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Lattice-dynamics approach to the theory of diatomic elastic dielectrics

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The equations of the dynamical theory of polarizable diatomic lattices, for the long-wavelength approximation, are shown to coincide with Mindlin's continuum equations for diatomic elastic dielectrics. The governing equations of the coupled mechanical and electrical fields account for the surface effects due to elastic deformations and electronic and atomic polarizations and accommodate the optical as well as the acoustical branches in dispersion relations. The material coefficients in the constitutive relations of the continuum theory are related to the lattice properties via the lattice formulation and their numerical values are computed for NaI, NaCl, KI, and KCl. The long-wavelength limits of the transverse- and longitudinal-optical branches of dispersion relations are predicted and compared with experimental values with close agreement.

I. INTRODUCTION

In a previous article,[1] a theory of lattice dynamics of cubic ionic crystals employing the shell model of Dick and Overhauser[2] was formulated and, through the long-wavelength-limit process, the connections were established between the lattice theory and Mindlin's continuum theory of elastic dielectrics with a polarization gradient.[3] This continuum theory with a polarization gradient[3] is an extension of the classical piezoelectricity. It provides additional electromechanical coupling which exists even for centrosymmetric materials and accommodates the surface effect due to electronic polarization and elastic deformation. It has been applied to account for the anomalous capacitance in thin dielectric films,[4] and for acoustical activity and, with the inclusion of the magnetic field, optical activity in quartz.[5] Theories of elastic dielectrics including the gradient of polarization or electric displacement have also been considered by many others.[6–8]

Extending the polarization-gradient theory[3] to diatomic, elastic dielectrics, two sets of mechanical displacements and two sets of electronic polarizations are introduced at each point of space which is occupied by the two interpenetrating, deformable and polarizable continua.[9] The dispersion relation obtained from this theory provides both the acoustical and optical branches and the surface effect includes the contributions from both electronic and ionic polarizations.

In the present paper, by the long-wavelength approximation, the relationship between the three-dimensional, dynamical theory of diatomic crystal lattices with shell-model atoms and Mindlin's continuum theory of diatomic, elastic dielectrics is established. The material coefficients are expressed in terms of the lattice properties and their numerical values are computed for NaI, NaCl, KI, and KCl. The long-wavelength limits of the optical dispersion frequencies, transverse and longitudinal, are calculated and compared to experimental values with close agreement.

II. INTERACTION ENERGY OF NaCl LATTICES WITH SHELL-MODEL ATOMS

In a compound lattice consisting of N different atoms, the positions of the atoms are given by

$$\vec{X}(l;k)=\vec{X}(l)+\vec{X}(k)\ , \tag{2.1}$$

where l indicates the cell origin and $\vec{X}(k)$ is the position vector from this cell origin to each different atom within the cell. Thus k takes on the values 1 through N, with $\vec{X}(k=1)=0$.

The components of the vectors $\vec{X}$ with respect to a rectangular Cartesian coordinate system are indicated by Greek indices as X_α. The summation convention is used only with respect to the Greek indices, while summation over the Latin indices is indicated by the symbol $\sum$.

The charge of the kth atom is given by

$$Z_k q=(X_k+Y_k)q\ , \tag{2.2}$$

where $X_k q$ and $Y_k q$ indicate the charges of the core and shell of the kth atom, respectively, and q denotes the charge of an electron, $q=1.6\times10^{-19}$ C. For a dielectric medium $\sum_k Z_k=0$.

For the shell model the positions of both the core and the shell before deformation are given by $\vec{X}(l;k)$. Their positions after deformation are, respectively,

$$\vec{x}^1(l;k)=\vec{X}(l;k)+\vec{U}(l;k)\ ,$$

$$\vec{\mathrm{x}}^2(l\,;k)=\vec{\mathrm{X}}(l\,;k)+\vec{\mathrm{U}}(l\,;k)+\vec{\mathrm{W}}(l\,;k)\;, \tag{2.3}$$

where $\vec{\mathrm{U}}$ is the displacement of the core and $\vec{\mathrm{W}}$ the displacement of the shell with respect to the core.

A theory of lattice dynamics for ionic crystals similar to the one derived by Woods, Cochran, and Brockhouse[10] was presented systematically in Ref. 1. To save space, some of the results in Ref. 1 will be given without rederivation.

The changes in the total potential energy of a finite lattice can be written as the sum of three parts[1]:

$$\psi=\psi^B+\psi^C+\psi^S\;, \tag{2.4}$$

where ψ^B and ψ^C denote, respectively, the energies due to the short- and long-range force interactions, and ψ^S represents the surface energy due to the presence of a boundary. The long-range interaction leads to the macroscopic electric field (Maxwell field) and to a local electric field (Lorentz field) which appears in the material coefficients. All of the long-range coefficients are expressible in terms of a single matrix, $C_{\alpha\beta}(\vec{\mathrm{y}}\,;k,k')$, which has been calculated by Kellermann[11] by an ingenious method of performing lattice sums. The short-range interactions are taken to act only between the shells of the first and second neighbors and are expressed by $B_{\alpha\beta}(\vec{\mathrm{y}}\,;k,k')$. Furthermore, the surface energy is accounted for by the interactions of dipoles induced on the boundary of a finite lattice going into a new equilibrium as compared with the configuration in the infinite lattice. The functions $T(L,k)$ and $B_\beta(L,k)$, expressing the surface energy, are calculated by a sum over the finite lattice.[1] A simplification is introduced by taking the one-ion-polarizable model, which amounts to setting, for $k=1$ denoting the alkali ion,

$$\vec{\mathrm{W}}(1)=0\;. \tag{2.5}$$

This approximation is well justified by the consideration that the polarizability of the alkali atom is an order of magnitude smaller than that of the halide atom.

For the harmonic approximation (2.4), the changes in the total potential energy of a finite NaCl-type lattice with shell-model atoms takes the following explicit form [Eq. (7.3) of Ref. 11]:

