Lattice Theory of the Elastic Dielectric*

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A homogeneously deformed and uniformly polarized elastic dielectric is considered. For small displacements of the medium from the deformed and polarized state, the equation of motion and the equation for the change in polarization due to the displacement are derived to the first order in the deformation parameter and the macroscopic electric field, using Toupin's general theory of the elastic dielectric. Born and Huang's treatment of the vibrations of an ionic lattice is extended to the case where the lattice is homogeneously deformed and has a uniform electric field. The equation of motion and the equation for the change in polarization due to small displacements from the deformed and polarized state are derived on lattice theory. A comparison of lattice-theoretical equations at long wavelength with the continuum-mechanical equations yields the expressions for the electrical susceptibility, the piezoelectric constants, and the second-order elastic constants together with their linear coefficients of variation with the deformation and the electrical field.

I. INTRODUCTION

THE general theory of the elastic dielectric in static equilibrium has been studied in detail by Toupin,[1] Eringen,[2] and Grindlay.[3] Toupin[4] has also considered the dynamics of an elastic dielectric and arrived at the equation of motion for small displacements from an initially polarized and elastically deformed state. Toupin has some criticisms to offer about the earlier analysis of the problem by Born and Huang,[5] and Mason.[6]

The lattice theory of vibrations of an ionic lattice in an initially unpolarized and strain-free state has been developed by Born and Huang.[7] They obtained the expressions for the dielectric, piezoelectric, and second-order elastic constants of such a lattice in terms of second-order coupling parameters. In nonionic crystals, the lattice theory was extended by Srinivasan[8] to the case of a lattice under homogeneous strain and the lattice-theoretical expressions for the third-order elastic constants of a nonionic crystal were obtained in terms of the second- and third-order coupling parameters. (This paper will be referred to as RSI, and the notation developed in this paper will be used extensively in what follows.) These expressions were applied by Srinivasan[9] to the case of germanium and silicon.

In the work presented here, the lattice theory of the vibration of an ionic lattice is extended to the case when the lattice is initially polarized uniformly and is in a state of homogeneous strain. The equation of motion is developed to the first power in the initial strain and electric field. This is compared with the corresponding equation of motion from Toupin's general theory. Expressions are derived for the linear coefficients of variation with strain and electric field of (i) the electric susceptibility, (ii) the piezoelectric constants, and (iii) the second-order elastic constants of an ionic lattice in terms of the second- and third-order coupling parameters.

The expressions so derived are applied to the fluorite lattice in the succeeding paper.

II. CONTINUUM THEORY

Consider a body subjected to a homogeneous deformation and a uniform electric field **E**. Using Toupin's[4] general theory of the dynamics of an elastic dielectric, the equation of motion for small displacements from an initially deformed and polarized state will be derived to the first order in the deformation parameters and the components of the electric field. It is convenient to use a rectangular Cartesian system of axes in what follows.

The reference or material configuration of the body is one free of strain and polarization. In this state let the coordinates of a material particle be denoted by X_i ($i=1, 2, 3$). When the body is homogeneously deformed, the spatial coordinate of the material particle becomes x_i. The deformation parameters ϵ_{ij} are given by

$$\partial x_i/\partial X_j=\delta_{ij}+\epsilon_{ij}. \tag{2.1}$$

The δ_{ij} are Kronecker deltas. The Lagrangian strain η_{ij} is given by

$$\eta_{ij}=\tfrac{1}{2}(\epsilon_{ij}+\epsilon_{ji}+\sum_k \epsilon_{kj}\epsilon_{ki}). \tag{2.2}$$

For a homogeneous strain, ϵ_{ij} and η_{ij} are independent of the material coordinates X_i.

The polarization in the deformed medium is **P** and the electric field **E**. Both are assumed to be uniform.

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Toupin[4] defines the material measure of polarization of the medium as

$$\pi_i = -\frac{v'}{v}\sum_k P_k \frac{\partial X_i}{\partial x_k}, \tag{2.3}$$

where v' is the volume of unit mass of the material in the deformed state and v is the volume of unit mass of the material in the reference configuration.

According to Toupin,[4] one could define an energy function Σ per unit volume of the undeformed state. Σ is a function of the components π_i and η_{ij} only. This function should be invariant to rigid rotations and to all the symmetry operations of the point-group symmetry of the medium.

As we are interested in developing the equations of motion for small displacements from the deformed state to first order in E_i and ϵ_{ij} (terms involving the product of E_i and ϵ_{ij} are to be considered as second-order quantities and omitted), we shall assume that the function Σ can be explicitly written out as a power series in η_{ij} and π_i. Since there are no stresses and no electric field in the reference configuration, we may write

$$\Sigma = \tfrac{1}{2}\sum_{ijkl} \bar{C}_{ij,kl}\eta_{ij}\eta_{kl} + \tfrac{1}{6}\sum_{ijklmn} \bar{C}_{ij,kl,mn}\eta_{ij}\eta_{kl}\eta_{mn} + \sum_{ikl} S_{i,kl}\pi_i\eta_{kl} + \tfrac{1}{2}\sum_{ijkl} S_{[ij,kl]}\eta_{ij}\pi_k\pi_l + \tfrac{1}{2}\sum_{iklmn} S_{i,kl,mn}\pi_i\eta_{kl}\eta_{mn} + \tfrac{1}{2}\sum_{ij} G_{ij}\pi_i\pi_j + \tfrac{1}{6}\sum_{ijk} G_{ijk}\pi_i\pi_j\pi_k + \cdots. \tag{2.4}$$

The symmetry of the coefficients is indicated by brackets over the suffixes as explained in RSI. Thus $\bar{C}_{ij,kl,mn}$ is symmetric in $(i \rightleftharpoons j)$, $(k \rightleftharpoons l)$, $(m \rightleftharpoons n)$, as well as $(ij) \rightleftharpoons (kl) \rightleftharpoons (mn)$. $S_{[ij,kl]}$ is symmetric only in $(i \rightleftharpoons j)$ and $(k \rightleftharpoons l)$. For our purpose no higher-order terms in the expansion Eq. (2.4) are needed.

The electric field $\mathbf{E}$ is given by

$$E_i = \sum_j \frac{\partial \Sigma}{\partial \pi_j}\frac{\partial X_j}{\partial x_i}. \tag{2.5}$$

The final equation of motion we obtain should be expressed in terms of E_i and ϵ_{ij}. The components P_i that may occur in this equation have to be replaced in terms of E_i and ϵ_{ij} to the first order. Equation (2.5) can therefore be inverted to give

$$P_i = \sum_j \mathcal{G}_{ij}E_j - \sum_{mn} E_{i,mn}\epsilon_{mn}. \tag{2.6}$$

$\mathcal{G}_{ij}$ are the components of the electrical-susceptibility tensor in the reference configuration. $E_{i,mn}$ are the components of the piezoelectric tensor in the reference configuration:

$$\mathcal{G}_{ij} = (G^{-1})_{ij}, \tag{2.7}$$

$$E_{i,mn} = \sum_j \mathcal{G}_{ij}S_{j,mn}. \tag{2.8}$$

If the material particles are given small displacements u_i from the deformed state, an additional polarization δP_i and an additional electric field $\delta E_i = e_i$ are generated. The additional polarization δP_i is given by

$$\delta P_i = p_i + \sum_l P_l \frac{\partial u_i}{\partial x_l} - \sum_k P_i \frac{\partial u_k}{\partial x_k}. \tag{2.9}$$

Here

$$p_i = \frac{v}{v'}\sum_j \delta\pi_j \frac{\partial x_i}{\partial X_j}, \tag{2.10}$$

where $\delta\pi_j$ is the change in the material polarization accompanying the displacement.

The change in the electric field e_i is given by[10]

$$e_i = \sum_{jklr} \mathcal{S}_{j,kl}\frac{\partial x_r}{\partial X_l}\frac{\partial X_j}{\partial x_i}\frac{\partial u_r}{\partial X_k} + \sum_{jkl} (\chi^{-1})_{kl}\frac{\partial X_k}{\partial x_i}\frac{\partial X_l}{\partial x_j}p_j - \sum_k E_k \frac{\partial u_k}{\partial x_i}. \tag{2.11}$$

Here

$$\mathcal{S}_{j,kl} = \frac{\partial^2 \Sigma}{\partial \pi_j \partial \eta_{kl}}, \tag{2.12}$$

$$(\chi^{-1})_{kl} = \frac{v'}{v}\frac{\partial^2 \Sigma}{\partial \pi_k \partial \pi_l}. \tag{2.13}$$

Equation (2.11) can be inverted to give

$$p_i = \sum_{jkl} \chi_{kl}\frac{\partial x_l}{\partial X_k}\frac{\partial x_j}{\partial X_l}\left(e_j + \sum_p E_p \frac{\partial u_p}{\partial x_j}\right) - \sum_{rsjk} \mathcal{E}_{j,ks}\frac{\partial x_i}{\partial X_j}\frac{\partial x_r}{\partial X_k}\frac{\partial u_r}{\partial X_s}. \tag{2.14}$$

Here

$$\mathcal{E}_{j,ks} = \sum_l \chi_{jl}\mathcal{S}_{l,ks}.$$

Using Eqs. (2.13) and (2.7), we can write χ_{kl} to the first order in E_i and ϵ_{ij}:

$$\chi_{kl} = \frac{v}{v'}\left[\mathcal{G}_{kl} + \sum_{mn} \mathcal{P}_{[kl,mn]}\epsilon_{mn} + \sum_p \mathcal{G}_{klp}E_p\right], \tag{2.15}$$

$$\mathcal{P}_{[kl,mn]} = -\sum_{vw} \mathcal{G}_{kv}\left(S_{[mn,vw]} - \sum_p G_{vwp}E_{p,mn}\right)\mathcal{G}_{wl}. \tag{2.16}$$

This quantity is symmetric in $(k \rightleftharpoons l)$ and $(m \rightleftharpoons n)$:

$$\mathcal{G}_{klp} = -\sum_{vwt} \mathcal{G}_{kv}G_{vwt}\mathcal{G}_{lw}\mathcal{G}_{pt}. \tag{2.17}$$

This quantity is symmetric in $k \rightleftharpoons l \rightleftharpoons p$.

χ_{kl} are the components of the electrical-susceptibility tensor in the deformed and polarized state. The linear

[10] There is a misprint in Eq. (6.19) of Toupin's paper (Ref. 4). The sign before the last term on the right-hand side of that equation should be positive.

[11] R. Srinivasan, following paper, Phys. Rev. 165, 1054 (1968).

coefficient of variation of the component χ_{kl} with the deformation parameter ϵ_{mn} is given by

$$\mathcal{G}_{[kl,mn]}=\mathcal{P}_{[kl,mn]}-\mathcal{G}_{kl}\delta_{mn}. \tag{2.18}$$

$\mathcal{G}_{klp}$ yields the linear coefficient of variation of χ_{kl} with the electric field E_p.

