

## Lattice-Dynamics Approach to the Theory of Elastic Dielectrics with Polarization Gradient

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(Received 2 October 1969)

A continuum theory of elastic dielectrics including polarization gradient is obtained as the long-wave approximation of a theory of lattice dynamics for the shell model of cubic ionic crystals. The additional energy associated with the formation and relaxation of a free surface is obtained by considering the unbalanced charges and dipole moments on the surface. The material coefficients of the continuum theory are related to the lattice properties, and their numerical values are calculated for NaI, NaCl, KI, and KCl. The surface energy density of a free half-space predicted by the continuum theory is compared with experimental results as well as other theoretical results based on discrete models.

### 1. INTRODUCTION

IN the recent continuum theories of elastic dielectrics the electromechanical interaction has been studied by Toupin<sup>1</sup> and Eringen<sup>2</sup> by considering the stored energy density to be a function of both strain and polarization. Mindlin<sup>3</sup> presents a linear theory which includes the polarization gradient in the energy density as well as the strain and polarization, and predicts surface effects due to deformation and polarization. He also indicates the relation between polarization gradient and the shell-shell and core-shell interactions of lattice theories of crystals.

The purpose of this investigation is (1) to obtain a continuum theory of elastic dielectrics of centrosymmetric cubic crystals by means of the long-wave approximation of the theory of lattice dynamics of crystals using the shell model introduced by Dick and Overhauser<sup>4</sup>; (2) to obtain the material coefficients of the continuum theory in terms of the lattice properties and calculate their numerical values.

In this formulation, a theory of lattice dynamics for ionic crystals similar to the one derived by Woods, Cochran, and Brockhouse,<sup>5</sup> which employs the one-ion-polarizable model, is used to obtain the potential energy of alkali halides. The energy due to the short-range forces is obtained by extending Kellermann's method<sup>6</sup> to include the interactions of the shells of both the first and second nearest neighbors as well as the interaction of a core with its own shell.

For lattices of finite extent the energy associated with the formation and relaxation of a surface is added to the potential energy described in the preceding paragraph. The surface energy is calculated for a half space using the methods described by Tosi<sup>7</sup> and Benson

and Yun,<sup>8</sup> and the results of the boundary-value problem given in Sec. 11.

For the resulting continuum theory, the values of the material coefficients are calculated for NaI, NaCl, KI, and KCl. The surface energy density predicted by this continuum theory is compared with the results obtained by Benson<sup>8</sup> and Shuttleworth<sup>7a</sup> based on discrete models, and other experimental data.<sup>7</sup>

### 2. SHELL MODEL

In this section a theory of lattice dynamics for ionic crystals similar to the one derived by Woods, Cochran, and Brockhouse<sup>5</sup> is presented systematically in order to obtain from it a continuum theory of dielectrics with polarization gradient by means of the long-wave approximation, and to calculate the numerical values of the material constants involved. In this theory, the polarizable ion is represented by the "shell model."<sup>4</sup> In the shell model the outermost electron shell is considered to be a rigid spherical "shell," which can move with respect to the massive ionic "core," which consists of the nucleus and the inner electron shells.

The notation followed is similar to the one used by Born and Huang.<sup>9</sup> For a composite lattice consisting of  $N$  different atoms, their positions are given by

$$\mathbf{X}(l; k) = \mathbf{X}(l) + \mathbf{X}(k), \quad (2.1)$$

where  $l$  indicates the cell origin and  $\mathbf{X}(k)$  is the position vector from this cell origin to each different atom within the cell, thus  $k$  takes on the value 1 through  $N$ , with  $\mathbf{X}(k=1)=0$ . The vector joining two lattice points is given by

$$\begin{aligned} \mathbf{X}(l-l'; k, k') &= \mathbf{X}(l; k) - \mathbf{X}(l'; k') \\ &= -\mathbf{X}(l'-l; k', k). \end{aligned} \quad (2.2)$$

The components of the vectors  $\mathbf{X}$  with respect to the rectangular Cartesian coordinate system are indicated by Greek indices  $X_\alpha$ . The summation convention is used only with respect to the Greek indices, while

<sup>7a</sup> Shuttleworth, Proc. Phys. Soc. (London) A62, 167 (1949).

<sup>8</sup> G. C. Benson and K. S. Yun, in *The Solid-Gas Interface*, edited by E. A. Flood (M. Dekker, Inc., New York, 1967), Vol. 1, p. 203.

<sup>9</sup> M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954).

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<sup>1</sup> R. A. Toupin, J. Ration. Mech. Anal. 5, 849 (1956).

<sup>2</sup> A. C. Eringen, Int. J. Eng. Sci. 1, 127 (1963).

<sup>3</sup> R. D. Mindlin, Int. J. Solids Structures 4, 637 (1968).

<sup>4</sup> B. J. Dick and A. W. Overhauser, Phys. Rev. 112, 90 (1958).

<sup>5</sup> A. B. D. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. 119, 980 (1960).

<sup>6</sup> E. W. Kellermann, Phil. Trans. Roy. Soc. London 238, 513 (1940).

<sup>7</sup> M. P. Tosi, Solid State Phys. 16, 92 (1964).

summation over the Latin indices is indicated by the symbol  $\sum$ .

The charge of the  $k$ th atom is given by

$$Z_k q = (X_k + Y_k) q, \quad (2.3)$$

where  $X_k q$  and  $Y_k q$  indicate the charges of the core and shell of the  $k$ th atom, respectively, and  $q$  denotes the charge of an electron,  $q = 1.6 \times 10^{-19}$  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  $\mathbf{X}(l; k)$ . Their positions after deformation are, respectively,

$$\begin{aligned} \mathbf{x}^1(l; k) &= \mathbf{X}(l; k) + \mathbf{U}(l; k), \\ \mathbf{x}^2(l; k) &= \mathbf{X}(l; k) + \mathbf{U}(l; k) + \mathbf{W}(l; k), \end{aligned} \quad (2.4)$$

where  $\mathbf{U}$  is the displacement of the core and  $\mathbf{W}$  the displacement of the shell with respect to the core (see Fig. 1).

According to the shell model, the potential energy consists of the following interaction energies between different ions: core-core, shell-shell, core-shell, shell-core, and the interaction energy of the core with its own shell. Under the two-body-interaction approximation, the potential  $\Phi$  which is invariant under rigid-body translation and rotation can be written as

$$\Phi = \frac{1}{2} \sum'_{lk'l'k'} \{ \Phi_N(r_1) + \Phi_T(r_2) + \Phi_{T'}(r_3) + \Phi_S(r_4) + K_k W_\alpha(l; k) W_\alpha(l; k) \}, \quad (2.5)$$

where

$$\begin{aligned} r_1 &= |\mathbf{x}^1(l; k) - \mathbf{x}^1(l'; k')|, \\ r_2 &= |\mathbf{x}^1(l; k) - \mathbf{x}^2(l'; k')|, \\ r_3 &= |\mathbf{x}^2(l; k) - \mathbf{x}^1(l'; k')|, \\ r_4 &= |\mathbf{x}^2(l; k) - \mathbf{x}^2(l'; k')|, \end{aligned} \quad (2.6)$$

where the prime over the summation sign indicates that the summation is to be suppressed for  $(l; k) = (l'; k')$ . And  $\Phi_N$ ,  $\Phi_S$ ,  $\Phi_T$ ,  $\Phi_{T'}$  represent the interaction energies between the various elements of the different ions, and  $K_k$  is the spring constant characterizing the interaction between the core and the shell of the same ion. This spring constant is related to the polarizability  $\alpha_k$  as follows:

$$K_k = Y_k^2 q^2 / \alpha_k \epsilon_0, \quad (2.7)$$

where  $\epsilon_0$  is the permittivity of vacuum with  $1/4\pi\epsilon_0 = 9 \times 10^9$  newton m<sup>2</sup>/C<sup>2</sup>.

$$\begin{aligned} \Phi &= \Phi_0 - \frac{1}{2} \sum'_{lk'l'k'} \{ [\Phi^{11}_{\alpha\beta}(l-l'; k, k') - \delta_{kk'} \delta_{ll'} \sum'_{l''k''} \Phi^{11}_{\alpha\beta}(l-l''; k, k'')] U_\alpha(l; k) U_\beta(l'; k') \\ &+ [\Phi^{12}_{\alpha\beta}(l-l'; k, k') - \delta_{kk'} \delta_{ll'} \sum'_{l''k''} \Phi^{12}_{\alpha\beta}(l-l''; k, k'')] U_\alpha(l; k) W_\beta(l'; k') \\ &+ [\Phi^{21}_{\alpha\beta}(l-l'; k, k') - \delta_{kk'} \delta_{ll'} \sum'_{l''k''} \Phi^{21}_{\alpha\beta}(l-l''; k, k'')] W_\alpha(l; k) U_\beta(l'; k') \\ &+ [\Phi^{22}_{\alpha\beta}(l-l'; k, k') - \delta_{kk'} \delta_{ll'} \sum'_{l''k''} \Phi^{22}_{\alpha\beta}(l-l''; k, k'')] W_\alpha(l; k) W_\beta(l'; k') + \sum'_{lk} \frac{1}{2} K_k W_\alpha(l; k) W_\alpha(l; k) \}, \end{aligned} \quad (2.12)$$

where  $\delta_{kk'}$  is the Kronecker delta.

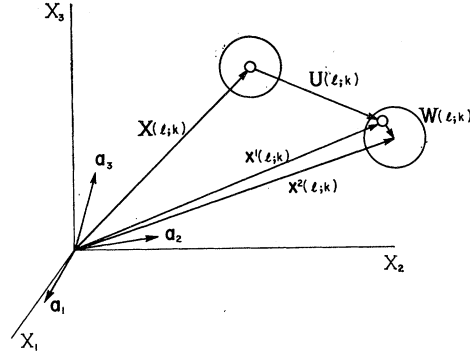


FIG. 1. Displacements of the core and the shell of a typical ion.

