to the second term in the right-hand side of (14) which is $\sim q^{-2}$, while the first and third terms are $\sim q^0$ and the fourth is $\sim q^2$. In this case the dispersion equation takes on the form

$$\sum_{\alpha,\beta}{}'\frac{q_\alpha q_\beta}{q^2}A_{\alpha\beta}(\mathbf{q},\omega)=0. \tag{69}$$

This equation is quadratic in ω^2. Its solutions are ω_1^2 and ω_2^2 which coincide with (22).

We note that in the vicinity of $\omega^2 \sim \omega_0^2$ the reciprocal dielectric tensor has a particularly simple form:

$$\varepsilon^{-1}_{\alpha\beta}(\mathbf{q},\omega)=-\frac{1}{\omega_0{}^2(\varepsilon_0-\varepsilon_\infty)}\{(\omega^2-\omega_0{}^2)\delta_{\alpha\beta}+\Pi_{\alpha\beta}(\mathbf{q})\}, \tag{70}$$

which is in agreement with (4.21) of [5].

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