If we are dealing with the susceptibility in the optical-frequency region we can relate $\mathcal{G}_{[kl,mn]}$ to the elasto-optic constants of the material.

Using Eqs. (2.12) and (2.15) we get

$$\mathcal{E}_{j,ks}=\frac{v}{v'}(E_{j,ks}+\sum_{mn}\hat{E}_{j,ks,mn}\epsilon_{mn}+\sum_{p}E_{[jp,ks]}E_p), \tag{2.19}$$

$$\hat{E}_{j,ks\,mn}=\sum_{v}\mathcal{G}_{jv}\Big[S_{v,ks,mn}-\sum_{w}(S_{[vw,ks]}E_{w,mn}+S_{[vw,mn]}E_{w,ks})+\sum_{wt}E_{w,ks}G_{vwt}E_{t,mn}\Big]. \tag{2.20}$$

This is symmetric in $(k\rightleftharpoons s)$, $(m\rightleftharpoons n)$, and $(ks)\rightleftharpoons(mn)$.

$$E_{[jp,ks]}=\sum_{vw}\mathcal{G}_{jv}S_{[ks,vw]}\mathcal{G}_{wp}+\sum_{v}S_{v,ks}\mathcal{G}_{v,jp}. \tag{2.21}$$

This is symmetric in $(j\rightleftharpoons p)$ and $(k\rightleftharpoons s)$.

$\mathcal{E}_{j,ks}$ are the components of the piezoelectric constant tensor in the deformed state. The linear coefficient of variation of $\mathcal{E}_{j,ks}$ with the deformation parameter ϵ_{mn} is

$$E_{[j,ks,mn]}=\hat{E}_{j,ks,mn}-E_{j,ks}\delta_{mn}. \tag{2.22}$$

$E_{[jp,ks]}$ gives the linear coefficient of variation of $\mathcal{E}_{j,ks}$ with the electric field.

Using Eqs. (2.6), (2.9), (2.14), (2.15), and (2.19), the expression for δP_i can be written as

$$\delta P_i=\frac{v}{v'}\Big\{\sum_{j}e_j\Big[\mathcal{G}_{ij}+\sum_{mn}(\mathcal{P}_{[ij,mn]}+\mathcal{G}_{in}\delta_{jm}+\mathcal{G}_{nj}\delta_{im})\epsilon_{mn}+\sum_{p}\mathcal{G}_{ijp}E_p\Big] -\sum_{js}\frac{\partial u_j}{\partial X_s}\Big[E_{i,js}+\sum_{mn}(\hat{E}_{i,js,mn}+E_{i,ns}\delta_{jm}+E_{n,js}\delta_{im}+E_{s,mn}\delta_{ij}-E_{i,mn}\delta_{js})\epsilon_{mn} +\sum_{p}(E_{[ip,js]}-\mathcal{G}_{is}\delta_{jp}-\mathcal{G}_{sp}\delta_{ij}+\mathcal{G}_{ip}\delta_{js})E_p\Big]\Big\}. \tag{2.23}$$

This equation will be compared with the corresponding equation from lattice theory to get the lattice-theoretical expressions for $\mathcal{P}_{[ij,mn]}$, $\mathcal{G}_{ijp}$, $\hat{E}_{i,js,mn}$, and $\hat{E}_{[ip,js]}$.

For the present case of a dielectric subjected to a homogeneous deformation and a uniform polarization and electrical field, the equation of motion given by Toupin[4] reduces to

$$\rho_0\frac{v}{v'}\ddot{u}_i=\sum_{kjl}\mathcal{C}_{ik,jl}\frac{\partial^2 u_j}{\partial x_l\partial x_k}+\sum_{kl}\mathcal{S}_{l,ik}\frac{\partial p_l}{\partial x_k}+\sum_{kl}\mathcal{T}_{kl}\frac{\partial^2 u_i}{\partial x_l\partial x_k}-E_i\,\mathrm{div}\mathbf{p}. \tag{2.24}$$

Here ρ_0 is the density of the material in the reference configuration.

$$\mathcal{C}_{ij,kl}=\frac{v}{v'}\sum_{pqrs}\frac{\partial^2\Sigma}{\partial\eta_{pq}\partial\eta_{rs}}\frac{\partial x_i}{\partial X_p}\frac{\partial x_j}{\partial X_q}\frac{\partial x_k}{\partial X_r}\frac{\partial x_l}{\partial X_s}, \tag{2.25}$$

$$\mathcal{T}_{kl}=\frac{v}{v'}\sum_{pq}\frac{\partial\Sigma}{\partial\eta_{pq}}\frac{\partial x_k}{\partial X_p}\frac{\partial x_l}{\partial X_q}. \tag{2.26}$$

Substituting in (2.24) for $\mathcal{S}_{l,ik}$, p_l, $\mathcal{C}_{ik,jl}$, and $\mathcal{T}_{kl}$ from (2.12), (2.14), (2.25), and (2.26), and looking for periodic solutions

$$u_i=u_i\exp(i\omega t),$$

we get

$$\rho_0\omega^2u_i=-\Big\{\sum_{jrs}\frac{\partial^2u_j}{\partial X_r\partial X_s}\Big[\bar{C}'_{ir,js}+\sum_{mn}\epsilon_{mn}(\bar{C}'_{ir,js,mn}+\bar{C}'_{rs,mn}\delta_{ij}+\bar{C}'_{ir,ns}\delta_{jm}+\bar{C}'_{nr,js}\delta_{im})+\sum_{p}E_p(\bar{C}'_{p,ir,js}+E_{p,rs}\delta_{ij} +E_{s,ir}\delta_{jp}+E_{r,js}\delta_{ip})\Big]+\sum_{jr}\frac{\partial e_j}{\partial X_r}\Big[E_{j,ir}+\sum_{mn}\epsilon_{mn}(\hat{E}_{j,ir,mn}+E_{n,ir}\delta_{jm}+E_{j,nr}\delta_{im})+\sum_{p}E_p(E_{[jp,ir]}-\mathcal{G}_{jr}\delta_{ip})\Big]\Big\}. \tag{2.27}$$

Here

$$\bar{C}'_{ir,js}=\bar{C}_{ir,js}-\sum_{p} S_{p,ir}E_{p,js}\,, \tag{2.28}$$

$$\bar{C}'_{ir,js,mn}=\bar{C}_{ir,js,mn}-\sum_{p}\left[S_{p,ir,js}E_{p,mn}+S_{p,js,mn}E_{p,ir}+S_{p,mn,ir}E_{p,js}\right]$$
$$+\sum_{pq}\left[S_{[ir,pq]}E_{p,js}E_{q,mn}+S_{[js,pq]}E_{p,mn}E_{q,ir}+S_{[mn,pq]}E_{p,ir}E_{q,js}\right]+\sum_{pqt} G_{pqt}E_{p,ir}E_{q,js}E_{t,mn}\,, \tag{2.29}$$

$$\bar{C}'_{p,ir,js}=\sum_{q}\mathcal{G}_{pq}\left[S_{q,ir,js}-\sum_{t}(S_{[qt,js]}E_{t,ir}+S_{[qt,ir]}E_{t,js})\right]-\sum_{qt}\mathcal{G}_{pqt}S_{q,ir}S_{t,js}\,. \tag{2.30}$$

The effective second-order elastic constants for wave propagation in an elastic dielectric are $\bar{C}'_{ir,js}$. The effective third-order elastic constants are $\bar{C}'_{ir,js,mn}$. The linear coefficient of variation of $\bar{C}'_{ir,js}$ with the electric field is given by $\bar{C}'_{p,ir,js}$.

The above equation must be supplemented with the equation

$$\mathrm{div}(\mathbf{e}+4\pi\delta\mathbf{P})=0\,. \tag{2.31}$$

In the next section, the equation of motion of a homogeneously deformed and uniformly polarized ionic lattice will be derived from lattice theory. Comparison with the Eq. (2.27) will yield the lattice-theoretical expressions for $\bar{C}'_{ir,js,mn}$ and $\bar{C}'_{p,ir,js}$.

III. LATTICE THEORY

Following the notation in RSI, the Greek alphabet is used to designate the particles in the basis cell. Capital letters L, M, N stand for cell indices and small letters i, j, k stand for component indices. A particle of type μ has a mass $M(\mu)$ and a charge $e(\mu)$. The theoretical expressions to be derived in the following are valid not only for rigid ions but also for polarizable ions when they are treated in the framework of the shell model of Cochran.

The potential energy between two particles $(L\lambda)$ and $(M\mu)$ is $\Phi(L\lambda,M\mu)$. It is composed of two parts,

$$\Phi(L\lambda,M\mu)={}^{N}\Phi(L\lambda,M\mu)+{}^{C}\Phi(L\lambda,M\mu)\,. \tag{3.1}$$

${}^{N}\Phi$ refers to the non-Coulomb interaction between the particles and could involve many body forces. ${}^{C}\Phi$ refers to the Coulomb interaction between the particles,

$${}^{C}\Phi(L\lambda,M\mu)=e(\lambda)e(\mu)/|X(L\lambda,M\mu)|\,. \tag{3.2}$$

The Coulomb part of the potential depends on the distance between two particles and hence satisfies the translational- and rotational-invariance conditions. The coupling parameters due to the non-Coulomb interaction must satisfy the conditions (2a)–(3f) of RSI, since the total potential energy must be invariant to rigid translations and rotations.

The lattice is assumed to be subjected to a homogeneous deformation. The coordinates $x_i(L\lambda)$ of the particles after deformation are related to the coordinates $X_i(L\lambda)$ before deformation by the relation

$$x_i(L\lambda)=X_i(L\lambda)+U_i(L\lambda)\,, \tag{3.3}$$

where

$$U_i(L\lambda)=\sum_{j}\epsilon_{ij}X_j(L\lambda)+w_i(\lambda)\,. \tag{3.4}$$

The ϵ_{ij} are the deformation parameters and $\mathbf{w}(\lambda)$ is the internal displacement of the λ sublattice. The polarization in the deformed state is given by

$$P_i=\frac{1}{v_a'}\sum_{\mu}e(\mu)x_i(0\mu)=\frac{1}{v_a'}\sum_{\mu}e(\mu)w_i(\mu)\,, \tag{3.5}$$

since the reference state is one of no polarization, i.e.,

$$\sum_{\mu}e(\mu)X_i(0\mu)=0\,. \tag{3.6}$$

v_a is the volume of the undeformed basis cell and v_a' is the volume of the basis cell after deformation. This polarization P_i is given by Eq. (2.6) to first order in the electric field and deformation.