Expansion of Eq. (2.6) in a Taylor series about its stable equilibrium configuration and the application of the harmonic approximation yields

$$\Phi = \Phi_0 + \Phi_1 + \Phi_2. \quad (2.8)$$

In Eq. (2.8)  $\Phi_0$  is a constant and  $\Phi_1$  vanishes since the stable equilibrium configuration corresponds to a state of minimum energy and  $\Phi_2$  involves quadratic terms in  $\mathbf{U}(l; k)$  and  $\mathbf{W}(l; k)$ . Noting that

$$\begin{aligned} \left. \frac{\partial^2 \Phi}{\partial x^i_\alpha(l; k) \partial x^j_\beta(l'; k')} \right|_{\mathbf{u}=\mathbf{w}=0} &= \Phi^{ij}_{\alpha\beta}(l-l'; k, k'), \\ \left. \frac{\partial^2 \Phi}{\partial x^i_\alpha(l; k) \partial x^j_\beta(l'; k')} \right|_{\mathbf{u}=\mathbf{w}=0} &= \sum'_{l'k'} \Phi^{ij}_{\alpha\beta}(l-l'; k, k'), \end{aligned} \quad (2.9)$$

where the second partial derivative

$$\partial^2 / \partial x^i_\alpha(l; k) \partial x^j_\beta(l'; k')$$

for  $\mathbf{U} = \mathbf{W} = 0$  can be defined by the operator as

$$\begin{aligned} L_{\alpha\beta}(l-l'; k, k') &= X_\alpha(l-l'; k, k') X_\beta(l-l'; k, k') - \frac{d^2}{r^2 dr^2} \\ &+ [r^2 \delta_{\alpha\beta} - X_\alpha(l-l'; k, k') X_\beta(l-l'; k, k')] \frac{d}{r^3 dr} \end{aligned} \quad (2.10)$$

and

$$r = r_i |_{\mathbf{u}=\mathbf{w}=0} \quad (i=1, 2, 3, 4). \quad (2.11)$$

By considering Eqs. (2.9) and (2.10), it can be seen that  $\Phi^{ij}_{\alpha\beta}$  are symmetric with respect to the Greek indices. The harmonic approximation of (2.5) is then

The kinetic energy, in view of the Born-Oppenheimer approximation,<sup>9</sup> can be written as

$$T = \sum_{lk} \frac{1}{2} m_k \dot{U}_\alpha(l; k) \dot{U}_\alpha(l; k), \tag{2.13}$$

where a dot indicates differentiation with respect to time. By letting  $L = T - \Phi$ , and applying Hamiltonian's principle, the equations of motion become

$$\begin{aligned} m_k \ddot{U}_\alpha(l; k) = & \sum'_{l'k'} \{ [\Phi^{11}_{\alpha\beta}(l-l'; k, k') - \delta_{kk'} \delta_{ll'} \sum'_{l''k''} \Phi^{11}_{\alpha\beta}(l-l''; k, k'')] U_\beta(l'; k') \\ & + [\Phi^{12}_{\alpha\beta}(l-l'; k, k') - \delta_{kk'} \delta_{ll'} \sum'_{l''k''} \Phi^{12}_{\alpha\beta}(l-l''; k, k'')] W_\beta(l'; k') \}, \tag{2.14} \\ 0 = & \sum'_{l'k'} \{ [\Phi^{21}_{\alpha\beta}(l-l'; k, k') - \delta_{kk'} \delta_{ll'} \sum'_{l''k''} \Phi^{21}_{\alpha\beta}(l-l''; k, k'')] U_\beta(l'; k') \\ & + [\Phi^{22}_{\alpha\beta}(l-l'; k, k') - \delta_{kk'} \delta_{ll'} \sum'_{l''k''} \Phi^{22}_{\alpha\beta}(l-l''; k, k'')] W_\beta(l'; k') \} - K_k W_\alpha(l; k). \end{aligned}$$

### 3. LATTICE WAVES

The equations of motion obtained above, Eqs. (2.14), comprise an infinite system of simultaneous linear differential equations. Due to the periodicity of the lattice, a reduction can be achieved by utilizing periodic plane-wave solutions of the form

$$U_\alpha(l; k) = U_\alpha(k) \exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t], \quad W_\alpha(l; k) = W_\alpha(k) \exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t], \tag{3.1}$$

where  $\mathbf{y}$  is a wave-number vector. Substitution of the above wave solutions into Eqs. (2.14) reduces the infinite number of differential equations to a  $3 \times 2 \times N$  system of linear algebraic equations:

$$\begin{aligned} -m_k \omega^2 U_\alpha(k) = & \sum_{k'} \{ N_{\alpha\beta}(\mathbf{y}; k, k') U_\beta(k') + T_{\alpha\beta}(\mathbf{y}; k, k') \} W_\beta(k'), \\ 0 = & \sum_{k'} \{ T'_{\alpha\beta}(\mathbf{y}; k, k') U_\beta(k') + S_{\alpha\beta}(\mathbf{y}; k, k') W_\beta(k') \} - K_k W_\alpha(k), \end{aligned} \tag{3.2}$$

where

$$N_{\alpha\beta}(\mathbf{y}; k, k') = \sum'_{l'} \{ \Phi^{11}_{\alpha\beta}(l-l'; k, k') \exp i[-\mathbf{y} \cdot \mathbf{X}(l-l'; k, k')] - \delta_{kk'} \sum_{k''} \Phi^{11}_{\alpha\beta}(l-l'; k, k'') \}, \tag{3.3}$$

and  $T_{\alpha\beta}$ ,  $T'_{\alpha\beta}$ , and  $S_{\alpha\beta}$  are defined in the same form as  $N_{\alpha\beta}$  in Eq. (3.3) except  $\Phi^{11}_{\alpha\beta}$  is replaced by  $\Phi^{12}_{\alpha\beta}$ ,  $\Phi^{21}_{\alpha\beta}$ , and  $\Phi^{22}_{\alpha\beta}$ , respectively.

Similarly, substitution of the wave solutions, Eqs. (3.1), into the potential- and kinetic-energy expressions, Eqs. (2.5) and (2.13), respectively, yields

$$\begin{aligned} \psi = \Phi - \Phi_0 = & -\frac{1}{2} \sum_{lk k'} \{ [N_{\alpha\beta}(\mathbf{y}; k, k') U_\alpha(k) U_\beta(k') + T_{\alpha\beta}(\mathbf{y}; k, k') U_\alpha(k) W_\beta(k') + T'_{\alpha\beta}(\mathbf{y}; k, k') W_\alpha(k) U_\beta(k') \\ & + S_{\alpha\beta}(\mathbf{y}; k, k') W_\alpha(k) W_\beta(k') - K_k W_\alpha(k) W_\alpha(k)] \exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t] \}^2, \end{aligned} \tag{3.4}$$

$$T = -\frac{1}{2} \omega^2 \sum_{lk} \{ m_k U_\alpha(k) U_\alpha(k) \exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t] \}^2. \tag{3.5}$$

In the above expressions the squared exponentials must be taken as the square of the real part of the exponential. This form of the potential-energy change, Eq. (3.4), is particularly useful for the long-wave approximation in obtaining the continuum equations.

The potential-energy density for the continuum can be obtained from Eq. (3.4) by the long-wave

approximation as

$$\begin{aligned} \lim_{\mathbf{y} \rightarrow 0} \frac{-1}{2v_a} \sum_{kk'} \{ & N_{\alpha\beta}(\mathbf{y}; k, k') U_\alpha(k) U_\beta(k') \\ & + T_{\alpha\beta}(\mathbf{y}; k, k') U_\alpha(k) W_\beta(k') \\ & + T_{\alpha\beta}'(\mathbf{y}; k, k') W_\alpha(k) U_\beta(k') \\ & + [S_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \delta_{\alpha\beta} K_k] W_\alpha(k) W_\beta(k') \} \\ & \times (\exp i[\mathbf{y} \cdot \mathbf{X}(k')])^2, \quad (3.6) \end{aligned}$$

where  $v_a = \mathbf{a}_1 \times \mathbf{a}_2 \cdot \mathbf{a}_3$  is the volume of the unit cell.

The potential energy can be written as the sum of two parts, one due to short-range forces and the other due to long-range forces:

$$\Phi = \Phi^B + \Phi^C, \quad (3.7)$$

where  $B$  and  $C$  are from the names of Born and Coulomb and denote the short- and long-range interactions, respectively. Consequently the coefficients defined by Eqs. (3.3) can also be written as the sum of their short- and long-range parts, as

$$N_{\alpha\beta} = N_{\alpha\beta}^B + N_{\alpha\beta}^C, \quad T_{\alpha\beta} = T_{\alpha\beta}^B + T_{\alpha\beta}^C, \quad \text{etc.} \quad (3.8)$$

#### 4. LONG-RANGE INTERACTIONS

For the shell model, Fig. 1, the long-range part of the potential energy is due to the Coulombic forces and

$$\begin{aligned} \Phi^C = & \Phi^C_0 + \Phi^C_1 - \frac{1}{2} \sum_{lkk'} \{ [Z_k Z_{k'} C_{\alpha\beta}^*(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Z_k Z_{k''} C_{\alpha\beta}(0; k, k'')] U_\alpha(k) U_\beta(k') \\ & + [Z_k Y_{k'} C_{\alpha\beta}^*(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Z_k Y_{k''} C_{\alpha\beta}(0; k, k'')] U_\alpha(k) W_\beta(k') \\ & + [Y_k Z_{k'} C_{\alpha\beta}^*(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Y_k Z_{k''} C_{\alpha\beta}(0; k, k'')] W_\alpha(k) U_\beta(k') \\ & + [Y_k Y_{k'} C_{\alpha\beta}^*(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Y_k Y_{k''} C_{\alpha\beta}(0; k, k'')] W_\alpha(k) W_\beta(k') \} \{ (\exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t])^2 \}, \quad (4.4) \end{aligned}$$

where, according to (3.3),

$$\begin{aligned} \Phi^C_0 = & \Phi^C |_{\mathbf{u}=\mathbf{w}=0}, \\ \Phi^C_1 = & \sum'_{lk} \frac{\partial \Phi^C}{\partial U_\alpha(l; k)} \Big|_{\mathbf{u}=\mathbf{w}=0} U_\alpha(l; k) \\ & + \frac{\partial \Phi^C}{\partial W_\alpha(l; k)} \Big|_{\mathbf{u}=\mathbf{w}=0} W_\alpha(l; k) \end{aligned} \quad (4.5)$$

and

$$\begin{aligned} C_{\alpha\beta}^*(\mathbf{y}; k, k') = & \sum'_{l'} \Phi^C_{\alpha\beta}(l-l'; k, k') \\ & \times \exp i[-\mathbf{y} \cdot \mathbf{X}(l-l'; k, k')], \quad (4.6) \\ C_{\alpha\beta}(0; k, k') = & \sum'_{l'} \Phi^C_{\alpha\beta}(l-l'; k, k'). \end{aligned}$$

In Eqs. (4.5) and (4.6) the prime on  $\sum$  suspends the summation for  $(l; k) = (l'; k')$ .