$$\begin{aligned}\psi=-\frac{1}{2}\sum_l \Big[&(\{B_{\alpha\beta}(\vec{\mathrm{y}}\,;1,1)-B_{\alpha\beta}(0\,;1,1)-B_{\alpha\beta}(0\,;1,2)+Z_1Z_1[C_{\alpha\beta}(\vec{\mathrm{y}}\,;1,1)\\&-C_{\alpha\beta}(0\,;1,1)+C_{\alpha\beta}(0\,;1,2)]\}U_\alpha(1)U_\beta(1)+[B_{\alpha\beta}(\vec{\mathrm{y}}\,;1,2)+Z_1Z_2C_{\alpha\beta}(\vec{\mathrm{y}}\,;1,2)]\,U_\alpha(1)U_\beta(2)\\&+[B_{\alpha\beta}(\vec{\mathrm{y}}\,;1,2)+Z_1Y_2C_{\alpha\beta}(\vec{\mathrm{y}}\,;1,2)]\,U_\alpha(1)W_\beta(2))\,(e^{i[\vec{\mathrm{y}}\cdot\vec{\mathrm{X}}(l;1)-\omega t]})^2+([B_{\alpha\beta}(\vec{\mathrm{y}}\,;2,1)+Z_2Z_1C_{\alpha\beta}(\vec{\mathrm{y}}\,;2,1)]U_\alpha(2)U_\beta(1)\\&+\{B_{\alpha\beta}(\vec{\mathrm{y}}\,;2,2)-B_{\alpha\beta}(0\,;2,2)-B_{\alpha\beta}(0\,;2,1)+Z_2Z_2[C_{\alpha\beta}(\vec{\mathrm{y}}\,;2,2)-C_{\alpha\beta}(0\,;2,2)+C_{\alpha\beta}(0\,;2,1)]\}\,U_\alpha(2)U_\beta(2)\\&+\{B_{\alpha\beta}(\vec{\mathrm{y}}\,;2,2)-B_{\alpha\beta}(0\,;2,2)-B_{\alpha\beta}(0\,;2,1)+Z_2Y_2\,[C_{\alpha\beta}(\vec{\mathrm{y}}\,;2,2)-C_{\alpha\beta}(0\,;2,2)]\}\,U_\alpha(2)W_\beta(2)\\&+[B_{\alpha\beta}(\vec{\mathrm{y}}\,;2,1)+Y_2Z_1C_{\alpha\beta}(\vec{\mathrm{y}}\,;2,1)]W_\alpha(2)U_\beta(1)+\{B_{\alpha\beta}(\vec{\mathrm{y}}\,;2,2)-B_{\alpha\beta}(0\,;2,2)-B_{\alpha\beta}(0\,;2,1)+Y_2Z_2\,[C_{\alpha\beta}(\vec{\mathrm{y}}\,;2,2)\\&-C_{\alpha\beta}(0\,;2,2)+C_{\alpha\beta}(0\,;2,1)]\}\,W_\alpha(2)U_\beta(2)+\{-K_2\delta_{\alpha\beta}+B_{\alpha\beta}(\vec{\mathrm{y}}\,;2,2)-B_{\alpha\beta}(0\,;2,2)\\&-B_{\alpha\beta}(0\,;2,1)Y_2Y_2\,[C_{\alpha\beta}(\vec{\mathrm{y}}\,;2,2)-C_{\alpha\beta}(0\,;2,2)]\}\,W_\alpha(2)W_\beta(2))(e^{i[\vec{\mathrm{y}}\cdot\vec{\mathrm{X}}(l;2)-\omega t]})^2\Big]\\&-\sum_l v_a(\hat{E}_\alpha\hat{P}_\alpha+\tfrac{1}{2}\epsilon_0\hat{E}_\alpha\hat{E}_\alpha)(e^{i[\vec{\mathrm{y}}\cdot\vec{\mathrm{X}}(l)-\omega t]})^2+\sum_L\{T(L\,;1)+T(L\,;2)+B_\beta(L\,;1)\,qZ_1\,U_\beta(1)\,e^{i[\vec{\mathrm{y}}\cdot\vec{\mathrm{X}}(L;1)]}\\&\qquad+B_\beta(L\,;2)q[Z_2\,U_\beta(2)+Y_2\,W_\beta(2)]e^{i[\vec{\mathrm{y}}\cdot\vec{\mathrm{X}}(L;2)-\omega t]}\}\;,\end{aligned} \tag{2.6}$$

where the summation over l is carried over the finite lattice and the summation over L is taken over the free boundary. The indices 1 and 2 denote, respectively, the positive (alkali) and the negative (halide) ions. K_2 is the spring constant characterizing the interaction between the core and shell of a negative ion and is related to the polarizability α_2 by

$$K_2=Y_2^2q^2/(4\pi\alpha_2\epsilon_0)\;. \tag{2.7}$$

$\vec{\mathrm{P}}$ is the total polarization and is defined as

$$\vec{\mathrm{P}}(l)=\frac{q}{v_a}\sum_k\,[Z_k\vec{\mathrm{U}}(l\,;k)+Y_k\vec{\mathrm{W}}(l\,;k)]\;, \tag{2.8}$$

where $v_a=2r_0^3$ is the volume of a unit cell. $\vec{\mathrm{E}}$ is the Maxwell electrostatic field and is related to $\vec{\mathrm{P}}$ by

$$\hat{E}_\alpha=-\frac{y_\alpha y_\beta}{|\vec{\mathrm{y}}|^2}\,\frac{\hat{P}_\beta}{\epsilon_0}\;, \tag{2.9}$$

where $\hat{E}_\alpha$ and $\hat{P}_\alpha$ are the amplitudes of the following periodic, plane-wave forms:

$$\vec{E}(l) = \hat{\vec{E}}\, e^{i[\vec{y}\cdot\vec{X}(l) - \omega t]}\ , \quad \vec{P} = \hat{\vec{P}}\, e^{i[\vec{y}\cdot\vec{X}(l) - \omega t]}\ .$$

Hence

$$\hat{\vec{P}} = \frac{q}{v_a} \sum_k \left[Z_k \vec{U}(k) + Y_k \vec{W}(k) \right] e^{i[\vec{y}\cdot\vec{X}(k)]}\ . \qquad (2.10)$$

In Ref. 1, the coefficients $B_{\alpha\beta}(\vec{y}\,;k,k')$ and $C_{\alpha\beta}(\vec{y}\,;k,k')$ were shown to be symmetric with respect to α and β by definition and with respect to k and k' because of the cubic symmetry of the crystal. Also, $T(L,k)$ and $B_\beta(L,k)$ were shown, by definition, to be independent of k, i.e.,

$$\begin{aligned}
&B_{\alpha\beta}(\vec{y}\,;k,k') = B_{\beta\alpha}(\vec{y}\,;k,k')\ ,\\
&B_{\alpha\beta}(\vec{y}\,;k,k') = B_{\alpha\beta}(\vec{y}\,;k',k)\ ,\\
&C_{\alpha\beta}(\vec{y}\,;k,k') = C_{\beta\alpha}(\vec{y}\,;k,k')\ ,\\
&C_{\alpha\beta}(\vec{y}\,;k\,;k') = C_{\alpha\beta}(\vec{y}\,;k',k)\ ,\\
&T(L\,;k) = T(L)\ ,\\
&B_\beta(L\,;k) = B_\beta(L)\ .
\end{aligned} \qquad (2.11)$$

III. LONG-WAVELENGTH APPROXIMATION

In order to obtain a continuum theory as the long-wavelength limit of the dynamical theory of diatomic lattices, a potential-energy density function which is defined as an average-energy representation of the medium will be obtained from (2.6) by the long wavelength approximation.

For long wavelengths including both the acoustical and optical modes, the distinction of the positive and negative ions must be retained. Let

$$\vec{U}(1) = \vec{u}^{\,1}\ , \quad \vec{U}(2) = \vec{u}^{\,2}\ , \quad \vec{W}(2) = \vec{w}\ , \qquad (3.1)$$

where $\vec{W}(1) = 0$ is due to the adoption of the one-ion-polarizable model. Substituting (3.1) into (2.10), expanding functions of $\vec{y}$ about $y = 0$ in a Taylor series and retaining the first terms, one has

$$\hat{\vec{P}} = (q/v_a)[(Z_2 - Z_1)(\vec{u}^{\,2} - \vec{u}^{\,1})/2 + Y_2\,\vec{w}\,]\ , \qquad (3.2)$$

where the charge neutrality $Z_1 + Z_2 = 0$ is employed. It can be seen that (3.2) includes both the ionic polarization (first term) and the electronic polarization (second term). To distinguish these contributions in the total polarization, define

$$q^* = \frac{Z_2 q}{v_a}\ , \quad \vec{P}^{\,2} = \frac{Y_2 q}{v_a}\,\vec{w}\ , \qquad (3.3)$$

where q^* is a charge density.