When the particles are given displacements $u_i(L\lambda)$ from this deformed configuration, the equation of motion is given by (31) of RSI to the first order in $U_i(L\lambda)$:

$$M(\lambda)\ddot{u}_i(L\lambda)=-\sum_{j}\sum_{\mu}\sum_{M}\Psi_{ij}(L\lambda,M\mu)u_j(M\mu)\,, \tag{3.7}$$

$$\Psi_{ij}(L\lambda,M\mu)=\Phi_{ij}(L\lambda,M\mu)+\sum_{l}\sum_{\nu}\sum_{N}\Phi_{ijl}(L\lambda,M\mu,N\nu)U_l(N\nu)\,. \tag{3.8}$$

Let us seek solutions of (3.7) of the type

$$u_i(L\lambda)=u_i(\lambda)[\exp i\omega t][\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(L\lambda)]=u_i(\lambda)[\exp i\omega t][\exp i2\pi\mathbf{y}\cdot\mathbf{x}(L\lambda)]\,. \tag{3.9}$$

Here $\mathbf{Y}$ is the wave vector in the reference configuration and $\mathbf{y}$ the wave vector in the deformed configuration. To first order in the deformation,

$$y_i = Y_i - \sum_j \epsilon_{ji} Y_j. \tag{3.10}$$

In Eqs. (2.23) and (2.27), the derivatives of the displacements with respect to material coordinates occur. So we shall use the first form of the solution (3.9). Substituting this form of the solution in (3.7), we get

$$M(\lambda)\omega^2(\mathbf{Y})u_i(\lambda) = \sum_{j\mu} u_j(\mu) \sum_M \Psi_{ij}(0\lambda,M\mu) \times \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu). \tag{3.11}$$

Consider

$$\sum_M \Psi_{ij}(0\lambda,M\mu) \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu).$$

The Coulomb part of this sum is

$$\sum_M {}^C\Phi_{ij}(0\lambda,M\mu) \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu) + \sum_{l\nu}\sum_{MN} {}^C\Phi_{ijl}(0\lambda,M\mu,N\nu)U_l(N\nu) \times \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu). \tag{3.12}$$

The first term can be written as

$$\sum_M{}' {}^C\Phi_{ij}(0\lambda,M\mu) \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu) - \delta_{\mu\lambda}\sum_\pi\sum_P{}' {}^C\Phi_{ij}(0\lambda,P\pi). \tag{3.13}$$

Substituting for $U_l(N\nu)$ from (3.4) into the second term of (3.12), and taking into account the fact that the Coulomb interaction is a two-body central interaction, we can write the second term of (3.12) as

$$\begin{aligned}\sum_l\sum_\nu w_l(\nu)[\delta_{\nu\mu}\sum_M{}' {}^C\Phi_{ijl}(0\lambda,M\mu,M\mu) \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu) + \delta_{\nu\lambda}\sum_M{}' {}^C\Phi_{ijl}(0\lambda,M\mu,0\lambda) \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu) \\ + \delta_{\mu\lambda}\sum_N{}' {}^C\Phi_{ijl}(0\lambda,0\lambda,N\nu) - \delta_{\mu\lambda}\delta_{\nu\lambda}\sum_P{}'\sum_\pi {}^C\Phi_{ijl}(0\lambda,0\lambda,P\pi)] + \sum_{mn}\epsilon_{mn}[\delta_{\mu\lambda}\sum_{N\nu}{}' {}^C\Phi_{ijm}(0\lambda,0\lambda,N\nu)X_n(0\lambda,N\nu) \\ - \sum_M{}' {}^C\Phi_{ijm}(0\lambda,M\mu,0\lambda)X_n(0\lambda,M\mu) \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu)].\end{aligned} \tag{3.14}$$

In the above, use has been made of the fact that

$${}^C\Phi_{ij}(0\lambda,0\lambda) = -\sum_\mu\sum_M{}' {}^C\Phi_{ij}(0\lambda,M\mu),$$

and

$${}^C\Phi_{ijm}(0\lambda,0\lambda,0\lambda) = -\sum_\mu\sum_M{}' {}^C\Phi_{ijm}(0\lambda,0\lambda,M\mu). \tag{3.15a}$$

The prime over the summation sign means that when $\lambda=\mu$, the term $M=0$ must be omitted.

From the expression (3.2) for ${}^C\Phi(0\lambda,M\mu)$, we can write

$$\sum_{M(\lambda\neq\mu)} {}^C\Phi_{ij}(0\lambda,M\mu) \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu) = \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(\lambda\mu) \times\left[-e(\lambda)e(\mu)\frac{\partial^2}{\partial X_i\partial X_j}\left(\sum_M \frac{1}{|\mathbf{X}(M)-\mathbf{X}|}\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(M)\right)\right]_{\mathbf{X}=-\mathbf{X}(\lambda\mu)}, \tag{3.15b}$$

$$\sum_{M(\lambda\neq\mu)} {}^C\Phi_{ijl}(0\lambda,0\lambda,M\mu) \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu) = \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(\lambda\mu) \times\left[-e(\lambda)e(\mu)\frac{\partial^3}{\partial X_i\partial X_j\partial X_l}\left(\sum_M \frac{\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(M)}{|\mathbf{X}(M)-\mathbf{X}|}\right)\right]_{\mathbf{X}=-\mathbf{X}(\lambda\mu)}. \tag{3.15c}$$

Using the theta transformation formula, Born and Huang[7] have shown that

$$\begin{aligned}\sum_M \frac{\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(M)}{|\mathbf{X}(M)-\mathbf{X}|} = [(1/\pi v_a Y^2)\exp(-(\pi^2/R^2)Y^2 + i2\pi\mathbf{Y}\cdot\mathbf{X}) + R\sum_M H(R|\mathbf{X}(M)-\mathbf{X}|)\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(M) \\ + (\pi/v_a R^2)\sum_{Y_h}{}' G(\pi^2|\mathbf{Y}_h+\mathbf{Y}|^2/R^2)\exp i2\pi(\mathbf{Y}_h+\mathbf{Y})\cdot\mathbf{X}].\end{aligned} \tag{3.16}$$

Here R is an arbitrary parameter chosen to ensure the rapid convergence of the two sums on the right. $\mathbf{Y}_h$ is a reciprocal lattice vector.

$$H(\xi) = \frac{2}{\pi^{1/2}}\frac{1}{\xi}\int_\xi^\infty e^{-u^2}du, \tag{3.17}$$

$$G(\xi) = e^{-\xi}/\xi. \tag{3.18}$$

The prime over the sum over $\mathbf{Y}_h$ means that the origin of the reciprocal lattice should be omitted in performing the sum. Substituting (3.16) in (3.15b) we get

$$\sum_M{}' \, {}^C\Phi_{ij}(0\lambda,M\mu)\, \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu) = (4\pi/v_a)e(\lambda)e(\mu)(Y_iY_j/Y^2)+e(\lambda)e(\mu)Q_{ij}(\mathbf{Y},\lambda\mu)\,, \tag{3.19a}$$

$$\sum_M{}' \, {}^C\Phi_{ijl}(0\lambda,0\lambda,M\mu)\, \exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu) = (4\pi/v_a)e(\lambda)e(\mu)[i2\pi Y_iY_jY_l/Y^2]+e(\lambda)e(\mu)R_{ijl}(\mathbf{Y},\lambda\mu)\,. \tag{3.19b}$$

Here

$$Q_{ij}(\mathbf{Y},\lambda\mu) = (4\pi/v_a)(Y_iY_j/Y^2)[\exp(-\pi^2Y^2/R^2)-1] - R^3\sum_M{}' H_{ij}(R|X(0\lambda,M\mu)|)\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu)$$
$$+\frac{4\pi^3}{R^2V_a}\sum_{Y_h}{}'(\mathbf{Y}_h+\mathbf{Y})_j(\mathbf{Y}_h+\mathbf{Y})_i G\left(\frac{\pi^2}{R^2}|\mathbf{Y}_h+\mathbf{Y}|^2\right)\exp(-i2\pi\mathbf{Y}_h\cdot\mathbf{X}(\lambda\mu))\,, \tag{3.20a}$$

$$R_{ijl}(\mathbf{Y},\lambda\mu) = (4\pi/v_a)i2\pi(Y_iY_jY_l/Y^2)[\exp(-\pi^2Y^2/R^2)-1] + R^4\sum_M{}' H_{ijl}(R|\mathbf{X}(0\lambda,M\mu)|)\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu)$$
$$+i\frac{8\pi^4}{v_aR^2}\sum_{Y_h}{}'(\mathbf{Y}_h+\mathbf{Y})_i(\mathbf{Y}_h+\mathbf{Y})_j(\mathbf{Y}_h+\mathbf{Y})_l G\left(\frac{\pi^2}{R^2}|\mathbf{Y}_h+\mathbf{Y}|^2\right)\exp(-i2\pi\mathbf{Y}_h\cdot\mathbf{X}(\lambda\mu))\,, \tag{3.20b}$$

$$H_{ij}(|\xi|) = \frac{\partial^2}{\partial\xi_i\partial\xi_j}H(|\xi|)\,,$$

$$H_{ijl}(|\xi|) = \frac{\partial^3}{\partial\xi_i\partial\xi_j\partial\xi_l}H(|\xi|)\,.$$

Now

$$\sum_M{}' \, {}^C\Phi_{ijm}(0\lambda,0\lambda,M\mu)X_n(0\lambda,M\mu)\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu) = \frac{1}{i2\pi}\frac{\partial}{\partial Y_n}\sum_M{}' \, {}^C\Phi_{ijm}(0\lambda,0\lambda,M\mu)\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu)$$

$$=\frac{4\pi}{v_a}e(\lambda)e(\mu)[(Y_iY_j\delta_{mn}+Y_jY_m\delta_{in}+Y_iY_m\delta_{jn})/Y^2-2Y_iY_jY_mY_n/Y^4]+e(\lambda)e(\mu)R_{ijm,n}(\mathbf{Y},\lambda\mu)\,, \tag{3.21}$$

where

$$R_{ijm,n}(\mathbf{Y},\lambda\mu) = \frac{1}{i2\pi}\frac{\partial}{\partial Y_n}R_{ijm}(\mathbf{Y},\lambda\mu)\,.$$