can be written as

$$\begin{aligned} \Phi^C = & \frac{1}{2} \sum'_{lkl'k'} \frac{q^2}{4\pi\epsilon_0} \\ & \times \left( \frac{X_k X_{k'}}{r_1} + \frac{X_k Y_{k'}}{r_2} + \frac{Y_k X_{k'}}{r_3} + \frac{Y_k Y_{k'}}{r_4} \right). \quad (4.1) \end{aligned}$$

One sees from Eqs. (2.5), with the definition, Eq. (3.7), that the four terms in Eq. (4.1) correspond, respectively, to  $\Phi^C_N$ ,  $\Phi^C_T$ ,  $\Phi^C_{T'}$ , and  $\Phi^C_S$ . The harmonic approximation of Eq. (4.1) has the same form as Eq. (2.12) with the coefficients  $\Phi^{ij}_{\alpha\beta}$  replaced by  ${}^C\Phi^{ij}_{\alpha\beta}$  using Eqs. (2.9) and (2.10) as

$$\begin{aligned} {}^C\Phi^{11}_{\alpha\beta}(l-l'; k, k') = & \Phi^C_{\alpha\beta}(l-l'; k, k') Z_k Z_{k'}, \\ {}^C\Phi^{12}_{\alpha\beta}(l-l'; k, k') = & \Phi^C_{\alpha\beta}(l-l'; k, k') Z_k Y_{k'}, \\ {}^C\Phi^{21}_{\alpha\beta}(l-l'; k, k') = & \Phi^C_{\alpha\beta}(l-l'; k, k') Y_k Z_{k'}, \\ {}^C\Phi^{22}_{\alpha\beta}(l-l'; k, k') = & \Phi^C_{\alpha\beta}(l-l'; k, k') Y_k Y_{k'}, \end{aligned} \quad (4.2)$$

where

$$\Phi^C_{\alpha\beta}(l-l'; k, k') = \frac{q^2}{4\pi\epsilon_0} L_{\alpha\beta}(l-l'; k, k') \frac{1}{r}. \quad (4.3)$$

For periodic waves Eq. (3.1), by considering Eqs. (3.3) and (3.4), the harmonic approximation of Eq. (4.1) can be written as

It should be noted that  $C_{\alpha\beta}(0; k, k')$  is not obtained from  $C_{\alpha\beta}^*(\mathbf{y}; k, k')$  as  $\mathbf{y} \rightarrow 0$ , but comes from the coefficients of the products of displacements under the first summation sign of Eq. (2.12) with  ${}^C\Phi^{ij}_{\alpha\beta}$  replacing  $\Phi^{ij}_{\alpha\beta}$ .

The coefficients  $C_{\alpha\beta}^*$  and the form of  $\Phi^C$  obtained here are the same as those obtained by Ewald<sup>9</sup> in studying the electrostatic field due to a dipole distribution in an infinite medium. Numerical values of  $C_{\alpha\beta}^*$  are given by Kellermann<sup>6</sup> for NaCl.

The potential  $\Phi^C$ , given in Eq. (4.4), is due to the interaction of the electrostatic forces acting between all the elements of the particles. As the purpose of this investigation is to study the relation between the lattice theory and the corresponding continuum theory of dielectrics, it is necessary to identify those parts of  $\Phi^C$  which correspond to the Maxwell and Lorentz fields, respectively, in the long-wave approximation.

The Maxwell electrostatic field is governed by the following field equations:

$$\nabla \cdot \mathbf{E} = -\frac{\nabla \cdot \mathbf{P}}{\epsilon_0}, \quad \nabla \times \mathbf{E} = 0. \quad (4.7)$$

In order to make use of the above field equations the dipole moment due to lattice deformations is averaged over a unit cell; thus the polarization is defined as

$$\mathbf{P}(l) = \frac{q}{v_a} \sum_k [Z_k \mathbf{U}(l; k) + Y_k \mathbf{W}(l; k)]. \quad (4.8)$$

For periodic lattice waves of the form

$$\mathbf{P}(l) = \hat{\mathbf{P}} \exp i[\mathbf{y} \cdot \mathbf{X}(l) - \omega t], \quad (4.9)$$

with

$$\hat{\mathbf{P}} = \frac{q}{v_a} \sum_k [Z_k \mathbf{U}(k) + Y_k \mathbf{W}(k)] \exp i[\mathbf{y} \cdot \mathbf{X}(k)], \quad (4.10)$$

and similarly assuming a periodic electric field

$$\mathbf{E}(l) = \hat{\mathbf{E}} \exp i[\mathbf{y} \cdot \mathbf{X}(l) - \omega t]. \quad (4.11)$$

Substitution of Eqs. (4.9) and (4.11) into (4.7) yields

$$\hat{E}_\alpha = -\frac{y_\alpha y_\beta}{|\mathbf{y}|^2} \frac{\hat{P}_\beta}{\epsilon_0}. \quad (4.12)$$

Consequently, the energy per unit cell, due to the Maxwell self-field, is given by

$$\begin{aligned} \psi^{\text{MS}} &= v_a \sum_l [E_\alpha(l) P_\alpha(l) + \frac{1}{2} \epsilon_0 E_\alpha(l) E_\alpha(l)] \\ &= -\frac{1}{2} \sum_{lkk'} \frac{q^2 y_\alpha y_\beta}{v_a \epsilon_0 |\mathbf{y}|^2} [Z_k Z_{k'} U_\alpha(k) U_\beta(k') \\ &\quad + Z_k Y_{k'} U_\alpha(k) W_\beta(k') + Z_{k'} Y_k W_\alpha(k) U_\beta(k') \\ &\quad + Y_k Y_{k'} W_\alpha(k) W_\beta(k')] \\ &\quad \times (\exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t])^2. \end{aligned} \quad (4.13)$$

Comparing Eqs. (4.4) and (4.13) it is seen that  $q^2 y_\alpha y_\beta / v_a \epsilon_0 |\mathbf{y}|^2$  is included in  $C^*_{\alpha\beta}(\mathbf{y}; k, k')$ .

In order to separate the part of the potential energy due to the Maxwell self-field it is convenient to write  $C^*_{\alpha\beta}$ , following Ewald,<sup>9</sup> as

$$C^*_{\alpha\beta}(\mathbf{y}; k, k') = C_{\alpha\beta}(\mathbf{y}; k, k') - \frac{q^2}{v_a \epsilon_0} \frac{y_\alpha y_\beta}{|\mathbf{y}|^2}. \quad (4.14)$$

In the long-wave limit,  $\mathbf{y} \rightarrow 0$ , the first term of Eq. (4.14) is regular and is equal to  $C_{\alpha\beta}(0; k, k')$  given in Eq. (4.6); the second part is not regular and corresponds to the Maxwell field. Substitution of Eq. (4.14) into (4.4) yields

$$\begin{aligned} \Phi^C &= \Phi^C_0 + \Phi^C_1 - \frac{1}{2} \sum_{lkk'} \left\{ [Z_k Z_{k'} C_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Z_k Z_{k''} C_{\alpha\beta}(0; k, k'')] U_\alpha(k) U_\beta(k') \right. \\ &\quad + [Z_k Y_{k'} C_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Z_k Y_{k''} C_{\alpha\beta}(0; k, k'')] U_\alpha(k) W_\beta(k') \\ &\quad + [Y_k Z_{k'} C_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Y_k Z_{k''} C_{\alpha\beta}(0; k, k'')] W_\alpha(k) U_\beta(k') \\ &\quad + [Y_k Y_{k'} C_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Y_k Y_{k''} C_{\alpha\beta}(0; k, k'')] W_\alpha(k) W_\beta(k') \\ &\quad \left. - \frac{q^2 y_\alpha y_\beta}{v_a \epsilon_0 |\mathbf{y}|^2} [Z_{k'} U_\beta(k') + Y_{k'} W_\beta(k')] [Z_k U_\alpha(k) + Y_k W_\alpha(k)] \right\} (\exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t])^2. \end{aligned} \quad (4.15)$$

Comparing the last term of the above expression with Eq. (4.13) it is seen that this is the part of the potential energy due to the Maxwell self-field.

### 5. SHORT-RANGE INTERACTIONS

By following the definition given in Eq. (3.7), invoking the harmonic approximation as in Eqs. (2.8) to (2.12), and substituting the waveforms given in Eq. (3.1), the part of the potential energy corresponding to short-range interactions is obtained by replacing  $N_{\alpha\beta}$ ,  $T_{\alpha\beta}$ ,  $T'_{\alpha\beta}$ , and  $S_{\alpha\beta}$  by  $N^B_{\alpha\beta}$ ,  $T^B_{\alpha\beta}$ ,  $T'^B_{\alpha\beta}$ , and  $S^B_{\alpha\beta}$ . The latter are defined in accordance with (3.3) by replacing  $\Phi$  by  $\Phi^B$ .

By using the definitions

$$\begin{aligned} B^{ij}_{\alpha\beta}(\mathbf{y}; k, k') &= \sum_{l'} {}^B \Phi^{ij}_{\alpha\beta}(l-l'; k, k') \exp i[-\mathbf{y} \cdot \mathbf{X}(l-l'; k, k')], \\ B^{ij}_{\alpha\beta}(0; k, k') &= \sum_{l'} {}^B \Phi^{ij}_{\alpha\beta}(l-l'; k, k'), \quad i, j = 1, 2 \end{aligned} \quad (5.1)$$

the potential energy due the short-range interactions, similar to Eq. (4.4), can be written as

$$\begin{aligned} \Phi^B = & \Phi_0^B + \Phi_1^B - \frac{1}{2} \sum_{lk k'} \{ [B_{\alpha\beta}^{11}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} B_{\alpha\beta}^{11}(0; k, k'')] U_\alpha(k) U_\beta(k') \\ & + [B_{\alpha\beta}^{12}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} B_{\alpha\beta}^{12}(0; k, k'')] U_\alpha(k) W_\beta(k') \\ & + [B_{\alpha\beta}^{21}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} B_{\alpha\beta}^{21}(0; k, k'')] W_\alpha(k) U_\beta(k') \\ & + [B_{\alpha\beta}^{22}(\mathbf{y}; k, k') - \delta_{kk'} (K_k \delta_{\alpha\beta} + \sum_{k''} B_{\alpha\beta}^{22}(0; k, k''))] W_\alpha(k) W_\beta(k') \} \cdot (\exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t])^2. \end{aligned} \quad (5.2)$$

From Eq. (5.2), it is seen that the self-energy is included in the part of the potential energy due to the short-range interactions.