The coefficients associated with the short- and long-range interactions are expanded, about $\vec{y} = 0$, in a Taylor series as follows:

$$\begin{aligned}
&B_{\alpha\beta}(\vec{y}\,;k,k') = B_{\alpha\beta;kk'} - B_{\gamma\alpha\delta\beta;kk'}\, y_\gamma y_\delta + O(y^4)\ ,\\
&C_{\alpha\beta}(\vec{y}\,;k,k') = C_{\alpha\beta;kk'} - C_{\gamma\alpha\delta\beta;kk'}\, y_\gamma y_\delta + O(y^4)\ ,
\end{aligned} \qquad (3.4)$$

where

$$B_{\alpha\beta;kk'} \equiv B_{\alpha\beta}(0\,;k,k')\ , \quad C_{\alpha\beta;kk'} \equiv C_{\alpha\beta}(0\,;k,k')\ . \qquad (3.5)$$

In (3.4), the vanishing of the linear term in y is due to the cubic symmetry. Comparing (3.4) with equations (8.5) and (8.7) of Ref. 1, one finds

$$\sum_{k'} B_{\gamma\alpha\delta\beta;kk'} = B_{\gamma\alpha\delta\beta}\ , \quad \sum_{k'} Z_k Z_{k'} C_{\gamma\alpha\delta\beta;kk'} = C_{\gamma\alpha\delta\beta}\ , \qquad (3.6)$$

where $k' = 1, 2$, and $B_{\gamma\alpha\delta\beta}$ and $C_{\gamma\alpha\delta\beta}$ are coefficients empolyed for the long-acoustical-wavelength approximation in Ref. 1.

By substituting (3.3)–(3.6) into (2.6), replacing $\hat{P}^2_\alpha(e^{i[\vec{y}\cdot\vec{X}(l) - \omega t]})$ by $P^2_\alpha(\vec{x}, t)$ and $i u^k_\alpha y_\gamma (e^{i[\vec{y}\cdot\vec{X}(l) - \omega t]})$ by $u^k_{\alpha,\gamma}(\vec{x}, t)$, etc., replacing the summations over l and L by integrations over the volume and the bounding surface, and employing the symmetry relations (2.11), one obtains the continuum representation of the potential-energy function:

$$\begin{aligned}
\psi = \frac{1}{2v_a} \int_V \Big\{ &[B_{\gamma\alpha\delta\beta;11} + Z_1^2 C_{\gamma\alpha\delta\beta;11} + (B_{\alpha\beta;12} - Z_1^2 C_{\alpha\beta;12})\, r_0^2\, \delta_{\gamma\delta}/2]\, u^1_{\alpha,\gamma} u^1_{\beta,\delta}\\
&+ 2[B_{\gamma\alpha\delta\beta;12} - Z_1^2 C_{\gamma\alpha\delta\beta;12} - (B_{\alpha\beta;12} - Z_1^2 C_{\alpha\beta;12})\, r_0^2\, \delta_{\gamma\delta}/2]\, u^1_{\alpha,\gamma} u^2_{\beta,\delta}\\
&+ [B_{\gamma\alpha\delta\beta;11} + Z_1^2 C_{\gamma\alpha\delta\beta;11} + (B_{\alpha\beta;12} - Z_1^2 C_{\alpha\beta;12})\, r_0^2\, \delta_{\gamma\delta}/2]\, u^2_{\alpha,\gamma} u^2_{\beta,\delta} + (B_{\alpha\beta;12} - Z_1^2 C_{\alpha\beta;12})(u^2_\alpha - u^1_\alpha)(u^2_\beta - u^1_\beta)\\
&+ \frac{2v_a}{qY_2}\, [B_{\gamma\alpha\delta\beta;12} + Z_1 Y_2 C_{\gamma\alpha\delta\beta;12} - (B_{\alpha\beta;12} + Z_1 Y_2 C_{\alpha\beta;12})\, r_0^2\, \delta_{\gamma\delta}/2]\, u^1_{\alpha,\gamma} P^2_{\beta,\delta}\\
&+ \frac{2v_a}{qY_2}\, [B_{\gamma\alpha\delta\beta;11} - Z_1 Y_2 C_{\gamma\alpha\delta\beta;11} + (B_{\alpha\beta;12} + Z_1 Y_2 C_{\alpha\beta;12})\, r_0^2\, \delta_{\gamma\delta}/2]\, u^2_{\alpha,\gamma} P^2_{\beta,\delta}\\
&+ \frac{2v_a}{qY_2} (B_{\alpha\beta;12} + Z_1 Y_2 C_{\alpha\beta;12})(u^2_\alpha - u^1_\alpha) P^2_\beta + \left(\frac{v_a}{qY_2}\right)^2 [B_{\gamma\alpha\delta\beta;11} + Y_2^2 C_{\gamma\alpha\delta\beta;11}\\
&+ (K_2\, \delta_{\alpha\beta} + B_{\alpha\beta;12})\, r_0^2\, \delta_{\gamma\delta}/2]\, P^2_{\alpha,\gamma} P^2_{\beta,\delta} + \left(\frac{v_a}{qY_2}\right)^2 (K_2 \delta_{\alpha\beta} + B_{\alpha\beta;12}) P^2_\alpha P^2_\beta \Big\}\, dV
\end{aligned}$$

$$-\int_V E_\alpha[\tfrac{1}{2}\epsilon_0 E_\alpha + P^2_\alpha + q^*(u^2_\alpha - u^1_\alpha)]\,dV + \int_S [T_0 + b^{20}_{\alpha\beta} P^2_\beta n_\alpha + c^{20}_{\alpha\beta}(u^2_\alpha - u^1_\alpha) n_\alpha]\,dA\ , \tag{3.7}$$

where

$$\begin{aligned} T_0 &= 2T(L)/A_a\ ,\\ b^{20}_{\alpha\beta} &= v_a B_\beta(L)\, n_\alpha(L)/A_a\ ,\\ c^{20}_{\alpha\beta} &= v_a q^* B_\beta(L)\, n_\alpha(L)/A_a\ . \end{aligned} \tag{3.8}$$

The expressions and values of $T(L)$ and $B_\beta(L)$ are given in Ref. 1. In (3.8), $A_a = 2\gamma^2_0$ is the area of a unit cell on the boundary and $n_\alpha(L\,;\,2)$ approach n_α, the unit normal to the Lth cell on the boundary in the continuum limit.