The Coulomb part of

$$\sum_M \Psi_{ij}(0\lambda,M\mu)\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu)$$

can now be written as

$$e(\lambda)[e(\mu)Q_{ij}(\mathbf{Y},\lambda\mu)-\sum_\pi e(\pi)Q_{ij}(0,\lambda\pi)\delta_{\mu\lambda}]+\sum_l\sum_\nu w_l(\nu)[-\delta_{\nu\mu}R_{ijl}(\mathbf{Y},\lambda\mu)e(\lambda)e(\mu)+\delta_{\nu\lambda}R_{ijl}(\mathbf{Y},\lambda\mu)e(\lambda)e(\mu)$$
$$+\delta_{\mu\lambda}R_{ijl}(0,\lambda\nu)e(\lambda)e(\nu)-\delta_{\mu\lambda}\delta_{\nu\lambda}e(\lambda)\sum_\pi e(\pi)R_{ijl}(0,\lambda\pi)]+\sum_{mn}\epsilon_{mn}[-e(\lambda)e(\mu)R_{ijm,n}(\mathbf{Y},\lambda\mu)+e(\lambda)\sum_\pi e(\pi)R_{ijm,n}(0,\lambda\pi)]$$
$$+\frac{4\pi}{v_a}e(\lambda)e(\mu)\frac{1}{Y^2}[Y_iY_j-\sum_{mn}\epsilon_{mn}(Y_iY_m\delta_{jn}+Y_jY_m\delta_{in}+Y_iY_j\delta_{mn}-2Y_iY_jY_mY_n/Y^2)]$$
$$+\frac{4\pi}{v_a}e(\lambda)e(\mu)\sum_l\sum_\nu i2\pi\frac{Y_iY_jY_l}{Y^2}[\delta_{\nu\lambda}-\delta_{\nu\mu}]w_l(\nu)\,. \tag{3.22}$$

The equation of motion can now be written as

$$M(\lambda)\omega^2u_i(\lambda)=\sum_{j\mu}[C^*_{ij}(\mathbf{Y},\lambda\mu)+\sum_{\nu l}D^*_{ijl}(\mathbf{Y},\lambda\mu\nu)w_l(\nu)+\sum_{mn}E^*_{ijmn}(\mathbf{Y},\lambda\mu)\epsilon_{mn}]u_j(\mu)$$
$$+e(\lambda)\sum_{\mu j}\frac{4\pi}{v_a}\frac{1}{Y^2}[Y_iY_j-\sum_{mn}\epsilon_{mn}(Y_iY_m\delta_{jn}+Y_jY_m\delta_{in}+Y_iY_j\delta_{mn}-2Y_iY_jY_mY_n/Y^2]e(\mu)u_j(\mu)$$
$$+e(\lambda)\sum_{\mu j}i2\pi Y_je(\mu)u_j(\mu)\times\sum_{l\nu}Y_iY_l(\delta_{\nu\lambda}-\delta_{\nu\mu})w_l(\nu)\,. \tag{3.23}$$

Here

$$C^*_{ij}(\mathbf{Y},\lambda\mu)=\sum_M {}^N\Phi_{ij}(0\lambda,M\mu)\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu)+e(\lambda)[e(\mu)Q_{ij}(\mathbf{Y},\lambda\mu)-\delta_{\mu\lambda}\sum_\pi e(\pi)Q_{ij}(0,\lambda\pi)], \quad (3.24a)$$

$$D^*_{ijl}(\mathbf{Y},\lambda\mu\nu)=\sum_{MN} {}^N\Phi_{ijl}(0\lambda,M\mu,N\nu)\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu)+e(\lambda)[e(\mu)R_{ijl}(\mathbf{Y},\lambda\mu)(\delta_{\nu\lambda}-\delta_{\nu\mu})$$
$$+e(\nu)R_{ijl}(0,\lambda\nu)\delta_{\mu\lambda}-\delta_{\mu\lambda}\delta_{\nu\lambda}\sum_\pi e(\pi)R_{ijl}(0,\lambda\pi)], \quad (3.24b)$$

$$E^*_{ijmn}(\mathbf{Y},\lambda\mu)=\sum_M\sum_N\sum_\nu {}^N\Phi_{ijl}(0\lambda,M\mu,N\nu)X_n(N\nu)\exp i2\pi\mathbf{Y}\cdot\mathbf{X}(0\lambda,M\mu)$$
$$+e(\lambda)[\delta_{\mu\lambda}\sum_\pi e(\pi)R_{ijm,n}(0,\lambda\pi)-e(\mu)R_{ijm,n}(\mathbf{Y},\lambda\mu)]. \quad (3.24c)$$

Following Born and Huang's procedure, $\mathbf{Y}$ is replaced by $\epsilon\mathbf{Y}$ and ω^2, C^*, D^*, E^*, and the displacement $u_i(\lambda)$ are expanded in powers of ϵ. Here ϵ is a convenient parameter which aids us in collecting terms of zero, first, and second orders separately. Later ϵ can be put equal to unity. We write

$$u_i(\lambda)=u_i^{(0)}(\lambda)+\epsilon u_i^{(1)}(\lambda)+\tfrac{1}{2}\epsilon^2u_i^{(2)}(\lambda)+\cdots, \quad (3.25a)$$

$$\omega^2(\epsilon\mathbf{Y})=\epsilon^2\omega^2(\mathbf{Y})+\cdots, \quad (3.25b)$$

$$C^*_{ij}(\epsilon\mathbf{Y},\lambda\mu)=C^*_{ij}(0,\lambda\mu)+i2\pi\epsilon\sum_r C^*_{ij,r}(0,\lambda\mu)Y_r-\tfrac{1}{2}(4\pi^2)\epsilon^2\sum_{rs} C^*_{ij,rs}(0,\lambda\mu)Y_rY_s+\cdots, \quad (3.25c)$$

$$D^*_{ijl}(\epsilon\mathbf{Y},\lambda\mu\nu)=D^*_{ijl}(0,\lambda\mu\nu)+i2\pi\epsilon\sum_r D^*_{ijl,r}(0,\lambda\mu\nu)Y_r-\tfrac{1}{2}(4\pi^2)\epsilon^2\sum_{rs} D^*_{ijl,rs}(0,\lambda\mu\nu)Y_rY_s+\cdots, \quad (3.25d)$$

$$E^*_{ijmn}(\epsilon\mathbf{Y},\lambda\mu)=E^*_{ijmn}(0,\lambda\mu)+i2\pi\epsilon\sum_r E^*_{ijmn,r}(0,\lambda\mu)Y_r-\tfrac{1}{2}(4\pi^2)\epsilon^2\sum_{rs} E^*_{ijmn,rs}(0,\lambda\mu)Y_rY_s+\cdots. \quad (3.25e)$$

Here

$$A_{ij\cdots,pq\cdots}=\cdots O_qO_pA_{ij\cdots},$$

and

$$O_p=\frac{1}{i2\pi}\frac{\partial}{\partial Y_p}.$$

A stands for C^*, D^*, or E^*.

Substituting in (3.23), and collecting the terms of zero order in ϵ,

$$\sum_{j\mu}[C^*_{ij}(0,\lambda\mu)+\sum_{l\nu} D^*_{ijl}(0,\lambda\mu\nu)w_l(\nu)+\sum_{mn} E^*_{ijmn}(0,\lambda\mu)\epsilon_{mn}]u_j^{(0)}(\mu)$$
$$+e(\lambda)\frac{4\pi}{v_aY^2}\sum_j[Y_iY_j-\sum_{mn}\epsilon_{mn}(Y_iY_j\delta_{mn}+Y_iY_m\delta_{jn}+Y_jY_m\delta_{in}-2Y_iY_jY_mY_n/Y^2)]\times\sum_\mu e(\mu)u_j^{(0)}(\mu)=0. \quad (3.26)$$

Since $\sum_\mu C^*_{ij}(0,\lambda\mu)$, $\sum_\mu D^*_{ijl}(0,\lambda\mu\nu)$, $\sum_\mu E^*_{ijmn}(0,\lambda\mu)$, and $\sum_\mu e(\mu)$ are all zero, the solution of the above equation is

$$u_j^{(0)}(\mu)=u_j^{(0)}, \quad (3.27)$$

independent of μ.

The first-order equation is

$$\sum_{\mu j}[C^*_{ij}(0,\lambda\mu)+\sum_{l\nu} D^*_{ijl}(0,\lambda\mu\nu)w_l(\nu)+\sum_{mn} E^*_{ijmn}(0,\lambda\mu)\epsilon_{mn}]u_j^{(1)}(\mu)$$
$$=-\sum_{js} i2\pi Y_su_j^{(0)}(\sum_\mu C^*_{ij,s}(0,\lambda\mu)+\sum_{\nu l} w_l(\nu)\sum_\mu D^*_{ijl,s}(0,\lambda\mu\nu)+\sum_{mn}\epsilon_{mn}\sum_\mu E^*_{ijmn,s}(0,\lambda\mu))$$
$$-e(\lambda)\left\{\frac{4\pi}{v_aY^2}\sum_j[Y_iY_j-\sum_{mn}\epsilon_{mn}(Y_iY_j\delta_{mn}+Y_iY_m\delta_{jn}+Y_jY_m\delta_{in}-2Y_iY_jY_mY_n/Y^2)]\sum_\mu e(\mu)u_j^{(1)}(\mu)\right.$$
$$\left.-\frac{4\pi}{v_a}\sum_j\frac{Y_iY_j}{Y^2}\sum_\nu e(\nu)w_j(\nu)\sum_k i2\pi Y_ku_k^{(0)}\right\}. \quad (3.28)$$

Now

$$C^*_{ij}(0,\lambda\mu)=\sum_M {}^N\Phi_{ij}(0\lambda,M\mu)+e(\lambda)[e(\mu)Q_{ij}(0,\lambda\mu)-\delta_{\mu\lambda}\sum_\pi e(\pi)Q_{ij}(0,\lambda\pi)]$$

$$=v_a\{{}^N[\lambda i,\mu j]+{}^C[\lambda i,\mu j]\}=V_a[\lambda i,\mu j], \quad (3.29a)$$

from (7a′) of RSI.

$$\sum_\mu C^*_{ij,s}(0,\lambda\mu)=\sum_{M\mu} {}^N\Phi_{ij}(0\lambda,M\mu)X_s(0\lambda,M\mu)+e(\lambda)\sum_\mu e(\mu)Q_{ij,s}(0,\lambda\mu)=v_a[{}^N(\lambda i,js)+{}^C(\lambda i,js)]=v_a(\lambda i,js), \quad (3.29b)$$

from (7b′) of RSI.

$$D^*_{ijl}(0,\lambda\mu\nu)=\sum_{mn} {}^N\Phi_{ijl}(0\lambda,M\mu,N\nu)+[e(\lambda)e(\mu)(\delta_{\nu\lambda}-\delta_{\nu\mu})R_{ijl}(0,\lambda\mu)+e(\lambda)e(\nu)\delta_{\mu\lambda}R_{ijl}(0,\lambda\nu)$$

$$-e(\lambda)\delta_{\mu\lambda}\delta_{\nu\lambda}\sum_\pi e(\pi)R_{ijl}(0,\lambda\pi)]=v_a\{{}^N[\lambda i,\mu j,\nu l]+{}^C[\lambda i,\mu j,\nu l]\}=v_a[\lambda i,\mu j,\nu l], \quad (3.29c)$$

from (14a) of RSI.