## 6. SURFACE ENERGY

The energy expression given in Eq. (3.4) and the more detailed expressions for the long- and short-range interaction energies given in Eqs. (4.15) and (5.2) apply for the case of an infinite lattice, since the summation over  $l$  is carried over the whole space. For a lattice of finite extent, the total potential energy is obtained by taking the summation on  $l$  over the finite lattice and adding to this, the change in the potential energy of the ions due to the presence of a boundary. This additional energy can be considered to be made up of two parts<sup>8</sup>: the work required to remove the part of the lattice on one side of the interface, while the rest of the lattice is held in its original equilibrium configuration, and the relaxation energy of the remaining part of the lattice due to the deformation and polarization of the lattice in going to a new equilibrium position.

Let the position of a lattice point on the surface be denoted by  $\mathbf{X}(L; K)$ , where  $L, K$  denote points on the free surface.

$$\begin{aligned} \sum_{LKlk} \frac{qZ_k}{4\pi\epsilon_0} \frac{X_\beta(l-L; k, K)}{|\mathbf{X}(l-L; k, K)|^3} & q[Z_K U_\beta(L; K) + Y_K W_\beta(L; K)] \\ & + \frac{1}{2} \sum_{LKL'K'} \left\{ \frac{q^2 [Z_K U_\alpha(L; K) + Y_K W_\alpha(L; K)] [Z_{K'} U_\alpha(L'; K') + Y_{K'} W_\alpha(L'; K')]}{4\pi\epsilon_0 |\mathbf{X}(L-L'; K, K')|^3} \right. \\ & - 3 \frac{q^2 X_\alpha(L-L'; K, K') X_\beta(L-L'; K, K')}{4\pi\epsilon_0 |\mathbf{X}(L-L'; K, K')|^5} \\ & \left. \times [Z_K U_\alpha(L; K) + Y_K W_\alpha(L; K)] [Z_{K'} U_\beta(L'; K') + Y_{K'} W_\beta(L'; K')] \right\}, \end{aligned} \quad (6.2)$$

where  $q[Z_K \mathbf{U}(L; K) + Y_K \mathbf{W}(L; K)]$  is the dipole moment of a point on the free surface. The first sum in this expression is the energy associated with interaction of the dipoles on the surface with the point charges inside while the second sum corresponds to the interaction of the dipoles on the surface with the other dipoles on the free surface. As can be seen, the term under the second summation sign in Eq. (6.2) is nonlinear in  $U_\alpha, W_\alpha$ . Neglecting this part, Eq. (6.2) becomes

$$\sum_{LKlk} \frac{q^2 Z_k}{4\pi\epsilon_0} \frac{X_\beta(l-L; k, K)}{|\mathbf{X}(l-L; k, K)|^3} [Z_K U_\beta(L; K) + Y_K W_\beta(L; K)]. \quad (6.3)$$

Introducing periodic waves, similar to those in Eq. (3.1), into Eq. (6.3), and combining them with Eq. (6.1), the additional potential energy for the finite lattice due to the presence of a surface is given as

Let  $\Phi(Ll; Kk)$  be the potential energy of interaction of a lattice point on the free surface  $\mathbf{X}(L; K)$  with an arbitrary point  $\mathbf{X}(l; k)$ , and let  $\Phi'(Ll; Kk)$  be the potential energy of interaction of a lattice point on the free surface with a point in the part of the body lying on one side of the free surface. Therefore, the part of the surface energy associated with the removal of part of the lattice, under the assumption that the ions remain immobile and unpolarized, is

$$\sum_{LKLk} [\Phi(Ll; Kk) - \Phi'(Ll; Kk)]. \quad (6.1)$$

This quantity is a constant for a given lattice and a given surface orientation.

The deformation and polarization of the lattice caused by the unbalanced forces due to the removal of the part of the lattice on the exterior side of the free surface contribute to the relaxation energy. Since the deformation is confined to a small vicinity of the free surface, only the particles on the first layer are considered to have dipole moments as well as charges, whereas the particles inside are assumed to have point charges only. Thus the relaxation energy can be written as<sup>8</sup>

$$\psi^S = \sum_{LK} \{T(L; K) + B_\beta(L; K)q[Z_K U_\beta(K) + Y_K W_\beta(K)] \cdot \exp i[\mathbf{y} \cdot \mathbf{X}(L) - \omega t]\}, \quad (6.4)$$

where

$$T(L; K) = \sum_{lk} [\Phi(Ll; Kk) - \Phi'(Ll; Kk)], \quad B_\beta(L; K) = \sum_{lk} \frac{qZ_k}{4\pi\epsilon_0} \frac{X_\beta(l; k) - X_\beta(L; K)}{|\mathbf{X}(l; k) - \mathbf{X}(L; K)|^3}. \quad (6.5)$$

The change in the total potential energy for a finite lattice is given by adding Eqs. (6.4), (4.15), and (5.2). Thus for  $\psi = \psi^B + \psi^C + \psi^S$ , one has

$$\begin{aligned} \psi = & -\frac{1}{2} \sum_{lkk'} \{ [B^{11}_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} B^{11}_{\alpha\beta}(0; k, k'') + Z_k Z_{k'} C_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Z_k Z_{k''} C_{\alpha\beta}(0; k, k'')] U_\alpha(k) U_\beta(k') \\ & + [B^{12}_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} B^{12}_{\alpha\beta}(0; k, k'') + Z_k Y_{k'} C_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Z_k Y_{k''} C_{\alpha\beta}(0; k, k'')] U_\alpha(k) W_\beta(k') \\ & + [B^{21}_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} B^{21}_{\alpha\beta}(0; k, k'') + Y_k Z_{k'} C_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \sum_{k''} Y_k Z_{k''} C_{\alpha\beta}(0; k, k'')] W_\alpha(k) U_\beta(k') \\ & + [B^{22}_{\alpha\beta}(\mathbf{y}; k, k') - \delta_{kk'} \{K_k \delta_{\alpha\beta} + \sum_{k''} B^{22}_{\alpha\beta}(0; k, k'')\} + Y_k Y_{k'} C_{\alpha\beta}(\mathbf{y}; k, k') \\ & - \delta_{kk'} \sum_{k''} Y_k Y_{k''} C_{\alpha\beta}(0; k, k'')] W_\alpha(k) W_\beta(k') \} (\exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t])^2 - \sum_l v_\alpha(\hat{E}_\alpha \hat{P}_\alpha + \frac{1}{2} \epsilon_0 \hat{E}_\alpha \hat{E}_\alpha) \\ & \times (\exp i[\mathbf{y} \cdot \mathbf{X}(l; k) - \omega t])^2 + \sum_{LK} \{T(L; K) + B_\beta(L; K)q[Z_K U_\beta(K) + Y_K W_\beta(K)] \exp i[\mathbf{y} \cdot \mathbf{X}(L; K) - \omega t]\}. \quad (6.6) \end{aligned}$$

### 7. ALKALI HALIDES

In this section the energy expression formulated in the previous section is applied to alkali halides, that is diatomic lattices, and expressions for the material coefficients are obtained by using the one-ion-polarizable model,<sup>5</sup> considering the short-range interactions of the first- and second-nearest neighbors as well as the interaction of the core with its own shell, which is an extension of Kellermann's work<sup>6</sup> where only the nearest-neighbor interactions are considered, and invoking the long-wave approximation. The numerical values of the material coefficients for NaCl, NaI, KCl, and KI, are calculated in Sec. 10.

Since the polarizability of the negative ion of an alkali halide is usually an order of magnitude greater than the polarizability of the positive ion, it is reasonable to neglect the polarizability of the positive ion. This simplified model is called the one-ion-polarizable model.<sup>5</sup>

The potential energy for alkali halides is obtained from Eq. (5.3), by specializing it for a diatomic lattice and letting  $k=1$  denote the positive ion,  $k=2$  the negative ion, and setting  $Y_1=0$  and  $\mathbf{W}(1)=0$ , for the one-ion-polarizable model.

As in Dick and Overhauser,<sup>4</sup> assuming that the short range forces between the ions act only through their shells, one has, similar to Eq. (2.5),

$$\Phi^B = \frac{1}{2} \sum'_{lkl'k'} \Phi^B_{S}(r_{il}) + \sum_{lk} \frac{1}{2} K_k W_\alpha(l; k) W_\alpha(l; k). \quad (7.1)$$

Considering Eqs. (2.9) and (5.1), one can define

$$\begin{aligned} B_{\alpha\beta}(\mathbf{y}; k, k') & \equiv B^{11}_{\alpha\beta}(\mathbf{y}; k, k') = B^{12}_{\alpha\beta}(\mathbf{y}; k, k') \\ & = B^{21}_{\alpha\beta}(\mathbf{y}; k, k') = B^{22}_{\alpha\beta}(\mathbf{y}; k, k'). \quad (7.2) \end{aligned}$$

Under the above specifications, by performing the summations over  $k, k'$ , the energy expression Eq. (6.6) assumes the following form:

$$\begin{aligned} \psi = & -\frac{1}{2} \sum_l \{ (B_{\alpha\beta}(\mathbf{y}; 1, 1) - B_{\alpha\beta}(0; 1, 1) - B_{\alpha\beta}(0; 1, 2) + Z_1 Z_1 [C_{\alpha\beta}(\mathbf{y}; 1, 1) - C_{\alpha\beta}(0; 1, 1) + C_{\alpha\beta}(0; 1, 2)]) U_\alpha(1) U_\beta(1) \\ & + (B_{\alpha\beta}(\mathbf{y}; 1, 2) + Z_1 Z_2 C_{\alpha\beta}(\mathbf{y}; 1, 2)) U_\alpha(1) U_\beta(2) \\ & + (B_{\alpha\beta}(\mathbf{y}; 1, 2) + Z_1 Y_2 C_{\alpha\beta}(\mathbf{y}; 1, 2)) U_\alpha(1) W_\beta(2) \} (\exp i[\mathbf{y} \cdot \mathbf{X}(l; 1) - \omega t])^2 \\ & + \{ (B_{\alpha\beta}(\mathbf{y}; 2, 1) + Z_2 Z_1 C_{\alpha\beta}(\mathbf{y}; 2, 1)) U_\alpha(2) U_\beta(1) \\ & + (B_{\alpha\beta}(\mathbf{y}; 2, 2) - B_{\alpha\beta}(0; 2, 2) - B_{\alpha\beta}(0; 2, 1) + Z_2 Z_2 [C_{\alpha\beta}(\mathbf{y}; 2, 2) - C_{\alpha\beta}(0; 2, 2) + C_{\alpha\beta}(0; 2, 1)]) U_\alpha(2) U_\beta(2) \\ & + (B_{\alpha\beta}(\mathbf{y}; 2, 2) - B_{\alpha\beta}(0; 2, 2) - B_{\alpha\beta}(0; 2, 1) + Z_2 Y_2 [C_{\alpha\beta}(\mathbf{y}; 2, 2) - C_{\alpha\beta}(0; 2, 2)]) U_\alpha(2) W_\beta(2) \\ & + (B_{\alpha\beta}(\mathbf{y}; 2, 1) + Y_2 Z_1 C_{\alpha\beta}(\mathbf{y}; 2, 1)) W_\alpha(2) U_\beta(1) \\ & + (B_{\alpha\beta}(\mathbf{y}; 2, 2) - B_{\alpha\beta}(0; 2, 2) - B_{\alpha\beta}(0; 2, 1) + Y_2 Z_2 [C_{\alpha\beta}(\mathbf{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}(\mathbf{y}; 2, 2) - B_{\alpha\beta}(0; 2, 2) - B_{\alpha\beta}(0; 2, 1) + Y_2 Y_2 [C_{\alpha\beta}(\mathbf{y}; 2, 2) - C_{\alpha\beta}(0; 2, 2)]) W_\alpha(2) W_\beta(2) \} \\ & \times (\exp i[\mathbf{y} \cdot \mathbf{X}(l; 2) - \omega t])^2 - \sum_l v_\alpha(\hat{E}_\alpha \hat{P}_\alpha + \frac{1}{2} \epsilon_0 \hat{E}_\alpha \hat{E}_\alpha) (\exp i[\mathbf{y} \cdot \mathbf{X}(l) - \omega t])^2 \\ & + \sum_L \{T(L; 1) + T(L; 2) + B_\beta(L; 1)qZ_1 U_\beta(1) \exp i[\mathbf{y} \cdot \mathbf{X}(L; 1) - \omega t] \\ & + B_\beta(L; 2)q[Z_2 U_\beta(2) + Y_2 W_\beta(2)] \exp i[\mathbf{y} \cdot \mathbf{X}(L; 2) - \omega t]\}. \quad (7.3) \end{aligned}$$

For cubic symmetry,

$$\begin{aligned} B_{\alpha\beta}(\mathbf{y}; 1,1) &= B_{\alpha\beta}(\mathbf{y}; 2,2), & B_{\alpha\beta}(\mathbf{y}; 1,2) &= B_{\alpha\beta}(\mathbf{y}; 2,1), \\ C_{\alpha\beta}(\mathbf{y}; 1,1) &= C_{\alpha\beta}(\mathbf{y}; 2,2), & C_{\alpha\beta}(\mathbf{y}; 1,2) &= C_{\alpha\beta}(\mathbf{y}; 2,1), \\ T(L; 1) &= T(L; 2) = T(L), & B_{\beta}(L; 1) &= B_{\beta}(L; 2) = B_{\beta}(L). \end{aligned} \quad (7.4)$$

The relation  $B_{\alpha\beta}(\mathbf{y}; 1,1) = B_{\alpha\beta}(\mathbf{y}; 2,2)$  is essentially an assumption which states the equality of the repulsion forces between the second neighbors, positive-positive, and negative-negative ions. The other equalities are seen to be exact by considering their definitions. Furthermore, for the short-range interactions being confined to the first and second neighbors, by performing the summations according to Eqs. (2.9), (5.1), and (7.2):

$$\begin{aligned} B_{\alpha'\alpha'}(\mathbf{y}; 1,1) &= (A_2 + B_2) [\cos(y_\alpha + y_\beta)r_0 + \cos(y_\alpha - y_\beta)r_0 + \cos(y_\alpha + y_\gamma)r_0 + \cos(y_\alpha - y_\gamma)r_0] \\ &\quad + 2B_2 [\cos(y_\beta + y_\gamma)r_0 + \cos(y_\beta - y_\gamma)r_0], \\ B_{\alpha'\alpha'}(\mathbf{y}; 1,2) &= 2[A_1 \cos y_\alpha r_0 + B_1 (\cos y_\beta r_0 + \cos y_\gamma r_0)], \\ B_{\alpha\beta}(\mathbf{y}; 1,1) &= (A_2 - B_2) [\cos(y_\alpha + y_\beta)r_0 - \cos(y_\alpha - y_\beta)r_0], \quad \alpha \neq \beta \\ B_{\alpha\beta}(\mathbf{y}; 1,2) &= 0, \quad \alpha \neq \beta \end{aligned} \quad (7.5)$$

where the primes above the Greek subscripts suspend the summation over the repeated indices,  $\alpha, \beta, \gamma$  represent the three orthogonal directions of the cubic lattice,  $r_0$  is the distance between the nearest neighbors and  $A_1, B_1, A_2, B_2$  are related to the derivatives of the short-range interaction potential between the first and second neighbors:

$$\begin{aligned} A_1 &= \left. \frac{d^2 \Phi^B_s(l-l'; 1,2)}{dr^2} \right|_{\mathbf{u}=\mathbf{w}=0}, & A_2 &= \left. \frac{d^2 \Phi^B_s(l-l'; 1,1)}{dr^2} \right|_{\mathbf{u}=\mathbf{w}=0}, \\ B_1 &= \left. \frac{d \Phi^B_s(l-l'; 1,2)}{r dr} \right|_{\mathbf{u}=\mathbf{w}=0}, & B_2 &= \left. \frac{d \Phi^B_s(l-l'; 1,1)}{r dr} \right|_{\mathbf{u}=\mathbf{w}=0}. \end{aligned} \quad (7.6)$$

## 8. LONG-WAVE APPROXIMATION

Going to the long-wave limit, in order to obtain the corresponding continuum theory, one has to define a potential-energy density as an average energy representative of the medium. For this purpose consider that the medium is divided into cubic cells with sides  $2r_0$  and centered around a particle. One can thus find the total energy of the medium as the sum of the energies of these cubical elements. One sees that the ions on the faces of the cube belong to two cubes, those on the edges belong to four cubes and those at the corners belong to eight cubes. Thus the energy of a cubical element can be found by weighting by  $1, \frac{1}{2}, \frac{1}{4}, \frac{1}{8}$  the energies of the ions at the center, on the faces, on the edges and at the corners. This method has actually been used by Evjen to evaluate the Madelung constant for a distribution of charged particles.<sup>7</sup>

The expansion of the functions of  $\mathbf{y}$  about  $\mathbf{y}=0$  are taken only up to the terms which retain  $\mathbf{W}$  and the first gradients of  $\mathbf{U}, \mathbf{W}$ .

For long acoustic waves the displacement amplitudes are taken as

$$\mathbf{U}(1) = \mathbf{U}(2) = \mathbf{u}, \quad \mathbf{W}(2) = \mathbf{w}. \quad (8.1)$$

Considering the definition of the polarization Eq. (4.10), one has

$$\hat{\mathbf{P}} = \frac{q}{v_a} [Z_1 \mathbf{u} e^{i\mathbf{y} \cdot \mathbf{x}(1)} + (Z_2 \mathbf{u} + Y_2 \mathbf{w}) e^{i\mathbf{y} \cdot \mathbf{x}(2)}] \simeq \frac{Y_2 q \mathbf{w}}{v_a}. \quad (8.2)$$

In obtaining Eq. (8.2), only the first terms in the expansions of  $e^{i\mathbf{y} \cdot \mathbf{x}(k)}$  are retained and the fact that  $Z_1 + Z_2 = 0$  is used.

In the resulting expression for the change in the potential energy, which can be obtained by using Eq. (7.4) and by substituting Eqs. (8.1) and (8.2) into Eq. (7.3), the summation over  $l$ , will be evaluated by considering that the medium is divided into cubes of sides  $2r_0$ . Let the origin of the coordinate system be  $X(l; 1)$ . Thus the centers of the cubes correspond to even values of  $l_1, l_2, l_3$  and are all occupied by positive ions. Consequently, the summation over  $l$  can be written in the following equivalent form:

$$\begin{aligned} &\sum_l \{\Phi(l; 1) + \Phi(l; 2)\} \\ &= \sum_{l(\text{even})} \{\Phi(l; 1) + \frac{1}{2} \sum_{m_1=1}^6 \Phi(l+m_1; 2) \\ &\quad + \frac{1}{4} \sum_{m_2=7}^{18} \Phi(l+m_2; 1) + \frac{1}{8} \sum_{m_3=19}^{26} \Phi(l+m_3; 2)\}. \end{aligned} \quad (8.3)$$

In the above representation  $\Phi(l; 1)$  denotes the energy of the ion at  $X(l; 1)$  and  $\Phi(l+m_1; 2), \Phi(l+m_2; 2), \Phi(l+m_3; 2)$  are the energies of the ions that are first, second, and third neighbors to that at  $\mathbf{X}(l; 1)$ . The summations over  $m_1, m_2, m_3$  are to be carried over the 6 first, 12 second, and 8 third neighbors. In this summation, the values of the functions at  $X(l+m; k)$  are to be expressed by the Taylor-series expansions about the point  $X(l; 1)$ .