Furthermore, introducing the definitions

$$\begin{aligned} S^k_{\alpha\gamma} &= \tfrac{1}{2}(u^k_{\gamma,\alpha} + u^k_{\alpha,\gamma}),\quad k = 1, 2\\ u^*_\alpha &= u^2_\alpha - u^1_\alpha\ ,\\ \omega^*_{\alpha\gamma} &= \tfrac{1}{2}(u^*_{\gamma,\alpha} - u^*_{\alpha,\gamma})\ , \end{aligned} \tag{3.9}$$

and converting the surface integrals into volume integrals, (3.7) takes the form

$$\begin{aligned} \psi = \psi_0 + \int_V \Big(&\tfrac{1}{2} a^{22}_{\alpha\beta} P^2_\alpha P^2_\beta + \tfrac{1}{2} b^{22}_{\gamma\alpha\delta\beta} P^2_{\alpha,\gamma} P^2_{\beta,\delta} + \frac{1}{2}\sum_{k,l} c^{kl}_{\gamma\alpha\delta\beta} S^k_{\alpha\gamma} S^l_{\beta\delta} + \sum_k d^{k2}_{\gamma\alpha\delta\beta} S^k_{\alpha\gamma} P^2_{(\beta,\delta)} + a^{*2}_{\alpha\beta} u^*_\alpha P^2_\beta + 2d^{*2}_{\alpha\beta}\,\omega^*_{\alpha\gamma} P^2_{[\beta,\gamma]}\\ &+ \tfrac{1}{2} a^{**}_{\alpha\beta} u^*_\alpha u^*_\beta + c^{**}_{\alpha\beta}\,\omega^*_{\alpha\gamma}\,\omega^*_{\beta\gamma} + b^{20}_{\alpha\beta} P^2_{\beta,\alpha} + c^{20}_{\alpha\beta} u^*_{\alpha,\beta}\Big)\,dV - \int_V (\tfrac{1}{2}\epsilon_0 E_\alpha E_\alpha + E_\alpha P^2_\alpha + q^* E_\alpha u^*_\alpha)\,dV\ , \end{aligned} \tag{3.10}$$

where

$$\begin{aligned} \psi_0 &= \int_S T_0\, dA\ ,\\ a^{22}_{\alpha\beta} &= (K_2\delta_{\alpha\beta} + B_{\alpha\beta;12}) 2r^3_0/q^2 Y^2_2\ ,\\ b^{22}_{\gamma\alpha\delta\beta} &= [B_{\gamma\alpha\delta\beta;11} + Y^2_2 C_{\gamma\alpha\delta\beta;11} + \tfrac{1}{2}(K_2\delta_{\alpha\beta} + B_{\alpha\beta;12})\, r^2_0 \delta_{\gamma\delta}] 2r^3_0/q^2 Y^2_2\ ,\\ c^{11}_{\gamma\alpha\delta\beta} &= c^{22}_{\gamma\alpha\delta\beta} = [B_{\gamma\alpha\delta\beta;11} + Z^2_1 C_{\gamma\alpha\delta\beta;11} + \tfrac{1}{2}(B_{\alpha\beta;12} - Z^2_1 C_{\alpha\beta;12}) r^2_0 \delta_{\gamma\delta}]/2r^3_0\ ,\\ c^{12}_{\gamma\alpha\delta\beta} &= c^{21}_{\gamma\alpha\delta\beta} = [B_{\gamma\alpha\delta\beta;12} - Z^2_1 C_{\gamma\alpha\delta\beta;12} - \tfrac{1}{2}(B_{\alpha\beta;12} - Z^2_1 C_{\alpha\beta;12})\, r^2_0 \delta_{\gamma\delta}]/2r^3_0\ ,\\ d^{12}_{\gamma\alpha\delta\beta} &= [B_{\gamma\alpha\delta\beta;12} + Z_1 Y_2 C_{\gamma\alpha\delta\beta;12} - \tfrac{1}{2}(B_{\alpha\beta;12} + Z_1 Y_2 C_{\alpha\beta;12})\, r^2_0 \delta_{\gamma\delta}]/qY_2\ ,\\ d^{22}_{\gamma\alpha\delta\beta} &= [B_{\gamma\alpha\delta\beta;11} - Z_1 Y_2 C_{\gamma\alpha\delta\beta;11} + \tfrac{1}{2}(B_{\alpha\beta;12} + Z_1 Y_2 C_{\alpha\beta;12})\, r^2_0 \delta_{\gamma\delta}]/qY_2\ ,\\ a^{*2}_{\alpha\beta} &= (B_{\alpha\beta;12} + Z_1 Y_2 C_{\alpha\beta;12})/qY_2\ ,\\ d^{*2}_{\alpha\beta} &= (B_{\alpha\beta;12} + Z_1 Y_2 C_{\alpha\beta;12})\, r^2_0/4qY_2\ ,\\ a^{**}_{\alpha\beta} &= (B_{\alpha\beta;12} - Z^2_1 C_{\alpha\beta;12})/2r^3_0\ ,\\ c^{**}_{\alpha\beta} &= \tfrac{1}{8}(B_{\alpha\beta;12} - Z^2_1 C_{\alpha\beta;12})\ . \end{aligned} \tag{3.11}$$

In (3.10), $P^2_{(\beta,\delta)}$ and $P^2_{[\beta,\delta]}$ represent the symmetric and antisymmetric parts of $P^2_{\beta,\delta}$, respectively.

ψ_0 is the portion of the surface energy which depends on the bounding surface and the particular lattice under consideration, but not on the deformation and polarization. Therefore, ψ_0 is present even at the initial state, i.e., when all the field variables are zero, in the bounded dielectric. Hence the difference in energy with respect to the initial state is

$$\begin{aligned} \psi - \psi_0 = \int_V [&W(S^1_{\alpha\gamma}, S^2_{\alpha\gamma}, P^2_{\alpha,\gamma}, u^*_\alpha, \omega^*_{\alpha\gamma})\\ &- \tfrac{1}{2}\epsilon_0 E_\alpha E_\alpha - E_\alpha(P^2_\alpha + q^* u^*_\alpha)]\,dV\ , \end{aligned} \tag{3.12}$$

where W is the energy density of deformation and polarization and is defined by the integrand of the first volume integral in (3.10). The remaining terms in (3.12) correspond to the energies associated with the Maxwell electrostatic field and with the electronic and ionic polarizations.

By noting that (3.10) should reduce to Eq. (8.9) of Ref. 1, which is the long-wavelength limit of the total-energy expression for monatomic lattices by setting $u^1_\alpha = u^2_\alpha = u_\alpha$ in (3.10), one obtains the following relations among the material coefficients of the diatomic and monatomic continua:

$$\begin{aligned} &\sum_{k,l} c^{kl}_{\gamma\alpha\delta\beta} = c_{\gamma\alpha\delta\beta}\ ,\quad \sum_k d^{k2}_{\gamma\alpha\delta\beta} = d_{\gamma\alpha\delta\beta}\ ,\\ &b^{22}_{\gamma\alpha\delta\beta} = b_{\gamma\alpha\delta\beta}\ ,\quad b^{20}_{\alpha\beta} = b^0_{\alpha\beta}\ ,\quad a^{22}_{\alpha\beta} = a_{\alpha\beta}\ . \end{aligned} \tag{3.13}$$

IV. CONTINUUM THEORY OF A DIATOMIC ELASTIC DIELECTRIC

In this section, the procedure employed by Mindlin[9] to obtain the coupled linear field equations and boundary conditions for diatomic, elastic dielectrics is briefly outlined.