$$\sum_\mu D^*_{ijl,s}(0,\lambda\mu\nu)=\sum_N\sum_{M\mu} {}^N\Phi_{ijl}(0\lambda,M\mu,N\nu)X_s(0\lambda,M\mu)+e(\lambda)\sum_\mu e(\mu)(\delta_{\nu\lambda}-\delta_{\nu\mu})R_{ijl,s}(0,\lambda\mu)$$

$$=v_a\{{}^N[\lambda i,\nu l,js]^\dagger+{}^C[\lambda i,\nu l,js]^\dagger\}=v_a[\lambda i,\nu l,js]^\dagger, \quad (3.29d)$$

from (14b′) of RSI.

$$[\lambda i,\nu l,js]=[\lambda i,\nu l,js]^\dagger-[\lambda s,\nu l]\delta_{ij}-[\lambda i,\nu s]\delta_{lj}; \quad (3.29d')$$

$[\lambda i,\nu l,js]^\dagger$ is not symmetric in $(j\rightleftharpoons s)$ while $[\lambda i,\nu l,js]$ is symmetric in $(j\rightleftharpoons s)$.

$$E^*_{ij,mn}(0,\lambda\mu)=\sum_M\sum_{N\nu} {}^N\Phi_{ijm}(0\lambda,M\mu,N\nu)X_n(N\nu)-e(\lambda)[e(\mu)R_{ijm,n}(0,\lambda\mu)-\delta_{\mu\lambda}\sum_\pi e(\pi)R_{ijm,n}(0,\lambda\pi)]$$

$$=v_a[\lambda i,\mu j,mn]^\dagger, \quad (3.29e)$$

$$\sum_\mu E^*_{ijmn,s}(0,\lambda\mu)=\sum_{M\mu}\sum_{N\nu} {}^N\Phi_{ijm}(0\lambda,M\mu,N\nu)X_n(N\nu)X_s(0\lambda,M\mu)-e(\lambda)\sum_\mu e(\mu)R_{ijm,ns}(0,\lambda\mu)$$

$$=v_a\{{}^N[\lambda i,(js),(mn)]+{}^C[\lambda i,(js),(mn)]\}=v_a[\lambda i,(js),(mn)], \quad (3.29f)$$

from (14d′) of RSI.

$$[\lambda i,js,mn]=[\lambda i,(js),(mn)]-(\lambda n,js)\delta_{im}-(\lambda s,mn)\delta_{ij}-(\lambda i,sn)\delta_{jm}, \quad (3.29f')$$

from (14c′) of RSI. $[\lambda i,(js),(mn)]$ is symmetric only in the interchange of $(js)\rightleftharpoons(mn)$, while $[\lambda i,js,mn]$ is symmetric in $(j\rightleftharpoons s)$, $(m\rightleftharpoons n)$, and $(js)\rightleftharpoons(mn)$.

Accompanying the displacement we have a change in polarization $\delta\mathbf{P}$ and a macroscopic electric field $\mathbf{e}$. Toupin[4] has emphasized the point that the independent variable in the electrical field is the spatial coordinate x_i and not the material coordinate X_i. So we write

$$\mathbf{e}(\mathbf{x})=\mathbf{e}\exp i2\pi\mathbf{y}\cdot\mathbf{x}. \quad (3.30)$$

The polarization wave accompanying the displacement can also be written as

$$\delta\mathbf{P}(\mathbf{x})=\delta\mathbf{P}\exp i2\pi\mathbf{y}\cdot\mathbf{x}. \quad (3.31)$$

The contribution to $\delta\mathbf{P}$ arises from the dipoles on the various sublattices,

$$\delta\mathbf{P}=\sum_\nu \delta\mathbf{P}(\nu). \quad (3.32)$$

$\mathbf{e}$ and $\delta\mathbf{P}$ can again be expanded in powers of ϵ as follows: Putting $\mathbf{y}=\epsilon\mathbf{y}$,

$$\delta\mathbf{P}=\delta\mathbf{P}^{(0)}+\epsilon\delta\mathbf{P}^{(1)}+\tfrac{1}{2}\epsilon^2\delta\mathbf{P}^{(2)}+\cdots, \quad (3.33)$$

$$\mathbf{e}=e^{(0)}+\epsilon\mathbf{e}^{(1)}+\tfrac{1}{2}\epsilon^2\mathbf{e}^{(2)}+\cdots, \quad (3.34a)$$

$$\delta\mathbf{P}^{(0)}(\nu)=(1/v_a')e(\nu)\mathbf{u}^{(0)}, \quad (3.34b)$$

$$\delta\mathbf{P}^{(1)}(\nu)=(1/v_a')[e(\nu)\mathbf{u}^{(1)}(\nu)-\sum_k i2\pi y_k u_k^{(0)}e(\nu)\mathbf{x}(0\nu)]. \quad (3.34c)$$

The second contribution to $\delta\mathbf{P}^{(1)}(\nu)$ arises as follows. Following Toupin,[4] we may consider $-\mathrm{div}(\delta\mathbf{P}^{(0)}(\nu)\times\exp i2\pi\mathbf{y}\cdot\mathbf{x})v_a'$ as an additional charge $\delta e(\nu)$; the dipole moment due to this additional charge is $\delta e(\nu)\mathbf{x}(0\nu)$. This contribution is also of the first order in ϵ. This interpretation receives support from the perfect agreement between the theoretical expression $\delta\mathbf{P}$ on lattice theory and the Eq. (2.23) and the lattice-theoretical equation of motion and Eq. (2.27).

The polarization of the medium is therefore

$$\delta\mathbf{P}^{(0)}=(1/v_a')\sum_\nu e(\nu)\mathbf{u}^{(0)}=0\,,\tag{3.35a}$$

$$\begin{aligned}\delta\mathbf{P}^{(1)}&=(1/v_a')[e(\nu)\mathbf{u}^{(1)}(\nu)-\sum_k i2\pi y_k u^{(0)}{}_k\sum_\nu e(\nu)\mathbf{x}(0\nu)]\\&=(1/v_a')[e(\nu)\mathbf{u}^{(1)}(\nu)-v_a'\sum_k i2\pi y_k u^{(0)}{}_k\mathbf{P}].\end{aligned}\tag{3.35b}$$

Born and Huang[7] have shown that if $\mathbf{e}$ and $\delta\mathbf{P}$ are related by Eq. (2.31), then

$$e_i^{(0)}=-4\pi\frac{y_i}{y^2}\sum_j y_j\delta P_j^{(0)}=0\,,\tag{3.36a}$$

$$\begin{aligned}e_i^{(1)}&=-4\pi\frac{y_i}{y^2}\sum_j y_j\delta P_j^{(1)}\\&=-\frac{4\pi}{v_a'}\frac{y_i}{y^2}\sum_j y_j[\sum e(\nu)u_j^{(1)}(\nu)\\&\qquad-v_a'\sum_k i2\pi y_k u^{(0)}{}_k P_j].\end{aligned}\tag{3.36b}$$

Taking into account the fact that to first order in ϵ_{mn},

$$v_a'=v_a(1+\sum_{mn}\epsilon_{mn}\delta_{mn})\,,$$

and using Eq. (3.10), we can write $e_i^{(1)}$ to first order in ϵ_{mn} and P_j as

$$\begin{aligned}e_i^{(1)}=&-\frac{4\pi}{v_a}\frac{1}{Y^2}\sum_{\mu j}[Y_iY_j-\sum_{mn}\epsilon_{mn}(Y_iY_m\delta_{jn}+Y_jY_m\delta_{in}+Y_iY_j\delta_{mn}-2Y_iY_jY_mY_n/Y^2)]e(\mu)u_j^{(1)}(\mu)\\&+\frac{4\pi}{v_a}\frac{Y_i}{Y^2}\sum_j Y_j\sum_\nu e(\nu)w_j(\nu)\sum_k i2\pi Y_k u_k^{(0)}.\end{aligned}\tag{3.37}$$

So the first-order equation of motion (3.28) can be written as

$$v_a\sum_{\mu j}[\lambda i,\mu j]'u_j^{(1)}(\mu)=-v_a\sum_{js}i2\pi Y_s u_j^{(0)}\{(\lambda i,js)+\sum_{\nu l}[\lambda i,\nu l,js]^\dagger w_l(\nu)+\sum_{mn}[\lambda i,(js),(mn)]\epsilon_{mn}\}+e(\lambda)e_i^{(1)}.\tag{3.38}$$

Here

$$[\lambda i,\mu j]'=[\lambda i,\mu j]+\sum_{\nu l}[\lambda i,\mu j,\nu l]w_l(\nu)+\sum_{mn}[\lambda i,\nu j,mn]^\dagger\epsilon_{mn}.\tag{3.39}$$

The matrix $[\lambda i,\mu j]'$ is of order $3n\times 3n$, where n is the number of particles in the basis cell. It is singular since $\sum_\mu[\lambda i,\mu j]'=0$. Following Born and Huang,[7] we form the matrix $\{\lambda i,\mu j\}'$ as follows. All rows and all columns of the matrix $[\lambda i,\mu j]$ having the index $\lambda=1$ or $\mu=1$ are omitted. The resulting matrix is inverted and bordered with zeros to make up the $3n\times 3n$ matrix $\{\lambda i,\mu j\}'$. To first order in ϵ_{mn} and $w_l(\nu)$,

$$\{\lambda i,\mu j\}'=\{\lambda i,\mu j\}-\sum_{\alpha\beta}\sum_{ab}\{\lambda i,\alpha a\}[\sum_{\nu l}[\alpha a,\beta b,\nu l]w_l(\nu)+\sum_{mn}[\alpha a,\beta b,mn]^\dagger\epsilon_{mn}]\{\beta b,\mu j\}.\tag{3.40}$$

$\{\lambda i,\mu j\}$ is obtained from $[\lambda i,\mu j]$ following the above procedure.