For the summation over  $L$ , the values of the functions



are similarly represented by their expansions about  $\mathbf{X}(L; 1)$ . By performing the above described expansions and summations, one has

$$\begin{aligned} \psi = & - \sum_{l(\text{even})} \{4(B_{\alpha\beta}(\mathbf{y}; 1,1) + B_{\alpha\beta}(\mathbf{y}; 1,2) - B_{\alpha\beta}(0; 1,1) - B_{\alpha\beta}(0; 1,2)) \\ & + Z_1^2 [C_{\alpha\beta}(\mathbf{y}; 1,1) - C_{\alpha\beta}(\mathbf{y}; 1,2) - C_{\alpha\beta}(0; 1,1) + C_{\alpha\beta}(0; 1,2)](1 + 0(\mathbf{y}^2))u_{\alpha}u_{\beta} \\ & + 4(B_{\alpha\beta}(\mathbf{y}; 1,1) + B_{\alpha\beta}(\mathbf{y}; 1,2) - B_{\alpha\beta}(0; 1,1) - B_{\alpha\beta}(0; 1,2)) \\ & - Z_1 Y_2 [C_{\alpha\beta}(\mathbf{y}; 1,1) - C_{\alpha\beta}(\mathbf{y}; 1,2) - C_{\alpha\beta}(0; 1,1) + C_{\alpha\beta}(0; 1,2)](1 + 0(\mathbf{y}^2))(v_a/Y_2 q)u_{\alpha}\hat{P}_{\beta} \\ & + 2(-K_2\delta_{\alpha\beta} - B_{\alpha\beta}(0; 2,1) + B_{\alpha\beta}(\mathbf{y}; 2,2) - B_{\alpha\beta}(0; 2,2)) \\ & + Y_2 Y_2 [C_{\alpha\beta}(\mathbf{y}; 2,2) - C_{\alpha\beta}(0; 2,2)](1 + \frac{1}{2}r_0^2\delta_{\gamma\delta}y_{\gamma}y_{\delta} + 0(\mathbf{y}^4))(v_a^2/Y_2^2 q^2)\hat{P}_{\alpha}\hat{P}_{\beta} \} \\ & \times (\exp i[\mathbf{y} \cdot \mathbf{X}(l) - \omega l])^2 - \sum_{l(\text{all})} v_a(\hat{E}_{\alpha}\hat{P}_{\alpha} + \frac{1}{2}\epsilon_0\hat{E}_{\alpha}\hat{P}_{\alpha})(\exp i[\mathbf{y} \cdot \mathbf{X}(l) - \omega l])^2 \\ & + \sum_L \{2T(L) + B_{\beta}(L)[v_a\hat{P}_{\beta}(1 + 0(\mathbf{y})) + qZ_1 u_{\beta}(0(\mathbf{y}))]\} \exp i[\mathbf{y} \cdot \mathbf{X}(L) - \omega l] \}. \end{aligned} \quad (8.4)$$

As a last step towards obtaining the continuum representation of the energy, consider the Taylor-series expansions of the coefficients  $B_{\alpha\beta}(\mathbf{y}; k, k')$  and  $C_{\alpha\beta}(\mathbf{y}; k, k')$  about  $\mathbf{y} = 0$ .

For the groups of the coefficients  $B_{\alpha\beta}(\mathbf{y}; k, k')$  of the short-range forces in Eq. (8.4), by considering the expressions obtained on the basis of first- and second-neighbor interactions, one has

$$\begin{aligned} B_{\alpha\beta}(\mathbf{y}; 1,1) + B_{\alpha\beta}(\mathbf{y}; 1,2) - B_{\alpha\beta}(0; 1,1) - B_{\alpha\beta}(0; 1,2) &= -B_{\gamma\alpha\delta\beta}y_{\gamma}y_{\delta} + O(\mathbf{y}^4), \\ B_{\alpha\beta}(\mathbf{y}; 2,2) - B(0; 2,2) &= -B'_{\gamma\alpha\delta\beta}y_{\gamma}y_{\delta} + O(\mathbf{y}^4), \\ B_{\alpha\beta}(0; 2,1) &= B_{\alpha\beta}, \end{aligned} \quad (8.5)$$

where, by considering Eq. (7.5), the independent coefficients are

$$\begin{aligned} B_{\alpha'\alpha'\alpha'\alpha'} &= [A_1 + 2(A_2 + B_2)]r_0^2, & B'_{\alpha'\alpha'\alpha'\alpha'} &= 2(A_2 + B_2)r_0^2, \\ B_{\alpha'\alpha'\beta'\beta'} &= (A_2 - B_2)r_0^2 = B_{\beta'\alpha'\alpha'\beta'}, & B'_{\alpha'\alpha'\beta'\beta'} &= (A_2 - B_2)r_0^2 = B'_{\beta'\alpha'\alpha'\beta'}, \\ B_{\gamma'\alpha'\gamma'\alpha'} &= (B_1 + A_2 + 3B_2)r_0^2, & B'_{\gamma'\alpha'\gamma'\alpha'} &= (A_2 + 3B_2)r_0^2, \\ B_{\alpha'\alpha'} &= 2(A_1 + 2B_1). \end{aligned} \quad (8.6)$$

Similarly,

$$\begin{aligned} C_{\alpha\beta}(\mathbf{y}; 1,1) - C_{\alpha\beta}(\mathbf{y}; 1,2) - C_{\alpha\beta}(0; 1,1) + C_{\alpha\beta}(0; 1,2) &= -C_{\gamma\alpha\delta\beta}y_{\gamma}y_{\delta} + O(\mathbf{y}^4), \\ C_{\alpha\beta}(\mathbf{y}; 2,2) - C_{\alpha\beta}(0; 2,2) &= 0. \end{aligned} \quad (8.7)$$

In the last expression of Eq. (8.7), even though the function is bounded at  $\mathbf{y} = 0$ , its expansion is not permitted, since it is not convergent. The numerical values of  $C_{\gamma\alpha\delta\beta}$  have been calculated by Kellermann<sup>6</sup> for the NaCl structure. For the independent coefficients he finds<sup>10</sup>

$$\begin{aligned} C_{\alpha'\alpha'\alpha'\alpha'} &= -1.28q^2/4\pi\epsilon_0 r_0 = C_1 r_0^2, \\ C_{\alpha'\alpha'\beta'\beta'} &= 0.35q^2/4\pi\epsilon_0 r_0 = C_{\beta'\alpha'\alpha'\beta'} = C_2 r_0^2, \\ C_{\gamma'\alpha'\gamma'\alpha'} &= 0.64q^2/4\pi\epsilon_0 r_0 = C_3 r_0^2. \end{aligned} \quad (8.8)$$

By using the expansions, Eqs. (8.5) and (8.7), in Eq. (8.4), and replacing  $u_{\alpha}u_{\beta}y_{\gamma}y_{\delta}(\exp i[\mathbf{y} \cdot \mathbf{X}(l) - \omega l])^2$  by  $u_{\alpha,\gamma}u_{\beta,\delta}$ ,  $\hat{P}_{\alpha}(\exp i[\mathbf{y} \cdot \mathbf{X}(L) - \omega l])$  by  $P_{\alpha}(x)$  etc., and replacing the summations over  $l$  and  $L$  by integrations over the volume and the bounding surface, one obtains

$$\begin{aligned} \psi = & \int_V \left( \frac{B_{\gamma\alpha\delta\beta} + Z_1^2 C_{\gamma\alpha\delta\beta}}{v_a} u_{\alpha,\gamma} u_{\beta,\delta} + \frac{B_{\gamma\alpha\delta\beta} - Z_1 Y_2 C_{\gamma\alpha\delta\beta}}{Y_2 q} u_{\alpha,\gamma} P_{\beta,\delta} + \frac{1}{2}(K_2\delta_{\alpha\beta} + B_{\alpha\beta}) \frac{v_a}{Y_2^2 q^2} P_{\alpha} P_{\beta} \right. \\ & \left. + \frac{1}{4}[(K_2\delta_{\alpha\beta} + B_{\alpha\beta})r_0^2\delta_{\gamma\delta} + B'_{\gamma\alpha\delta\beta}] \frac{v_a}{Y_2^2 q^2} P_{\alpha,\gamma} P_{\beta,\delta} \right) dV - \int_V (E_{\alpha} P_{\alpha} + \frac{1}{2}\epsilon_0 E_{\alpha} E_{\alpha}) dV + \int_S (T_0 + b^0_{\alpha\beta} P_{\beta} n_{\alpha}) dA, \end{aligned} \quad (8.9)$$

<sup>10</sup> Note that Kellermann's definition of the coefficients with mixed indices are switched here. The same comment holds for his  $C_{12}$  and  $C_{44}$ .

where

$$\begin{aligned} T_0 &= 2T(L)/A_a, \\ b^0_{\alpha\beta} &= v_a B_\beta(L) n_\alpha(L)/A_a. \end{aligned} \quad (8.10)$$

$A_a = 2r_0^2$  denotes the area of a cell on the boundary and  $n_\alpha(L) \equiv n_\alpha(L; 1) \equiv n_\alpha(L; 2)$  is the unit normal to the  $L$ th cell on the boundary in the continuum limit. The invariance of the energy under rigid-body rotations eliminates the antisymmetric part of the displacement gradient. Furthermore, by converting the surface integral over  $b^0_{\alpha\beta} P_\beta n_\alpha$  to a volume integral, Eq. (8.9) can be written as

$$\begin{aligned} \psi &= \psi_0 + \int_V (b^0_{\alpha\beta} P_{\beta,\alpha} + \frac{1}{2} a_{\alpha\beta} P_\alpha P_\beta \\ &\quad + \frac{1}{2} b_{\gamma\alpha\delta\beta} P_{\alpha,\gamma} P_{\beta,\delta} + \frac{1}{2} c_{\gamma\alpha\delta\beta} S_{\alpha\gamma} S_{\beta\delta} \\ &\quad + d_{\gamma\alpha\delta\beta} P_{\alpha,\gamma} S_{\beta\delta} - E_\alpha P_\alpha - \frac{1}{2} \epsilon_0 E_\alpha E_\alpha) dV, \end{aligned} \quad (8.11)$$

where

$$\psi_0 = \int_S T_0 dA \quad (8.12)$$

and

$$\begin{aligned} S_{\alpha\gamma} &= \frac{1}{2}(u_{\alpha,\gamma} + u_{\gamma,\alpha}), \\ b^0_{\alpha\beta} &= \frac{r_0 q}{4\pi\epsilon_0} \sum_{(l,k)} Z_k \frac{X_\beta(l;k) - X_\beta(L;2)}{|\mathbf{X}(l;k) - \mathbf{X}(L;2)|^3} n_\alpha(L), \\ &\quad (l,k) \text{ over the half space,} \\ a_{\alpha\beta} &= 2(K_2 \delta_{\alpha\beta} + B_{\alpha\beta}) \frac{r_0^3}{Y_2^2 q^2}, \\ b_{\gamma\alpha\delta\beta} &= [(K_2 \delta_{\alpha\beta} + B_{\alpha\beta}) r_0^2 \delta_{\gamma\delta} + B'_{\gamma\alpha\delta\beta}] \frac{r_0^3}{Y_2^2 q^2}, \\ c_{\gamma\alpha\delta\beta} &= \frac{B_{\gamma\alpha\delta\beta} + Z_1^2 C_{\gamma\alpha\delta\beta}}{r_0^3}, \\ d_{\gamma\alpha\delta\beta} &= \frac{B_{\gamma\alpha\delta\beta} - Z_1 V_2 C_{\gamma\alpha\delta\beta}}{Y_2 q}. \end{aligned} \quad (8.13)$$

$\psi_0$  is the part of the surface energy, which depends on the bounding surface and the particular lattice under consideration, but not on the deformation and polarization. Therefore,  $\psi_0$  is present even at the initial state, that is when all the field variables are zero, in the bounded dielectric. Therefore, the difference in energy with respect to the initial state is

$$\psi - \psi_0 = \int_V H dV, \quad (8.14)$$

where  $H$  is the total potential-energy density with respect to the initial state

$$H = W(S_{\alpha\gamma}, P_\alpha, P_{\alpha,\gamma}) - \frac{1}{2} \epsilon_0 E_\alpha E_\alpha - E_\alpha P_\alpha, \quad (8.15)$$

and  $W$  is the energy density associated with deformation and polarization

$$\begin{aligned} W &= b^0_{\alpha\beta} P_{\beta,\alpha} + \frac{1}{2} a_{\alpha\beta} P_\alpha P_\beta + \frac{1}{2} b_{\gamma\alpha\delta\beta} P_{\alpha,\gamma} P_{\beta,\delta} \\ &\quad + \frac{1}{2} c_{\gamma\alpha\delta\beta} S_{\alpha\gamma} S_{\beta\delta} + d_{\gamma\alpha\delta\beta} P_{\alpha,\gamma} S_{\beta\delta}. \end{aligned} \quad (8.16)$$

Comparison of Eqs. (8.15) and (8.16) with Eqs. (2.2), (2.6), and (3.1) of Mindlin (Ref. 3) shows that they have the same form for centrosymmetric cubic crystals.