Consider the body of an elastic dielectric which consists of two interpenetrating deformable and polarizable continua and occupies a volume V boundedby a surface S, separating V from an outer vacuum V'. At each material point x_α, two sets of mechanical displacements u_α^k and two sets of polarizations P_α^k $(k=1,2)$ are introduced. Define electric-enthalpy density and kinetic-energy density by

$$H=W(S_{\alpha\gamma}^k,\, P_\alpha^k,\, P_{\alpha\gamma}^k,\, u_\alpha^*,\, \omega_{\alpha\gamma}^*)-(\tfrac{1}{2}\epsilon_0 E_\alpha E_\alpha+E_\alpha P_\alpha)\ ,$$

$$T=\sum_k \frac{1}{2}\rho^k \dot{u}_\alpha^k \dot{u}_\alpha^k ,\quad k=1,2 \tag{4.1}$$

where the variables in W, the potential-energy density of deformation and polarization, are defined by (3.9), a dot over the symbol represents the partial derivative with respect to t and ρ^1 and ρ^2 are the mass densities of the two continua corresponding to the positive and negative ions in a unit cell. Hence

$$\rho^1=m^1/v_a\ ,\quad \rho^2=m^2/v_a\ , \tag{4.2}$$

where m^k are the masses of the atoms. P_α is the sum of the electronic and ionic polarizations

$$P_\alpha=P_\alpha^1+P_\alpha^2+q^* u_\alpha^*\ . \tag{4.3}$$

Introduce the electric potential ϕ of the Maxwell self-field as

$$E_\alpha=-\phi_{,\alpha}\ ; \tag{4.4}$$

then Mindlin's extension of Toupin's variational principle[12] takes the form

$$\delta\int_{t_0}^{t_1} dt\int_V (T-H)\,dV-\delta\int_{t_0}^{t_1} dt\int_{V'} \frac{1}{2}\epsilon_0 \phi_{,\alpha}\phi_{,\alpha}\,dV$$
$$+\sum_k\int_{t_0}^{t_1} dt\int_V (f_\alpha^k\,\delta u_\alpha^k+E_\alpha^0\,\delta P_\alpha^k+E_\alpha^0 q^*\,\delta u_\alpha^*)\,dV$$
$$+\sum_k\int_{t_0}^{t_1} dt\int_S t_\alpha^k\,\delta u_\alpha^k\,dS=0,\quad k=1,2 \tag{4.5}$$

where f_α^k, E_α^0, and t_α^k are, respectively, the external body forces, external electric field, and surface tractions. By partial differentiation,

$$\delta W=\sum_k (T_{\alpha\beta}^k\,\delta S_{\alpha\beta}^k-E_\alpha^k\,\delta P_\alpha^k+E_{\alpha\beta}^k\,\delta P_{\beta,\alpha}^k)$$
$$+T_\alpha^*\,\delta u_\alpha^*+T_{\alpha\beta}^*\,\delta\omega_{\alpha\beta}^*\ , \tag{4.6}$$

where

$$T_{\alpha\beta}^k=\frac{\partial W}{\partial S_{\alpha\beta}^k}\ ,\quad E_\alpha^k=-\frac{\partial W}{\partial P_\alpha^k}\ ,\quad E_{ij}^k=\frac{\partial W}{\partial P_{\beta,\alpha}^k}\ ,$$

$$T_\alpha^*=\frac{\partial W}{\partial u_\alpha^*}\ ,\quad T_{\alpha\beta}^*=\frac{\partial W}{\partial\omega_{\alpha\beta}^*}\ . \tag{4.7}$$

By substituting (4.3), (4.4), and (4.6) into (4.1) and employing the chain rule of differentiation, one has

$$\delta H=-\sum_k [T_{\alpha\beta,\alpha}^k+(-1)^k(T_{\alpha\beta,\alpha}^*-T_\beta^*-q^*\phi_{,\beta})]\,\delta u_\beta^k$$
$$-\sum_k (E_\beta^k+E_{\alpha\beta,\alpha}^k)\delta P_\beta^k$$
$$+\sum_k [\epsilon_0\phi_{,\alpha\alpha}-P_{\alpha,\alpha}^k-(-1)^k q^* u_{\alpha,\alpha}^k]\delta\phi$$
$$+\sum_k \{[T_{\alpha\beta}^k+(-1)^k T_{\alpha\beta}^*]\,\delta u_\beta^k\}_{,\alpha}$$
$$+\sum_k (E_{\alpha\beta}^k\,\delta P_\beta^k)_{,\alpha}-\sum_k \{[\epsilon_0\phi_{,\alpha}-P_\alpha^k-(-1)^k$$
$$\times q^* u_\alpha^k]\,\delta\phi\}_{,\alpha}\ , \tag{4.8}$$

and

$$\delta(\tfrac{1}{2}\epsilon_0\phi_{,\alpha}\phi_{,\alpha})=\epsilon_0\phi_{,\alpha\alpha}\delta\phi-\epsilon_0(\phi_{,\alpha}\,\delta\phi)_{,\alpha}\ . \tag{4.9}$$

By integration by parts and accounting for δu_α^k vanishing at t_0 and t_1, it can be shown that, from (4.11),

$$\delta\int_{t_0}^{t_1} T\,dt=-\sum_k\int_{t_0}^{t_1} \rho^k \ddot{u}_\alpha^k\,\delta u_\alpha^k\,dt\ . \tag{4.10}$$

Then the insertion of (4.8)–(4.10) into the variational principle (4.5), application of the divergence theorem, and the requirement of independent variations δu_α^k, δP_α^k, and $\delta\phi$ lead to the following field equations in V:

$$T_{\alpha\beta,\alpha}^k+(-1)^k(T_{\alpha\beta,\alpha}^*-T_\beta^*-q^*\phi_{,\beta})+f_\beta^k+(-1)^k q^* E_\beta^0$$
$$=\rho^k\ddot{u}_\alpha^k\ ,$$
$$E_\beta^k+E_{\alpha\beta,\alpha}^k-\phi_{,\beta}+E_\beta^0=0\ , \tag{4.11}$$
$$-\epsilon_0\phi_{,\alpha\alpha}+P_{\alpha,\alpha}^1+P_{\alpha,\alpha}^2+q^* u_{\alpha,\alpha}^*=0\ ;$$

and in V':

$$\phi_{,\alpha\alpha}=0\ ; \tag{4.12}$$

and the boundary conditions on S:

$$n_\alpha[T_{\alpha\beta}^k+(-1)^k T_{\alpha\beta}^*]=t_\beta^k\ ,$$
$$n_\alpha E_{\alpha\beta}^k=0\ , \tag{4.13}$$
$$n_\alpha(-\epsilon_0\,[\phi_{,\alpha}]+P_\alpha^1+P_\alpha^2+q^* u_\alpha^*)=0\ ,$$

where $[\phi_{,\alpha}]$ is the jump in $\phi_{,\alpha}$ across S.