The solution of (3.38) can then be written as

$$\begin{aligned}u_i^{(0)}=&-\sum_{js}i2\pi Y_s u_j^{(0)}[\sum_{\rho r}\{\lambda i,\rho r\}'[(\rho r,js)+\sum_{\nu l}[\rho r,\nu l,js]^\dagger w_l(\nu)+\sum_{mn}[\rho r,(js),(mn)]\epsilon_{mn}]]\\&+e(\lambda)\sum_j e_j^{(1)}\sum_\rho\frac{1}{v_a}e(\rho)\{\lambda i,\rho j\}'.\end{aligned}\tag{3.41}$$

With the help of (3.35b), the polarization $\delta P^{(1)}$ can be written as

$$\begin{aligned}\delta P_i^{(1)}=\frac{v_a}{v_a'}\Bigg[&-\sum_{js}i2\pi Y_s u_j^{(0)}\bigg[\frac{1}{v_a}\sum_{\lambda\rho r}e(\lambda)\{\lambda i,\rho r\}'((\rho r,js)+\sum_{\nu l}[\rho r,\nu l,js]^\dagger w_l(\nu)+\sum_{mn}[\rho r,(js),(mn)]\epsilon_{mn})\bigg]\\&+\sum_j e_j^{(1)}\sum_{\lambda\rho}\frac{e(\lambda)e(\rho)}{v_a^2}\{\lambda i,\rho j\}'-\sum_k i2\pi Y_k u_k^{(0)}P_i\Bigg].\end{aligned}\tag{3.42}$$

If there were no initial deformation or polarization

$$u_i^{(1)}(\lambda)=-\sum_{js} i2\pi Y_s u_j^{(0)} A(\lambda i,js)+\sum_j e_j^{(1)} \sum_\rho \frac{1}{v_a} e(\rho)\{\lambda i,\rho j\}, \tag{3.43a}$$

$$\delta P_i^{(1)}=\frac{1}{v_a}\sum_\lambda e(\lambda)u_i^{(1)}(\lambda)=-\sum_{js} i2\pi Y_s u_j^{(0)}\left[\frac{1}{v_a}\sum_\lambda e(\lambda)A(\lambda i,js)\right]+\sum_j e_j^{(1)}\sum_{\lambda\rho}\frac{1}{v_a^2}e(\lambda)e(\rho)\{\lambda i,\rho j\}. \tag{3.43b}$$

Here

$$A(\lambda i,js)=\sum_{\rho r}\{\lambda i,\rho r\}(\rho r,js). \tag{3.43b$'$}$$

Comparing with Eqs. (2.6) and (3.5), one can identify $w_i(\lambda)$ with $u_i^{(1)}(\lambda)$, $\delta\mathbf{P}^{(1)}$ with $\mathbf{P}$, $\mathbf{e}^{(1)}$ with $\mathbf{E}$, and $i2\pi Y_s u_j^{(0)}$ with ϵ_{js}. To the first order in ϵ_{js} and E_p,

$$w_i(\lambda)=-\sum_{mn}A(\lambda i,mn)\epsilon_{mn}+\sum_p E_p\sum_\pi\frac{1}{v_a}e(\pi)\{\lambda i,\pi p\}, \tag{3.44a}$$

$$P_i=-\frac{1}{v_a}\sum_{mn}\epsilon_{mn}\Big[\sum_\lambda e(\lambda)A(\lambda i,mn)\Big]+\sum_p E_p\left[\frac{1}{v_a^2}\sum_{\lambda\pi}e(\lambda)\{\lambda i,\pi p\}e(\pi)\right]. \tag{3.44b}$$

The piezoelectric constant $E_{i,mn}$ in the undeformed unpolarized state is given by

$$E_{i,mn}=\frac{1}{v_a}\sum_\lambda e(\lambda)A(\lambda i,mn), \tag{3.45}$$

and the electric susceptibility in the undeformed and unpolarized state is given by

$$\mathcal{G}_{ij}=\frac{1}{v_a^2}\sum_{\lambda\pi}e(\lambda)\{\lambda i,\pi j\}e(\pi). \tag{3.46}$$

The above results were obtained by Born and Huang.[7]

For the case of the initially deformed and polarized lattice we substitute for $w_l(\nu)$ and P_i from (3.44a) and (3.44b) in (3.42), and obtain an expression for $\delta P_i^{(1)}$ involving only ϵ_{mn} and E_p. We compare this expression with (2.23).

First let us consider the coefficient of $e_j^{(1)}$ in the resulting expression. This is

$$\frac{v_a}{v_a'}\Bigg\{\frac{1}{v_a^2}\sum_{\lambda\rho}e(\lambda)e(\rho)\Big(\{\lambda i,\rho j\}-\sum_{mn}\epsilon_{mn}\Big[\sum_{\alpha\beta}\sum_{ab}\{\lambda i,\alpha a\}\{\beta b,\rho j\}[\alpha a,\beta b,mn]^\dagger-\sum_{\nu l}[\alpha a,\beta b,\nu l]A(\nu l,mn)\Big]$$
$$-\frac{1}{v_a}\sum_p E_p\Big[\sum_{\alpha a}\sum_{\beta b}\sum_{\nu l}\{\lambda i,\alpha a\}e(\pi)\{\pi p,\nu l\}\{\beta b,\rho j\}[\alpha a,\beta b,\nu l]\Big]\Big)\Bigg\}. \tag{3.47}$$

Comparing with the coefficient of e_j in (2.23), one gets

$$\mathcal{G}_{ijp}=-\frac{1}{v_a^3}\sum_{\lambda\rho\pi}\sum_{\alpha a}\sum_{\beta b}\sum_{\nu l}[\alpha a,\beta b,\nu l]e(\lambda)\{\lambda i,\alpha a\}e(\pi)\{\pi p,\nu l\}e(\rho)\{\rho j,\beta b\}. \tag{3.48}$$

The right-hand side has the proper symmetry, namely, $i\rightleftharpoons j\rightleftharpoons p$.

$$\mathcal{P}_{[ij,mn]}+\mathcal{G}_{in}\delta_{jm}+\mathcal{G}_{jn}\delta_{im}=-\frac{1}{v_a^2}\sum_{\lambda\rho}\sum_{\alpha a}\sum_{\beta b}e(\lambda)\{\lambda i,\alpha a\}e(\rho)\{\beta b,\rho j\}\Big\{[\alpha a,\beta b,mn]^\dagger-\sum_{\nu l}[\alpha a,\beta b,\nu l]A(\nu l,mn)\Big\}. \tag{3.49}$$

Using (3.29d$'$), the right side of (3.49) becomes

$$-(1/v_a^2)\sum_{\lambda\rho}\sum_{\alpha a}\sum_{\beta b}e(\lambda)\{\lambda i,\alpha a\}e(\rho)\{\beta b,\rho j\}\Big\{[\alpha a,\beta b,mn]-\sum_{\nu l}[\alpha a,\beta b,\nu l]A(\nu l,mn)\Big\}$$
$$-(1/v_a^2)\delta_{in}\sum_{\lambda\rho}e(\lambda)e(\rho)\{\lambda m,\rho j\}-(1/v_a^2)\delta_{jn}\sum_{\lambda\rho}e(\lambda)e(\rho)\{\lambda i,\rho m\}. \tag{3.50}$$

Using (3.46), one can therefore write

$$\mathcal{P}_{[ij,mn]}=-(1/v_a^2)\sum_{\lambda\rho}\sum_{\alpha a}\sum_{\beta b} e(\lambda)\{\lambda i,\alpha a\}e(\rho)\{\beta b,\rho j\}\{[\alpha a,\beta b,mn]-\sum_{\nu l}[\alpha a,\beta b,\nu l]A(\nu l,mn)\}$$
$$-[\mathcal{G}_{in}\delta_{jm}+\mathcal{G}_{jn}\delta_{im}+\mathcal{G}_{jm}\delta_{in}+\mathcal{G}_{im}\delta_{jn}]. \quad (3.51)$$

The right side has the proper symmetry ($i\rightleftharpoons j$) and ($m\rightleftharpoons n$).

The coefficient of $-i2\pi Y_s u_j^{(0)}$ in (3.42), after substituting for $w_l(\nu)$, P_i, and $\{\lambda i,\rho r\}'$ from (3.44a), (3.44b), and (3.40), is

$$\frac{v_a}{v_a'}\Bigg\{\frac{1}{v_a}\sum_\lambda e(\lambda)\Big[A(\lambda i,js)+\sum_{mn}\epsilon_{mn}\Big(\sum_{\rho r}\{\lambda i,\rho r\}[[\rho r,(js),(mn)]-\sum_{\tau t}[\rho r,\tau t,mn]^\dagger A(\tau t,js)-\sum_{\tau t}[\rho r,\tau t,js]^\dagger A(\tau t,mn)$$
$$+\sum_{\alpha a}\sum_{\beta b}[\rho r,\alpha a,\beta b]A(\alpha a,js)A(\beta b,mn)]\Big)\Big]+\sum_p E_p\Bigg(\frac{1}{v_a^2}\sum_{\rho r}\{\lambda i,\rho r\}[\sum_{\nu l}[\rho r,\nu l,js]^\dagger-\sum_{\tau t}[\rho r,\tau t,\nu l]A(\tau t,js)$$
$$+\sum_\beta e(\beta)\{\nu l,\beta p\}]\Bigg)+\sum_p E_p\mathcal{G}_{ip}\delta_{sj}\Bigg\}. \quad (3.52)$$

Comparing with the coefficient of $-\partial u_j/\partial X_s$ in (2.23), one gets

$$\hat{E}_{[ip,js]}-\mathcal{G}_{is}\delta_{jp}-\mathcal{G}_{sp}\delta_{ij}+\mathcal{G}_{ip}\delta_{js}=(1/v_a^2)\sum_{\lambda\beta}\sum_{\rho r}\sum_{\nu l} e(\lambda)\{\lambda i,\rho r\}e(\beta)\{\beta p,\nu l\}[[\rho r,\nu l,js]-\sum_{\tau t}[\rho r,\nu l,\tau t]A(\tau t,js)]$$
$$+(1/v_a^2)\delta_{is}\sum_{\lambda\beta} e(\lambda)e(\beta)[\lambda j,\beta p]+(1/v_a^2)\delta_{sp}\sum_{\lambda\beta} e(\lambda)[\lambda i,\beta j]e(\beta)+\mathcal{G}_{ip}\delta_{js}, \quad (3.53)$$

so that

$$\hat{E}_{[ip,js]}=\{(1/v_a^2)\sum_{\lambda\beta}\sum_{\rho r}\sum_{\nu l} e(\lambda)\{\lambda i,\rho r\}e(\beta)\{\beta p,\nu l\}[[\rho r,\nu l,js]-\sum_{\tau t}[\rho r,\nu l,\tau t]A(\tau t,js)]\}$$
$$+[\mathcal{G}_{jp}\delta_{is}+\mathcal{G}_{ij}\delta_{sp}+\mathcal{G}_{sp}\delta_{ij}+\mathcal{G}_{ip}\delta_{js}]. \quad (3.54)$$

The right-hand side has the proper symmetry ($i\rightleftharpoons p$) and ($j\rightleftharpoons s$).