## 9. CONTINUUM THEORY OF ELASTIC DIELECTRICS

In this section, the procedure used by Mindlin<sup>3</sup> to obtain the linear field equations for elastic dielectrics is briefly outlined.

In a body occupying a volume  $V$  bounded by a surface  $S$ , the total potential energy is given as

$$\psi = \int_V H dV + \int_S T_0 dA, \quad (9.1)$$

where

$$H = W(S_{\alpha\gamma}, P_\alpha, P_{\alpha,\gamma}) - (\frac{1}{2} \epsilon_0 E_\alpha E_\alpha + E_\alpha P_\alpha). \quad (9.2)$$

$T_0$  is a constant surface energy in the absence of all fields,  $S_{\alpha\beta} = \frac{1}{2}(u_{\alpha,\gamma} + u_{\gamma,\alpha})$  is the linear strain, and  $u_\alpha$ ,  $P_\alpha$ , and  $E_\alpha$  are the displacement, the polarization, and the electrostatic field, respectively.

Introducing the electrostatic potential  $\phi$  as  $E_\alpha = -\phi_{,\alpha}$ , the field equations and the boundary conditions are obtained for arbitrary variations  $\delta u_\alpha$ ,  $\delta P_\alpha$ , and  $\delta\phi$  from the following variational equation:

$$\begin{aligned} \delta \int_{t_0}^{t_1} dt \int_V (\frac{1}{2} \rho \dot{u}_\alpha \dot{u}_\alpha - H) dV + \int_{t_0}^{t_1} dt \\ \times \left[ \int_V (f_\alpha \delta u_\alpha + E^0_\alpha \delta P_\alpha) dV + \int_S t_\alpha \delta u_\alpha dA \right] = 0, \end{aligned} \quad (9.3)$$

where  $f_\alpha$ ,  $E^0_\alpha$ , and  $t_\alpha$  are the external body force, external electric field, and the surface traction.

The variational equation gives the following field equations, in  $V$ :

$$\begin{aligned} T_{\gamma\alpha,\gamma} + f_\alpha &= \rho \dot{u}_\alpha, \\ E_{\gamma\alpha,\gamma} + \bar{E}_\alpha - \phi_{,\alpha} + E^0_\alpha &= 0, \\ -\epsilon_0 \phi_{,\alpha\alpha} + P_{\alpha,\alpha} &= 0, \end{aligned} \quad (9.4)$$

and the boundary conditions, on  $S$ ,

$$\begin{aligned} n_\gamma T_{\gamma\alpha} &= t_\alpha, \\ n_\gamma E_{\gamma\alpha} &= 0, \\ n_\alpha (-\epsilon_0 \llbracket \phi_\alpha \rrbracket + P_\alpha) &= 0, \end{aligned} \quad (9.5)$$

where  $\llbracket \phi_\alpha \rrbracket$  is the jump in  $\phi_\alpha$  across the surface and

$$T_{\beta\alpha} = T_{\alpha\beta} = \frac{\partial W}{\partial S_{\alpha\beta}}, \quad E_{\alpha\beta} = \frac{\partial W}{\partial P_{\beta,\alpha}}, \quad \bar{E}_\alpha = -\frac{\partial W}{\partial P_\alpha}. \quad (9.6)$$

TABLE I. Lattice parameters and the elastic constants.

	$r_0^a$ $10^{-8}$ cm	$\alpha_2^b$ $10^{-24}$ cm <sup>3</sup>	$c_{11}$	$c_{12}$ $10^{12}$ dyn/cm <sup>2c</sup>	$c_{44}$	$K_2$ $10^6$ dyn/cm	$A_1$	$A_2$ $10^8$ dyn/cm	$B_1$	$B_2$
NaI	3.23	7.10	0.359 <sup>d</sup> 0.359	0.075 <sup>d</sup> 0.071	0.077 <sup>d</sup> 0.072	12.5	21.01 20.35	-0.10 ...	-1.37 -2.06	-0.23 ...
NaCl	2.81	3.66	0.486 0.486	0.127 0.129	0.128 0.129	24.3	27.14 27.10	-0.07 ...	-3.03 -3.03	0.00 ...
KI	3.53	7.10	0.270 0.270	0.043 0.053	0.042 0.052	12.5	17.32 16.24	+0.11 ...	-2.82 -1.58	+0.44 ...
KCl	3.14	3.66	0.400 0.400	0.062 0.083	0.062 0.083	24.3	20.23 22.09	+0.14 ...	-4.40 -2.18	+0.79 ...

<sup>a</sup> Reference 9, p. 26.

<sup>b</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), p. 165.

<sup>c</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), p. 93.

<sup>d</sup> NaI values from Table III, p. 988, Ref. 5.

For cubic symmetry, the second- and fourth-rank tensors are of the following form<sup>11</sup>:

$$A_{\alpha\beta} = A\delta_{\alpha\beta},$$

$$A_{\gamma\alpha\delta\beta} = (A_{11} - A_{12} - 2A_{44})\delta_{\gamma\alpha\delta\beta} + A_{12}\delta_{\alpha\gamma}\delta_{\beta\delta} + A_{44}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) + A_{77}(\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma}), \quad (9.7)$$

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

Using the symmetry conditions (9.7), the energy density of deformation and polarization  $W$  becomes

$$W = b^0 P_{\alpha,\alpha} + \frac{1}{2} a P_{\alpha} P_{\alpha} + \frac{1}{2} [(b_{11} - b_{12} - 2b_{44})\delta_{\gamma\alpha\delta\beta} P_{\alpha,\gamma} P_{\beta,\delta} + b_{12} P_{\alpha,\alpha} P_{\beta,\beta} + \frac{1}{2} b_{44} (P_{\alpha,\beta} + P_{\beta,\alpha})(P_{\alpha,\beta} + P_{\beta,\alpha}) + \frac{1}{2} b_{77} (P_{\alpha,\beta} - P_{\beta,\alpha})(P_{\alpha,\beta} - P_{\beta,\alpha}) + \frac{1}{2} [(c_{11} - c_{12} - 2c_{44})\delta_{\gamma\alpha\delta\beta} S_{\alpha\gamma} S_{\beta\delta} + c_{12} S_{\alpha\alpha} S_{\beta\beta} + 2c_{44} S_{\alpha\beta} S_{\alpha\beta}] + [(d_{11} - d_{12} - 2d_{44})\delta_{\gamma\alpha\delta\beta} P_{\alpha,\gamma} S_{\beta\delta} + d_{12} P_{\alpha,\alpha} S_{\beta\beta} + d_{44} (P_{\alpha,\beta} + P_{\beta,\alpha}) S_{\alpha\beta}]. \quad (9.8)$$

The surface energy of the system is defined as the total energy the system has in the absence of all external forces and fields. By applying the chain rule, the divergence theorem, and using the equilibrium equations and the boundary conditions, one obtains

$$\psi = \int_V H dV + \int_S T_0 dA = \int_S (T_0 + \frac{1}{2} b^0_{\alpha\beta} P_{\beta} n_{\alpha}) dA. \quad (9.9)$$

Thus the surface energy density (energy per unit area) is defined as

$$S = T_0 + \frac{1}{2} [b^0_{\alpha\beta} P_{\beta} n_{\alpha}]_S, \quad (9.10)$$

where  $T_0$  and  $b^0_{\alpha\beta}$  depend on the orientation of the boundary surface.

## 10. NUMERICAL VALUES OF MATERIAL COEFFICIENTS

The numerical value of the surface parameter  $b^0_{\alpha\beta}$ , which is  $b^0\delta_{\alpha\beta}$  in this case, is obtained by evaluating the

<sup>11</sup> W. P. Mason, *Crystal Physics of Interaction Processes* (Academic Press Inc., New York, 1966).

second of Eqs. (8.13) for the surface (1,0,0) as

$$b^0 = -0.282(q/4\pi\epsilon_0 r_0). \quad (10.1)$$

The value of the other surface parameter  $T_0$  in Eq. (8.10) is taken from Benson,<sup>8</sup> who has evaluated the sum given in Eq. (6.5) for both the (1,0,0) and (1,1,0) surfaces.