For centrosymmetric cubic crystals, the energy function of deformation and polarization is taken as

$$W=\frac{1}{2}\sum_{k,l}(a^{kl}_{\alpha\beta}P^k_\alpha P^l_\beta+b^{kl}_{\gamma\alpha\delta\beta}P^k_{\alpha,\gamma}P^l_{\beta,\delta}+c^{kl}_{\gamma\alpha\delta\beta}S^k_{\alpha\gamma}S^l_{\beta\delta}+2d^{kl}_{\gamma\alpha\delta\beta}S^k_{\alpha\gamma}P^l_{(\beta,\delta)})$$
$$+\sum_k(a^{**}u^*_\alpha P^k_\beta+2d^{*k}\omega^*_{\alpha\beta}P^k_{[\beta,\alpha]})+\tfrac{1}{2}a^{**}u^*_\alpha u^*_\alpha+c^{**}\omega^*_{\alpha\beta}\omega^*_{\alpha\beta}$$
$$+\sum_k(b^{k0}P^k_{\alpha,\alpha}+c^{k0}S^k_{\alpha\alpha})\ . \qquad (4.14)$$

The second- and fourth-rank tensors of the material coefficients in (4.14) for centrosymmetric, cubic symmetry are of the following form[9]:

$$a^{kl}_{\alpha\beta}=a^{kl}\,\delta_{\alpha\beta}\ ,$$
$$b^{kl}_{\alpha\beta\gamma\delta}=b^{kl}\,\delta_{\gamma\alpha\delta\beta}+b^{kl}_{12}\,\delta_{\alpha\gamma}\,\delta_{\beta\delta}+b^{kl}_{44}\,(\delta_{\alpha\beta}\,\delta_{\gamma\delta}+\delta_{\alpha\delta}\,\delta_{\beta\gamma})$$
$$+\,b^{kl}_{77}\,(\delta_{\alpha\beta}\,\delta_{\gamma\delta}-\delta_{\alpha\gamma}\,\delta_{\beta\delta})\ , \qquad (4.15)$$
$$c^{kl}_{\alpha\beta\gamma\delta}=c^{kl}\,\delta_{\gamma\alpha\delta\beta}+c^{kl}_{12}\,\delta_{\alpha\gamma}\,\delta_{\beta\delta}+b^{kl}_{44}\,(\delta_{\alpha\beta}\,\delta_{\gamma\delta}+\delta_{\alpha\delta}\,\delta_{\beta\gamma})\ ,$$
$$d^{kl}_{\alpha\beta\gamma\delta}=d^{kl}\,\delta_{\gamma\alpha\delta\beta}+d^{kl}_{12}\,\delta_{\alpha\gamma}\,\delta_{\beta\delta}+d^{kl}_{44}\,(\delta_{\alpha\beta}\,\delta_{\gamma\delta}+\delta_{\alpha\delta}\,\delta_{\beta\gamma})\ ,$$

where $\delta_{\gamma\alpha\delta\beta}$ is unity when all its indices are alike and zero otherwise, and

$$b^{kl}=b^{kl}_{11}-b^{kl}_{12}-b^{kl}_{44}\ ,\quad c^{kl}=c^{kl}_{11}-c^{kl}_{12}-c^{kl}_{44}\ ,$$
$$d^{kl}=d^{kl}_{11}-d^{kl}_{12}-d^{kl}_{44}\ .$$

Substitution of (4.14) and (4.15) into (4.7) yields the constitutive equations

$$T^k_{\alpha\beta}=c^{k0}\,\delta_{\alpha\beta}+\sum_l(c^{kl}\,\delta_{\alpha\beta\gamma\delta}S^l_{\gamma\delta}+c^{kl}_{12}\,\delta_{\alpha\beta}\,S^l_{\gamma\gamma}+2\,c^{kl}_{44}S^l_{\alpha\beta})$$
$$+\sum_l(d^{kl}\,\delta_{\alpha\beta\gamma\delta}P^l_{\delta,\gamma}+d^{lk}_{12}\,\delta_{\alpha\beta}\,P^l_{\gamma,\gamma}+2\,d^{lk}_{44}P^l_{(\beta,\alpha)})\ ,$$
$$-E^k_\beta=\sum_l a^{kl}\,P^l_\beta+a^{**}u^*_\beta\ , \qquad (4.16)$$
$$E^k_{\alpha\beta}=b^{k0}\,\delta_{\alpha\beta}+\sum_l(b^{kl}\,\delta_{\alpha\beta\gamma\delta}P^l_{\delta,\gamma}+b^{kl}_{12}\,\delta_{\alpha\beta}\,P^l_{\gamma,\gamma}$$
$$+2\,b^{kl}_{44}P^l_{(\beta,\alpha)}+2\,b^{kl}_{77}P^l_{[\beta,\alpha]})+2\,d^{*k}\,\omega^*_{ij}$$
$$+\sum_l(d^{kl}\,\delta_{\alpha\beta\gamma\delta}S^k_{\gamma\delta}+d^{kl}_{12}\,\delta_{\alpha\beta}\,S^l_{\gamma\gamma}+2\,d^{kl}_{44}S^l_{\alpha\beta})\ ,$$
$$T^*_\beta=a^{**}u^*_\beta+\sum_l a^{*l}\,P^l_\beta\ ,$$
$$T^*_{\alpha\beta}=2\,c^{**}\,\omega^*_{ij}+2\sum_l d^{*l}\,P^l_{[\beta,\alpha]}\ .$$

In a state of equilibrium and in the absence of external forces ($f^k_\alpha, E^0_\alpha=0$), it can be shown that the surface energy, per unit area, of deformation and polarization induced by the presence of a free boundary is

$$W^S=\tfrac{1}{2}n_\alpha[b^{10}P^1_\alpha+b^{20}P^2_\alpha+c^{20}u^*_\alpha]_S\ . \qquad (4.17)$$

It may be noted that the energy-density function (4.14) of the continuum is the same as the integrand of the first volume integral of (3.10), which is obtained from the lattice formulation through the long-wavelength limit. In comparing these two expressions, one should take into account (4.15) and the fact that P^1_α does not appear in the lattice formulation because of the one-ion-polarizable model employed. Also note that, in (3.10),

$$c^{20}_{\alpha\beta}\,u^*_{\alpha,\beta}=c^{20}_{\alpha\beta}\,(S^2_{\alpha\beta}-S^1_{\alpha\beta})=c^{20}(S^2_{\alpha\alpha}-S^1_{\alpha\alpha})\ . \qquad (4.18)$$

Hence (4.18) is equivalent to $\sum_k c^{k0}S^k_{\alpha\alpha}$ in (4.14) and the additional condition $c^{10}+c^{20}=0$, which is obtained by requiring that, in the initial state, there is no resultant force across any surface, exterior or interior, of the continuum.

V. NUMERICAL VALUES OF MATERIAL COEFFICIENTS

The material coefficients appearing in the constitutive relations (4.16) of the continuum theory described in Sec. IV are related to the short- and long-range interaction coefficients by (3.11). Their values are evaluated as follows.

A. Short-range interaction coefficients

By expanding the short-range interaction functions $B_{\alpha\beta}(\vec{y};k,k')$, given in (7.5) of Ref. 1, into Taylor series of y_α and comparing the resulting expressions with (3.4) and (3.5), one finds

$$B_{\alpha\alpha;11}=4(A_2+2B_2)\ ,\qquad B_{\alpha\alpha;12}=2(A_1+2B_1)\ ,$$
$$B_{\alpha\beta;11}=0\ ,\qquad B_{\alpha\beta;12}=0\ ,$$
$$B_{\alpha\alpha\alpha\alpha;11}=2(A_2+B_2)r_0^2\ ,\qquad B_{\alpha\alpha\alpha\alpha;12}=A_1r_0^2\ , \qquad (5.1)$$
$$B_{\beta\alpha\beta\alpha;11}=(A_2+3B_2)r_0^2\ ,\qquad B_{\beta\alpha\beta\alpha;12}=B_1r_0^2\ ,$$
$$B_{\alpha\alpha\beta\beta;11}=(A_2-B_2)r_0^2\ ,\qquad B_{\alpha\alpha\beta\beta;12}=0\ ,$$

where α,β,γ represent the three orthogonal directions of the cubic lattice and r_0 is the distance between the nearest neighbors. In (5.1) and the subsequent equations of this section, summations over repeated Greek indices are suspended. The values of these short-range interaction coefficients, shown in Table II for NaI, NaCl, KI, and KCl, are computed by employing the numerical values of A_1, A_2, B_1, and B_2, obtained from Ref. 1, and other lattice parameters shown in Table I.