Comparing the coefficient of ϵ_{mn} in the term containing $-\partial u_j/\partial X_s$ in (2.23) with the coefficient of ϵ_{mn} in (3.52), and using (3.29d′), (3.29f′), and (3.48b′), one gets

$$\hat{E}_{i,js,mn}+E_{i,ns}\delta_{jm}+E_{n,js}\delta_{im}+E_{s,nm}\delta_{ij}-E_{i,mn}\delta_{js}$$
$$=(1/v_a)\sum_{\lambda\rho r} e(\lambda)\{\lambda i,\rho r\}\{[\rho r,js,mn]-\sum_{\tau t}[\rho r,\tau t,mn]A(\tau t,js)-\sum_{\tau t}[\rho r,\tau t,js]A(\tau t,mn)$$
$$+\sum_{\alpha a}\sum_{\beta b}[\rho r,\alpha a,\beta b]A(\alpha a,mn)A(\beta b,js)\}+E_{i,sn}\delta_{jm}-E_{i,mn}\delta_{js}-E_{m,js}\delta_{in}-E_{j,mn}\delta_{is}.$$

Therefore,

$$\hat{E}_{i,js,mn}=(1/v_a)\sum_{\lambda\rho r} e(\lambda)\{\lambda i,\rho r\}\{[\rho r,js,mn]-\sum_{\tau t}[\rho r,\tau t,js]A(\tau t,mn)-\sum_{\tau t}[\rho r,\tau t,mn]A(\tau t,js)$$
$$+\sum_{\alpha a}\sum_{\beta b}[\rho r,\alpha a,\beta b]A(\alpha a,js)A(\beta b,mn)\}-[E_{n,js}\delta_{im}+E_{m,js}\delta_{in}+E_{s,mn}\delta_{ij}+E_{j,mn}\delta_{is}]. \quad (3.55)$$

The right side has the requisite symmetry $j\rightleftharpoons s$, $m\rightleftharpoons n$, and $(js)\rightleftharpoons(mn)$.

Comparing the second-order terms in ϵ in the equation of motion (3.23) and summing over λ, one gets

$$\rho_0 v_a\omega^2 u_i^{(0)}=\sum_{jrs}4\pi^2 Y_r Y_s u_j^{(0)}(-\tfrac{1}{2})\{\sum_{\lambda\mu}C^*_{ij,rs}(0,\lambda\mu)+\sum_{\nu l}w_l(\nu)[\sum_{\lambda\mu}D^*_{ijl,rs}(0,\lambda\mu\nu)]+\sum_{mn}\epsilon_{mn}[\sum_{\lambda\mu}E^*_{ijmn,rs}(0,\lambda\mu)]\}$$
$$+\sum_{\mu jr}i2\pi Y_r u_j^{(1)}(\mu)\{\sum_\lambda C^*_{ij,r}(0,\lambda\mu)+\sum_{\nu l}w_l(\nu)[\sum_\lambda D^*_{ijl,r}(0,\lambda\mu\nu)]+\sum_{mn}\epsilon_{mn}[\sum_\lambda E^*_{ijmn,r}(0,\lambda\mu)]\}$$
$$+\sum_r i2\pi Y_r[(4\pi/V_a)(Y_i/Y^2)\sum_{j\mu}Y_j e(\mu)u_j^{(1)}(\mu)]\sum_\lambda e(\lambda)w_r(\lambda). \quad (3.56)$$

Now

$$\sum_{\lambda\mu}C^*_{ij,rs}(0,\lambda\mu)=\sum_{\lambda\mu}\sum_M {}^N\Phi_{ij}(0\lambda,M\mu)X_r(0\lambda,M\mu)X_s(0\lambda,M\mu)+\sum_{\lambda\mu}e(\lambda)e(\mu)Q_{ij,rs}(0,\lambda\mu)$$
$$=-2v_a[{}^N\hat{C}_{[ij,rs]}+{}^C\hat{C}_{[ij,rs]}]=-2V_a\hat{C}_{[ij,rs]}, \quad (3.57a)$$

from (8) of RSI.

$$\sum_{\lambda\mu} D^*_{ijl,rs}(0,\lambda\mu\nu)=\sum_{M\mu}\sum_{N\lambda} {}^N\Phi_{ijl}(0\lambda,M\mu,N\nu)X_r(0\lambda,M\mu)X_s(0\lambda,M\mu)+\sum_{\lambda\mu} e(\lambda)e(\mu)R_{ijl,rs}(0,\lambda\mu)[\delta_{\nu\lambda}-\delta_{\nu\mu}]$$

$$=-\sum_{\lambda\mu}\sum_{M'N'} {}^N\Phi_{lij}(0\nu,N'\lambda,M'\mu)[X_r(0\nu,N'\lambda)-X_r(0\nu,M'\mu)][X_s(0\nu,N'\lambda)-X_s(0\nu,M'\mu)]$$

$$+\sum_{\lambda\mu} e(\mu)e(\lambda)R_{ijl,rs}(0,\lambda\mu)[\delta_{\nu\lambda}-\delta_{\nu\mu}]=-2\sum_{\lambda\mu}\sum_{M'N'} {}^N\Phi_{lij}(0\nu,N'\lambda,M'\mu)X_r(0\nu,M'\mu)X_s(0\nu,N'\lambda)$$

$$+2e(\nu)\sum_{\mu} e(\mu)R_{ijl,rs}(0,\nu\mu)=-2v_a[\nu l,(jr),(is)], \quad (3.57b)$$

from (3.29f).

$$\sum_{\lambda\mu} E^*_{ijmn,rs}(0,\lambda\mu)=\sum_{\lambda}\sum_{M\mu}\sum_{N\nu} {}^N\Phi_{ijm}(0\lambda,M\mu,N\nu)X_n(N\nu)X_r(0\lambda,M\mu)X_s(0\lambda,M\mu)-\sum_{\lambda\mu} e(\lambda)e(\mu)R_{ijm,nrs}(0,\lambda\mu)$$

$$=-2v_a\{{}^N\hat{C}_{ij,[mn],rs}+{}^C\hat{C}_{ij,[mn],rs}\}=-2v_a\hat{C}_{ij,[mn],rs}, \quad (3.57c)$$

from (15) of RSI.

$$\sum_{\lambda} C^*_{ij,r}(0,\lambda\mu)=-v_a(\mu j,ir), \quad (3.57d)$$

$$\sum_{\lambda} D^*_{ijl,r}(0,\lambda\mu\nu)=-v_a[\nu l,\mu j,ir]^\dagger, \quad (3.57e)$$

$$\sum_{\lambda} E^*_{ijmn,r}(0,\lambda\mu)=-v_a[\mu j,(mn),(ir)], \quad (3.57f)$$

$$\sum_{r} i2\pi Y_r[(4\pi/v_a)(Y_i/Y^2)\sum_{j} Y_je(\mu)u_j^{(1)}(\mu)]\sum_{\lambda} e(\lambda)w_l(\lambda)=-v_a\sum_{r} i2\pi Y_re_i^{(1)}P_r, \quad (3.58)$$

to the first order in ϵ_{mn} and P_i. Thus, (3.56) becomes

$$\rho_0\omega^2u_i^{(0)}=4\pi^2\sum_{jrs} Y_rY_su_j^{(0)}[\hat{C}_{[ij,rs]}+\sum_{\nu l} w_l(\nu)[\nu l,(jr),(is)]+\sum_{mn}\epsilon_{mn}\hat{C}_{ij,[mn],rs}]$$

$$-\sum_{\mu jr} i2\pi Y_ru_j^{(1)}(\mu)\{(\mu j,ir)+\sum_{\nu l} w_l(\nu)[\nu l,\mu j,ir]^\dagger+\sum_{mn}\epsilon_{mn}[\mu j,(mn),(ir)]\}-\sum_{r} i2\pi Y_re_i^{(1)}P_r. \quad (3.59)$$

Substituting for $u_j^{(1)}(\mu)$ from (3.41) and collecting the coefficients of $-i2\pi Y_re_j^{(1)}$, we get

$$(1/v_a)(\sum_{\beta} e(\beta)A(\beta j,ir)+\sum_{l} w_l(\nu)\sum_{\mu\beta}\sum_{a}\{\mu a,\beta j\}e(\beta)\times[[\mu a,\nu l,ir]^\dagger-\sum_{\sigma s}[\mu a,\nu l,\sigma s]A(\sigma s,ir)]$$

$$+\sum_{mn}\epsilon_{mn}\sum_{\mu\beta}\sum_{a}\{\mu a,\beta j\}e(\beta)\times[-\sum_{\sigma s}[\mu a,\sigma s,mn]^\dagger A(\sigma s,ir)+[\mu a,(mn),(ir)]]+P_r\delta_{ij}). \quad (3.60)$$

Substituting for $w_l(\nu)$ and P_r from (3.44a) and (2.6), and making use of (3.53) and (3.55), it can be shown that the coefficient of $-i2\pi Y_re_j^{(1)}$ agrees exactly with the coefficient of $-\partial e_j/\partial X_r$ in (2.27).

Now, let us consider the coefficient of $4\pi^2Y_rY_su_j^{(0)}$ in (3.59) after substituting for $u_j^{(1)}(\mu)$ from (3.41). This is

$$2\hat{C}_{[ij,rs]}-\sum_{\mu a}(\mu a,ir)A(\mu a,js)-\sum_{\mu a}(\mu a,is)A(\mu a,jr)+\sum_{l\nu} w_l(\nu)\{[\nu l,(ir),(js)]+[\nu l,(is),(jr)]-\sum_{\beta b}[[\nu l,\beta b,js]^\dagger A(\beta b,ir)$$

$$+[\nu l,\beta b,ir]^\dagger A(\beta b,js)+[\nu l,\beta b,jr]^\dagger A(\beta b,is)+[\nu l,\beta b,is]^\dagger A(\beta b,jr)]+\sum_{\alpha a}\sum_{\beta b}[\alpha a,\beta b,\nu l][A(\alpha a,ir)A(\beta b,js)$$

$$+A(\alpha a,is)A(\beta b,jr)]\}+\sum_{mn}\epsilon_{mn}\{2\hat{C}_{ij,[mn],rs}-\sum_{\alpha a}[[\alpha a,(js),(mn)]A(\alpha a,ir)+[\alpha a,(ir),(mn)]A(\alpha a,js)$$

$$+[\alpha a,(jr),(mn)]A(\alpha a,is)+[\alpha a,(is),(mn)]A(\alpha a,jr)]$$

$$+\sum_{\alpha a}\sum_{\beta b}[\alpha a,\beta b,mn]^\dagger[A(\alpha a,ir)A(\beta b,js)+A(\alpha a,is)A(\beta b,jr)]\}. \quad (3.61)$$

This should be compared with the coefficient of $-\partial^2u_j/\partial X_r\partial X_s$ in (2.27), namely,

$$\bar{C}'_{ir,js}+\bar{C}'_{is,jr}+\sum_{mn}\epsilon_{mn}(2\bar{C}'_{rs,mn}\delta_{ij}+\bar{C}'_{ir,ns}\delta_{jm}+\bar{C}'_{is,nr}\delta_{jm}+\bar{C}'_{js,nr}\delta_{im}+\bar{C}'_{ns,jr}\delta_{im}+\bar{C}'_{ir,js,mn}+\bar{C}'_{is,jr,mn})$$

$$+\sum_{p} E_p(\bar{C}'_{p,ir,js}+\bar{C}'_{p,is,jr}+2E_{p,rs}\delta_{ij}+E_{s,ir}\delta_{jp}+E_{r,is}\delta_{jp}+E_{r,js}\delta_{ip}+E_{s,jr}\delta_{ip}). \quad (3.62)$$