The rest of the material coefficients are obtained by considering Eqs. (8.6) through (8.7) and (8.13) with Eqs. (9.7):

$$a = 2[K_2 + 2(A_1 + 2B_1)]r_0^3(Y_2q)^{-2},$$

$$b_{11} = [K_2 + 2(A_1 + 2B_1) + 2(A_2 + B_2)]r_0^5(Y_2q)^{-2},$$

$$b_{12} = (A_2 - B_2)r_0^5(Y_2q)^{-2},$$

$$b_{44} = \frac{1}{2}[K_2 + 2(A_1 + 2B_1) + 2(A_2 + B_2)]r_0^5(Y_2q)^{-2},$$

$$b_{77} = \frac{1}{2}[K_2 + 2(A_1 + 2B_1) + 4B_2]r_0^5(Y_2q)^{-2},$$

$$c_{11} = [A_1 + 2(A_2 + B_2) + C_1]r_0^{-1}, \quad (10.2)$$

$$c_{12} = (A_2 - B_2 + C_2)r_0^{-1},$$

$$c_{44} = \frac{1}{2}(B_1 + A_2 + B_2 + C_2 + C_3)r_0^{-1},$$

$$d_{11} = [A_1 + 2(A_2 + B_2) - Z_1 Y_2 C_1]r_0^2(Y_2q)^{-1},$$

$$d_{12} = [A_2 - B_2 - Z_1 Y_2 C_2]r_0^2(Y_2q)^{-1},$$

$$d_{44} = \frac{1}{2}[B_1 + 2(A_2 + B_2) - Z_1 Y_2 (C_2 + C_3)]r_0^2(Y_2q)^{-1},$$

where  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$  can be evaluated by using the minimum property of the potential energy at equilibrium and matching the experimental values of the elastic constants  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$  with their corresponding theoretical expressions. The Cauchy conditions still hold for the shell model due to the central nature of the interaction. The other fundamental coefficient  $K_2$  is related to the polarizability  $\alpha_2$  of the negative ion through Eq. (2.7). The experimental values used in these computations as well as the calculated values of  $K_2$ ,  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$  for NaI, NaCl, KI, and KCl are given in Table I. Of the two sets of values for  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$ , the upper row corresponds to the values obtained by matching  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ , whereas those of the lower row are computed by restricting the short-range interactions to the first neighbors only, i.e., for  $A_2 = B_2 = 0$ , and matching  $c_{11}$ . In both cases the minimum property of the energy is used. The other constants appearing in the equations for the material

TABLE II. Material coefficients.

	$a$ ( $10^{19}$ ) dyn cm <sup>2</sup> /C <sup>2</sup>	$-b^0$ ( $10^7$ ) dyn cm/C	$b_{11}$	$b_{12}$ $10^4$ dyn cm <sup>4</sup> /C <sup>2</sup>	$b_{44}$	$b_{77}$	$d_{11}$	$d_{12}$ $10^7$ dyn cm/C	$d_{44}$
NaI	1.37	1.26	0.712	$7 \times 10^{-7}$ ...	0.356	0.356	3.81	-1.51 -1.50	-2.10 -2.09
NaCl	1.74	1.44	0.688	$-2 \times 10^{-7}$ ...	0.344	0.344	4.67	-1.80 -1.80	-2.44 -2.44
KI	1.76	1.15	1.110	$-31 \times 10^{-7}$ ...	0.555	0.555	3.42	-1.42 -1.47	-1.93 -1.95
KCl	2.43	1.29	1.200	$-32 \times 10^{-7}$ ...	0.600	0.600	3.92	-1.55 -1.60	-2.12 -2.18

coefficients are

$$Y_2 = -7, \quad Z_1 = +1, \quad q = 1.6 \times 10^{-19} \text{ C}, \quad (10.3)$$

$$1/4\pi\epsilon_0 = 9 \times 10^{18} \text{ dyn cm}^2/\text{C}^2.$$

Of the material coefficients appearing in the energy of deformation and polarization, Eq. (9.8),  $a$ ,  $b_{\alpha\beta}$ ,  $d_{\alpha\beta}$  (and  $c_{12}$ ,  $c_{44}$  for the lower row of Table I) are computed using the quantities given in Table I and Eq. (10.2). The numerical values of these material coefficients for NaI, NaCl, KI, and KCl are given in Table II.

## 11. SOME QUANTITATIVE PREDICTIONS

The surface energy density is given by Eq. (9.10). Part of this energy depends on the value of the polarization on the surface, which can be obtained as the solution of a boundary-value problem. In order to evaluate the surface energy expression (9.10), and the displacement of the half space bounded by the free surface (1,0,0) of a centrosymmetric cubic crystal, Mindlin's solution<sup>3</sup> for this problem is used.

$$u_1 = -\frac{b^0 d_{11}}{c_{11}\lambda(a + \epsilon_0^{-1})} e^{-x_1/\lambda},$$

$$P_1 = \frac{b^0}{\lambda(a + \epsilon_0^{-1})} e^{-x_1/\lambda}, \quad (11.1)$$

$$\phi = -\frac{b^0}{(a\epsilon_0 + 1)} e^{-x_1/\lambda},$$

$$S = T_0 - \frac{(b^0)^2}{2\lambda(a + \epsilon_0^{-1})},$$

TABLE III. Surface energy density for the (1,0,0) surface.

	Benson <sup>a</sup> (erg/cm <sup>2</sup> )			Shuttleworth <sup>b</sup> (erg/cm <sup>2</sup> ) $S$	Experi- mental <sup>b</sup> (erg/cm <sup>2</sup> ) $S$	This analysis (erg/cm <sup>2</sup> )	
	$T_0$	$T$	$S$			$T$	$S$
NaI	170	-52	118	...	...	-39	131
NaCl	210	-52	158	214	276 300	-59	151
KI	140	-27	113	...	...	-22	118
KCl	175	-34	141	171	110 252	-24	151

<sup>a</sup> Ref. 8, Table 8-5, p. 229.

<sup>b</sup> Ref. 7, Table XXV, p. 102.

where

$$\lambda^2 = \frac{b_{11}}{(a + \epsilon_0^{-1})} \left( 1 - \frac{d_{11}^2}{c_{11}b_{11}} \right). \quad (11.2)$$

### A. Surface Energy

By substituting the values of  $T_0$  as given by Benson<sup>8</sup> and the coefficients given in Tables I and II into the last of Eqs. (11.1), the surface energy density is obtained for NaI, NaCl, KI, and KCl. These values are compared in Table III with the results obtained by Benson<sup>8</sup> and Shuttleworth<sup>7a</sup> based on discrete models and the experimental data given in Table XXV of Ref. 7.

### B. Displacement of Free Surface

The displacement of the particles at the free surface is calculated to be of the order of 1-3% of the interparticle distance.<sup>8</sup> Table IV gives the displacement of the free surface as predicted by the present analysis.

When comparing the results in Table IV, with those obtained from a discrete model, one should remember that the continuum analysis does not identify the particles, but gives an average displacement of the positive and negative ions.

### C. Rate of Decay of Surface Effects

From the solution of the boundary-value problem for the continuum, Eqs. (11.1) and (11.2), one sees that the surface effects decay as  $e^{-x_1/\lambda}$ . From a discrete analysis for the NaCl-type crystals, Madelung<sup>8</sup> found that the displacements decay as an exponential function of the distance from the free surface of the crystal. Furthermore, the surface effects are found to be confined to the first very few layers of the surface. The parameter  $r_0/\lambda$  characterizing the rate of decay is computed to be of the order of  $\sim 1.75$  (see Table IV). Consequently the effects

TABLE IV. Surface displacement and the decay parameter  $\lambda$ .

	$\mu$ ( $10^{-8}$ cm)	$u/r_0$ (%)	$\lambda$ ( $10^{-8}$ cm)	$r_0/\lambda$
NaI	0.0670	2.08	1.54	2.11
NaCl	0.0798	2.84	1.30	2.13
KI	0.0492	1.39	2.25	1.65
KCl	0.0373	1.19	2.41	1.30

at the second and third layers are approximately 15 and 3% of those at the first layer.

#### D. Dispersion Relation

Acoustical plane waves in the infinite medium according to this continuum theory are found to be dispersive. The dispersion relation for the longitudinal and transverse acoustic waves propagating in the (1,0,0) direction are

$$\omega_i = V_i y_1 \left( 1 - \frac{M_i}{1 + N_i y_1^{-2}} \right)^{1/2}, \quad i = 1, 2, 3 \quad (11.3)$$

where  $i=1$  corresponds to the longitudinal waves and  $i=2,3$  correspond to the transverse waves, and

$$v_1 = \left( \frac{c_{11}}{\rho} \right)^{1/2}, \quad M_1 = \frac{d_{11}^2}{c_{11} b_{11}}, \quad N_1 = \frac{a + \epsilon_0^{-1}}{b_{11}},$$

$$v_2 = v_3 = \left( \frac{c_{44}}{\rho} \right)^{1/2}, \quad M_2 = M_3 = \frac{d_{44}^2}{c_{44}(b_{44} + b_{77})},$$

$$N_2 = N_3 = \frac{a}{b_{44} + b_{77}}. \quad (11.4)$$

The corresponding group velocities are

$$v_{gi} = \frac{d\omega_i}{dy_1} = v_i \left( 1 - \frac{M_i}{1 + N_i y_1^{-2}} \right)^{-1/2}$$

$$\times \left[ 1 - \frac{M_i(1 + 2N_i y_1^{-2})}{(1 + N_i y_1^{-2})^2} \right]. \quad (11.5)$$

One notices that the group velocities are bounded by  $v_1$  and  $v_2$ , the phase velocities of the longitudinal and transverse waves of the classical theory of elasticity.

## 12. CONCLUSIONS

The shell model which allows for a mechanism of ionic polarization is used in obtaining the total potential

energy of ionic crystals. In this formulation the energy due to the long-range forces is taken to be electrostatic in nature, while the energy due to the short-range forces is obtained by considering the interactions between the shells of the first and second nearest neighbors and the interaction of a shell with its own core. A continuum theory of elastic dielectrics is obtained from the lattice formulation by the long-wave approximation. In this continuum theory, the potential-energy density is seen to be a function of strain, polarization, the polarization gradient. For the case of centrosymmetric crystals this theory is the same as the one presented by Mindlin.<sup>3</sup> However, this means of formulation allows one to obtain the values of the material coefficients using the properties of the discrete model and the experimentally obtained values of  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$ .

As can be seen from Eqs. (10.2) and Table II the new dielectric coefficients  $b_{11}$ ,  $b_{44}$ ,  $b_{77}$  depend on  $K_2$ ,  $A_1$ ,  $A_2$ ,  $B_1$ ,  $B_2$  whereas the coefficient  $b_{12}$  depends only on  $A_2$  and  $B_2$  which is due to the short-range interactions between the second neighbors. Therefore, the numerical value of  $b_{12}$  is many orders of magnitude less than the numerical values of  $b_{11}$ ,  $b_{44}$ , and  $b_{77}$ .

In this paper the surface energy associated with the creation of a free surface is considered to be made up of two parts: one is associated with the removal of part of the material and is a constant for a given surface and the other is due to the relaxation of the free surface and is a function of the field variables. The constant part is present at the initial undeformed, unpolarized state and the relaxation part is included in the total potential-energy density and accounts for the presence of surface effects.

Also, in order to obtain the value of the surface energy density it is necessary to solve a boundary-value problem with a free surface, since the definition of the surface energy density, Eq. (9.10) involves the polarization on the surface, which is given by the solution of the specific boundary-value problem.