TABLE I. Lattice parameters.

	r_0 (10^{-8} cm)	A_1	A_2 (10^3 dyn/cm)	B_1	B_2	K_2 (10^6 dyn/cm)
NaI	3.23	21.01	−0.10	−1.37	−0.23	1.59
NaCl	2.81	27.14	−0.07	−3.03	0.00	3.09
KI	3.53	17.32	+0.11	−2.82	+0.44	1.59
KCl	3.14	20.23	+0.14	−4.40	+0.79	3.09

B. Long-range interaction coefficients

The functions for long-range interactions were calculated by Kellermann as the sum of infinite series and the values were given in Tables 2 and 2a in his classical article[11] as functions of the wave number. By comparing (1.9), (1.10), and (1.12) of Ref. 11 with (3.2), (4.4), and (4.6) of Ref. 1, one finds

$$c\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix} = Z_k Z_{k'} C^*_{\alpha\beta}(\vec{y}\,;k,k') - \delta_{kk'} \sum_{k''} C_{\alpha\beta}(0,k,k'') Z_k Z_{k''} \,, \qquad (5.2)$$

where

$$C^*_{\alpha\beta}(\vec{y},k,k') = C_{\alpha\beta}(\vec{y}\,;k,k') - \frac{q^2}{v_a\epsilon_0}\,\frac{y_\alpha y_\beta}{|\vec{y}|^2} \,. \qquad (5.3)$$

On the right-hand side of (5.3), the first term is regular as $\vec{y}\to 0$, while the second term, which characterizes the Maxwell electric field, is not analytic at $\vec{y}=0$; i.e., the limit of this term depends on the direction at which $\vec{y}$ approaches zero.

By employing the relations (5.2), (5.3), and expansion (3.4) and numerical differentiation of the results given in Tables 2 and 2a and Eq. (4.12) of Kellermann[11] with proper accounting for the limits, one obtains

$$\begin{aligned}
&C_{\alpha\alpha;11} = \frac{4\pi}{3}\,\frac{e^2}{2r_0^3}\,, && C_{\alpha\alpha;12} = \frac{4\pi}{3}\,\frac{e^2}{2r_0^3}\,,\\
&C_{\alpha\beta;11} = 0\,, && C_{\alpha\beta;12} = 0\,,\\
&C_{\alpha\alpha\alpha\alpha;11} = -0.95\,\frac{e^2}{2r_0}\,, && C_{\alpha\alpha\alpha\alpha;12} = 1.61\,\frac{e^2}{2r_0}\,,\\
&C_{\beta\alpha\beta\alpha;11} = 0.50\,\frac{e^2}{2r_0}\,, && C_{\beta\alpha\beta\alpha;12} = -0.78\,\frac{e^2}{2r_0}\,,\\
&C_{\alpha\alpha\beta\beta;11} = -0.289\,\frac{e^2}{2r_0}\,, && C_{\alpha\alpha\beta\beta;12} = -0.985\,\frac{e^2}{2r_0}\,.
\end{aligned} \qquad (5.4)$$

It can be seen that these values when inserted into the compatibility relations (3.6) agree with the exact values, 2.56 $e^2/(2r_0)$, 1.28 $e^2/(2r_0)$, and 0.696 $e^2/(2r_0)$ for $C_{\alpha\alpha\alpha\alpha}$, $C_{\beta\alpha\beta\alpha}$, and $C_{\alpha\alpha\beta\beta}$, respectively.

Upon substituting the values of the short- and long-range interaction coefficients given in Table II into (3.11), one obtains the numerical values of the material coefficients of Mindlin's theory as shown in Table III.

VI. WAVE PROPAGATION

The purpose of this section is to compute the limiting frequencies, as $y\to 0$, of the optical branches of the dispersion relations for plane waves by employing Mindlin's continuum theory and the numerical values obtained in Sec. V.

By substitution of constitutive equations (4.16) into the field equations (4.11), the equations of motions in terms of u^k_α, P^k_α, and ϕ for cubic crystals are obtained as follows:

TABLE II. Auxilliary values for computing material coefficients.

	$B_{\alpha\alpha;11}$	$B_{\alpha\alpha;12}$ (10^3 dyn/cm)	$B_{\alpha\alpha\alpha\alpha;11}$	$B_{\alpha\alpha\alpha\alpha;12}$	$B_{\alpha\alpha\beta\beta;11}$	$B_{\alpha\alpha\beta\beta;12}$ (10^{-12} dyn cm)	$B_{\beta\alpha\beta\alpha;11}$	$B_{\beta\alpha\beta\alpha;12}$
NaI	−2.24	36.54	−0.69	21.92	+0.14	0	−0.82	−1.43
NaCl	−0.28	42.16	−0.11	21.43	−0.06	0	−0.06	−2.39
KI	+3.96	23.36	+1.37	21.58	−0.41	0	+1.78	−3.51
KCl	+6.88	22.86	+1.83	19.95	−0.64	0	+2.47	−4.34
	$C_{\alpha\alpha;11}$	$C_{\alpha\alpha;12}$ (10^3 dyn/cm)	$C_{\alpha\alpha\alpha\alpha;11}$	$C_{\alpha\alpha\alpha\alpha;12}$	$C_{\alpha\alpha\beta\beta;11}$	$C_{\alpha\alpha\beta\beta;12}$ (10^{-12} dyn cm)	$C_{\beta\alpha\beta\alpha;11}$	$C_{\beta\alpha\beta\alpha;12}$
NaI	14.32	14.32	−3.39	5.74	−1.03	−3.51	1.78	−2.78
NaCl	21.75	21.75	−3.89	6.60	−1.18	−4.04	2.05	−3.20
KI	10.97	10.97	−3.10	5.25	−0.94	−3.21	1.63	−2.55
KCl	15.59	15.59	−3.49	5.91	−1.06	−3.61	1.83	−2.86

$$\sum_l [c^{kl}\delta_{\alpha\beta\gamma\delta} u^l_{\delta,\gamma\alpha} + c^{kl}_{12} u^l_{\alpha,\alpha\beta} + c^{kl}_{44}(u^l_{\beta,\alpha\alpha} + u^l_{\alpha,\alpha\beta})] + \sum_l [d^{lk}\delta_{\alpha\beta\gamma\delta} P^l_{\delta,\gamma\alpha} + d^{lk}_{12} P^l_{\alpha,\alpha\beta} + d^{lk}_{44}(P^l_{\beta,\alpha\alpha} + P^l_{\alpha,\alpha\beta})]$$