If the lattice were undeformed and unpolarized, one would get

$$2\hat{C}_{[ij,rs]}-\sum_{\mu a}(\mu a,ir)A(\mu a,js)-\sum_{\mu a}(\mu a,is)A(\mu a,jr)=\bar{C}'_{ir,js}+\bar{C}'_{is,jr}. \tag{3.63}$$

This leads to the Kun-Huang relation on the second-order coupling parameters

$$\hat{C}_{[ij,rs]}=\hat{C}_{ij,rs}, \tag{3.64}$$

i.e., $\hat{C}_{[ij,rs]}$ must be symmetric in the interchange $(ij)\rightleftharpoons(rs)$. The second-order elastic constants are given by

$$\bar{C}'_{ir,js}=C_{ir,js}-\sum_{\mu a}(\mu a,ir)A(\mu a,js)=\hat{C}_{ij,rs}+\hat{C}_{jr,is}-\hat{C}_{ir,js}-\sum_{\mu a}(\mu a,ir)A(\mu a,js). \tag{3.65}$$

Substituting for $w_l(\nu)$ from (3.44a) into (3.61), the coefficient of ϵ_{mn} is

$$\begin{aligned}&2\hat{C}_{ij,[mn],rs}-\sum_{\alpha a}\{E[\alpha a,[js,mn]]A(\alpha a,ir)+E[\alpha a,[mn,ir]]A(\alpha a,js)+E[\alpha a,[ir,js]]A(\alpha a,mn)\}\\&-\sum_{\alpha a}\sum_{\beta b}\sum_{\nu l}[\alpha a,\beta b,\nu l]A(\alpha a,ir)A(\beta b,js)A(\nu l,mn)-\sum_{\alpha a}\{E[\alpha a,[jr,mn]]A(\alpha a,is)+E[\alpha a,[mn,is]]A(\alpha a,jr)\\&+E[\alpha a,[is,jr]]A(\alpha a,mn)\}-\sum_{\alpha a}\sum_{\beta b}\sum_{\nu l}[\alpha a,\beta b,\nu l]A(\alpha a,is)A(\beta b,jr)A(\nu l,mn)-\sum_{\alpha a}[2(\alpha a,rs)A(\alpha a,mn)\delta_{ij}\\&+(\alpha a,sn)A(\alpha a,ir)\delta_{jm}+(\alpha a,rn)A(\alpha a,is)\delta_{jm}+(\alpha a,rn)A(\alpha a,js)\delta_{im}+(\alpha a,sn)A(\alpha a,jr)\delta_{im}]. \end{aligned}\tag{3.66}$$

Here we have used (3.29d′) and (3.29f′).

$$E[\alpha a,[jr,mn]]=[\alpha a,jr,mn]-C[\alpha a,[jr,mn]], \tag{3.66′}$$

$$C[\alpha a,[jr,mn]]=\sum_{\nu l}[\alpha a,\nu l,mn]A(\nu l,jr), \tag{3.66″}$$

from Eqs. (28a), and (28b) of RSI.

Comparing this with the coefficient of ϵ_{mn} in (3.62), one can get the Kun-Huang relation among the third-order coupling parameters, as was done in RSI. This relation is

$$2[\hat{C}_{ij,[mn],rs}-\hat{C}_{[jn,rs]}\delta_{im}-\hat{C}_{[ni,rs]}\delta_{jm}-C_{rs,mn}\delta_{ij}];$$

it must be symmetric in $(ir)\rightleftharpoons(js)$. As in RSI, we can write the expression for $\bar{C}'_{ir,js,mn}$ as

$$\begin{aligned}\bar{C}'_{ir,js,mn}=C_{ir,js,mn}&-\sum_{\alpha a}\{E[\alpha a,[js,mn]]A(\alpha a,ir)+E[\alpha a,[mn,ir]]A(\alpha a,js)+E[\alpha a,[ir,js]]A(\alpha a,mn)\}\\&-\sum_{\alpha a}\sum_{\beta b}\sum_{\nu l}[\alpha a,\beta b,\nu l]A(\alpha a,ir)A(\beta b,js)A(\nu l,mn),\end{aligned} \tag{3.67}$$

where

$$\begin{aligned}C_{ir,js,mn}=\hat{C}_{ij,[mn],rs}+\hat{C}_{rj,[mn],is}-\hat{C}_{ir,[mn],js}&-[\hat{C}_{[nj,rs]}-\hat{C}_{[nr,js]}]\delta_{im}-[\hat{C}_{[in,rs]}+\hat{C}_{[nr,is]}]\delta_{jm}\\&+[\hat{C}_{[nj,is]}-\hat{C}_{[in,js]}]\delta_{rm}-[C_{rs,mn}\delta_{ij}+C_{is,mn}\delta_{rj}-C_{js,mn}\delta_{ir}].\end{aligned} \tag{3.68}$$

The coefficient of E_p after substituting for $w_l(\nu)$ from (3.44a) is

$$\begin{aligned}&(1/v_a)\sum_{\nu l}\{[\nu l,(ir),(js)]-\sum_{\alpha a}[[\nu l,\alpha a,js]^{\dagger}A(\alpha a,ir)+[\nu l,\alpha a,ir]^{\dagger}A(\alpha a,js)]+\sum_{\alpha a}\sum_{\beta b}A(\alpha a,ir)[\alpha a,\beta b,\nu l]A(\beta b,js)\}\\&\times\{\nu l,\pi p\}e(\pi)+(1/v_a)\sum_{\nu l}\{[\nu l,(is),(jr)]-\sum_{\alpha a}[[\nu l,\alpha a,jr]^{\dagger}A(\alpha a,is)+[\nu l,\alpha a,is]^{\dagger}A(\alpha a,jr)]\\&+\sum_{\alpha a}\sum_{\beta b}A(\alpha a,is)[\alpha a,\beta b,\nu l]A(\beta b,jr)\}\{\nu l,\pi p\}e(\pi).\end{aligned} \tag{3.69}$$

This is to be compared with

$$(\bar{C}'_{p,ir,js}+E_{p,rs}\delta_{ij}+E_{s,ir}\delta_{jp}+E_{r,js}\delta_{ip})+(\bar{C}'_{p,is,jr}+E_{p,rs}\delta_{ij}+E_{r,is}\delta_{jp}+E_{s,jr}\delta_{ip}),$$

from (3.62). Using (3.29d′) and (3.29f′) we get

$$\begin{aligned}\bar{C}'_{p,ir,js}+E_{p,rs}\delta_{ij}+E_{s,ir}\delta_{jp}+E_{r,js}\delta_{ip}=(1/v_a)\sum_{\nu\pi l}e(\pi)\{\nu l,\pi p\}\{[\nu l,js,ir]-\sum_{\alpha a}[[\nu l,\alpha a,js]A(\alpha a,ir)+[\nu l,\alpha a,ir]A(\alpha a,js)]\\+\sum_{\alpha a}\sum_{\beta b}A(\alpha a,ir)[\nu l,\alpha a,\beta b]A(\beta b,js)\}+E_{p,rs}\delta_{ij}-E_{j,ir}\delta_{ps}-E_{i,js}\delta_{pr}.\end{aligned} \tag{3.70}$$

Thus

$$\bar{C}'_{p,ir,js}=(1/v_a)\sum_{\nu l}\sum_{\pi} e(\pi)\{\nu l,\pi p\}\{[\nu l,js,ir]-\sum_{\alpha a}[[\nu l,\alpha a,js]A(\alpha a,ir)+[\nu l,\alpha a,ir]A(\alpha a,js)]$$
$$+\sum_{\alpha a}\sum_{\beta b}A(\alpha a,ir)[\nu l,\alpha a,\beta b]A(\beta b,js)\}-[E_{j,ir}\delta_{ps}+E_{s,ir}\delta_{pj}+E_{i,js}\delta_{pr}+E_{r,js}\delta_{pi}]. \quad (3.71)$$

The right-hand side has the requisite symmetry $(i\rightleftharpoons r)$, $(j\rightleftharpoons s)$, and $(ir)\rightleftharpoons(js)$.

Thus we have derived the lattice-theoretical expressions for $\bar{C}'_{ir,js,mn}$, $\mathcal{G}_{ij}$, $\mathcal{G}_{ijp}$, $\mathcal{P}_{[ij,mn]}$, $\hat{E}_{[ip,js]}$, $\hat{E}_{i,js,mn}$, and $\bar{C}'_{p,ir,js}$. The expressions derived here will be applied to the case of the fluorite lattice in the following paper.[11]

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Lattice Theory of the Elastic Dielectric: Application to the Fluorite Lattice*

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The lattice theory of the elastic dielectric developed in the preceding paper is applied to the fluorite lattice. Expressions are derived for the third-order elastic constants of the fluorite lattice in Axe's shell model. The values of the third-order elastic constants and the pressure derivatives of the second-order elastic constants are calculated for calcium, strontium, and barium fluorides on the rigid-ion and shell models. In calcium fluoride, the calculated values of the pressure derivatives of the second-order elastic constants are in fair agreement with Wong and Schuele's experimental values. The static dielectric constant and its strain dependence are also calculated for the three fluorides in the shell model.

I. INTRODUCTION

In the preceding paper, lattice-theoretical expressions were derived for the electrical susceptibility, the piezoelectric constants, the second-order elastic constants, and their linear coefficients of variation with strain and electric field for an ionic lattice. This paper will be referred to as RSII in the following. In the present paper, these theoretical expressions are applied to the fluorite lattice to calculate the third-order elastic constants and the strain dependence of the static dielectric constants of calcium, strontium, and barium fluorides.

The reasons for the choice of the fluorite lattice are as follows. The simplest ionic crystals to which the theoretical expressions could be applied are the alkali halides. However, the third-order elastic constants of the alkali halides have been calculated already by Bross,[1] N'Ranyan,[2] and Ghate.[3] The strain dependence of the dielectric constants has, however, not been calculated. In these crystals every atom is at a center of inversion and there is therefore no internal displacement when the lattice is elastically deformed. On the other hand, in the fluorite structure the anions are not at centers of inversion and they undergo internal displacements when the lattice is strained. The absence of internal displacements makes the theoretical expressions for the third-order elastic constants quite simple in the alkali halides. There is no such simplification in the fluorite lattice. Another consequence of the structure of the alkali halides is the fact that the polarizability of the ions plays no role in determining the values of the elastic constants. For elastic deformations, the ions behave as though they were rigid. This is not the case for the fluorite lattice. The polarizability of the anion influences the values of some of the elastic constants. Experiments to measure the third-order elastic constants of some crystals of fluorite structure are in progress in the Materials Research Laboratory, Pennsylvania State University.

Of the crystals of fluorite structure dealt with in this paper, calcium fluoride has been the subject of some theoretical discussion. Srinivasan,[4] Rajagopal,[5] and

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