$$+ (-1)^k \sum_l [d^{*l}(P^l_{\beta,\alpha\alpha} - P^l_{\alpha,\alpha\beta}) + (-1)^l c^{**}(u^l_{\beta,\alpha\alpha} - u^l_{\alpha,\alpha\beta})]$$

$$- (-1)^k[a^{*1}P^1_\beta + a^{*2}P^2_\beta + a^{**}(u^2_\beta - u^1_\beta) + q^*\phi_{,\beta} - q^* E^0_\beta] + f^k_\beta = \rho^k u^k_{\beta,tt} ,$$

$$\sum_l [d^{kl}\delta_{\alpha\beta\gamma\delta} u^l_{\delta,\gamma\alpha} + d^{kl}_{12} u^l_{\alpha,\alpha\beta} + d^{kl}_{44}(u^l_{\beta,\alpha\alpha} + u^l_{\alpha,\alpha\beta}) + (-1)^l d^{*k}(u^l_{\beta,\alpha\alpha} - u^l_{\alpha,\alpha\beta})] \tag{6.1}$$

$$+ \sum_l [b^{kl}\delta_{\alpha\beta\gamma\delta} P^l_{\delta,\gamma\alpha} + b^{kl}_{12} P^l_{\alpha,\alpha\beta} + b^{kl}_{44}(P^l_{\beta,\alpha\alpha} + P^l_{\alpha,\alpha\beta}) + b^{kl}_{77}(P^l_{\beta,\alpha\alpha} - P^l_{\alpha,\alpha\beta})]$$

$$- a^{1k}P^1_\beta - a^{2k}P^2_\beta - a^{*2}(u^2_\beta - u^1_\beta) - \phi_{,\beta} + E^0_\beta = 0 ,$$

$$- \epsilon_0\phi_{,\alpha\alpha} + P^1_{\alpha,\alpha} + P^2_{\alpha,\alpha} + q^*(u^2_{\alpha,\alpha} - u^1_{\alpha,\alpha}) = 0 .$$

In applying these equations to the one-ion-polarizable case, one should set $P^1_\alpha = 0$; consequently $E^1_\alpha = E^1_{\alpha\beta} = 0$ from (4.16). Therefore, the second set of equations in (6.1) is reduced to one, for k only takes on the value of 2.

By introducing longitudinal plane waves propagating along the x_1 axis,

$$(u^k_1,\ P^2_1,\ \phi) = (A^k_1,\ B_1, C)\, e^{i(\nu_1 x_1 - \omega t)} ,$$

and then transverse plane waves,

$$(u^k_2, P^2_2, \phi) = (A^k_2, B_2, C)\, e^{i(\nu_1 x_1 - \omega t)} ,$$

into the equations of motion (6.1) with $f^k_\beta = E^0_\beta = 0$, and setting the determinants of the matrices for A^k_1, B_1, C and A^k_2, B_2, C, equal to zero, dispersion relations are obtained, respectively, for longitudinal and transverse waves. Of the four branches in each case, only two are real, corresponding to the acoustical and optical branches.[9] At $y_1 = 0$, frequencies of the acoustical branches approach zero and the limiting frequencies of the transverse- and longitudinal-optical waves are

$$\omega_{\mathrm{TO}} = \left(\frac{a^{**}}{\bar{\rho}}\,(1 - F_1)\right)^{1/2} ,$$

TABLE III. Material coefficients.

	$c^{11}_{11}=c^{22}_{11}$	$c^{12}_{11}=c^{21}_{11}$	$c^{11}_{12}=c^{22}_{12}$	$c^{12}_{12}=c^{21}_{12}$	$c^{11}_{44}=c^{22}_{44}$	$c^{12}_{44}=c^{21}_{44}$	$c^{20}=-c^{10}$	c^{**}
	(10^{12} dyn/cm^2)							(10^3 dyn/cm)
NaI	0.111	0.068	−0.013	0.052	0.186	−0.152	0.030	2.77
NaCl	0.091	0.153	−0.028	0.091	0.227	−0.163	0.052	2.55
KI	0.068	0.098	−0.015	0.037	0.127	−0.099	0.021	1.55
KCl	0.031	0.169	−0.027	0.058	0.128	−0.082	0.033	0.91
	d^{22}_{11}	d^{12}_{11}	d^{22}_{12}	d^{12}_{12}	d^{22}_{44}	d^{12}_{44}	d^{*2}	a^{*2}
	(10^7 dyn cm/C)							(10^{22} dyn/cm C)
NaI	5.146	−1.335	0.632	−2.196	1.926	−4.578	1.483	5.687
NaCl	6.324	−1.668	0.745	−2.524	2.604	−5.665	1.940	9.828
KI	4.788	−1.615	0.626	−2.009	1.793	−4.250	1.486	4.771
KCl	5.811	−1.885	0.720	−2.259	2.429	−5.197	1.898	7.701
	b^{22}_{11}	b^{22}_{12}	b^{22}_{44}	b^{22}_{77}	$-b^{20}$		a^{22}	a^{**}
	(10^5 dyn cm^4/C^2)				(10^7 dyn cm /C)		(10^{20} dyn cm^2/C^2)	(10^{26} dyn/cm^4)
NaI	0.366	−0.027	0.274	0.228	1.26		0.874	3.297
NaCl	0.369	−0.021	0.254	0.218	1.44		1.106	4.600
KI	0.599	−0.033	0.410	0.352	1.15		1.131	1.408
KCl	0.673	−0.026	0.424	0.378	1.29		1.534	1.175

TABLE IV. Comparison of the predicted and experimental values of dispersion frequencies.

	ω_{TO} (10^{13} sec^{-1}) Predicted	Experimental[a]	$(1-F_1)^{1/2}$	ω_{LO} (10^{13} sec^{-1}) Predicted	Experimental[a]	$(1-F_2)^{1/2}$
NaI	2.5	2.2[b]	0.94	3.9	3.3[b]	0.88
NaCl	2.7	3.1	0.90	5.3	5.0	0.88
KI	1.5	1.9	0.93	2.7	2.6	0.89
KCl	1.3	2.7	0.82	3.8	4.0	0.89

[a] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971), p. 190.

[b] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., Oxford, England, 1954), Table 17, p. 85 for NaI values.

$$\omega_{LO}=\left(\frac{a^{**}+(q^*)^2\epsilon_0^{-1}}{\bar{\rho}}(1-F_2)\right)^{1/2}, \tag{6.2}$$

where

$$\begin{aligned}\bar{\rho}&=\rho^1\rho^2/(\rho^1+\rho^2)=m^1m^2/v_a(m_1+m_2),\\ F_1&=(a^{*2})^2/a^{22}a^{**},\\ F_2&=(a^{*2}+q^*\epsilon_0^{-1})^2/(a^{22}+\epsilon_0^{-1})[a^{**}+(q^*)^2\epsilon_0^{-1}].\end{aligned} \tag{6.3}$$

$\bar{\rho}$ is the effective density, and m^1 and m^2 are the atomic masses of the positive and negative ions. F_1 and F_2 in (6.2) may be regarded as the corrections of the frequencies brought by the shell model over the rigid-ion model. The values of frequencies predicted by (6.2) are calculated and compared with measured ones as shown in Table IV. It can also be seen from the values of $(1-F_1)^{1/2}$ and $(1-F_2)^{1/2}$ shown that the modification of the values of dispersion frequencies may range from 5 to 15%.

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