# Electrostrictive Constants of Insulating Crystals*

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The electrostrictive constants of insulating crystals have been related to the microscopic coupling parameters of lattice theory. This is done within the framework of the Born-Huang method of long waves. It is shown that the electrostrictive constants, as commonly defined, include the effects of Maxwell stresses and local stresses in the crystal. The connection between the theory and the properties of displacive ferroelectrics in the unpolarized phase is discussed. The relation between the observed temperature dependence of the electrostrictive coefficients and the temperature dependent "ferroelectric mode" is exhibited. Order-of-magnitude agreement is obtained between the theory and experiment for $SrTiO_3$.

## I. INTRODUCTION

THE piezoelectric coefficients have been related to the microscopic properties of the crystalline lattice by Born and Huang in their classic text on lattice dynamics.[1] This theory is applicable when the induced stress in a material is proportional to the applied field. If, however, the crystal possesses a center of symmetry, this linear effect is absent, and the stress is proportional to the square of the field. In this paper it will be shown how one can relate this quadratic behavior to the microscopic properties of the lattice. The quadratic dependence of stress on field has been called electrostriction by a number of investigators, and this is the terminology that will be adopted here.

Electrostrictive effects are generally small and difficult to measure in most materials. Ferroelectrics, however, exhibit pronounced electromechanical behavior. These materials undergo a transition to a polarized phase at a certain temperature. Above the transition temperature they are paraelectric, having a large dielectric constant which obeys a Curie-Weiss law. One may classify these materials as belonging to one of two categories[2]; those that are piezoelectric in the unpolarized phase, and those that are electrostrictive in the unpolarized phase. The ferroelectric materials that are piezoelectric in the unpolarized phase have been recently discussed by Cochran[3] and will not concern us in the present work. Barium titanate and its isomorphs belong to the second category since in the high-temperature cubic phase each ion is at a center of symmetry. The electrostrictive properties of these materials are of interest for several reasons. It appears that the explanation of the observed first-order phase transition in $BaTiO_3$ requires the presence of suitable electrostrictive terms in the expression for the free energy of the material.[4] Electrostrictive behavior also leads to the difference between the value of the clamped and free nonlinear dielectric constant in the paraelectric phase.[5] One basic assumption of Devonshire's theory[4] is that the piezoelectric coefficients of the material in the polarized phase are related simply to the electrostrictive coefficients of the material in the unpolarized phase. The microscopic basis for such assumption has been discussed by Anderson.[6] In this sense one could, therefore, say that the electromechanical behavior of barium titanate in all phases is electrostrictive.

The calculation relating the electrostrictive coefficients to the microscopic coupling parameters of the lattice also presents some new and interesting problems not encountered in the linear theory. Toupin has stated that, in general, one cannot consider the stress tensor as a polynomial in the electric field and elements of infinitesimal strain measure.[7] He has demonstrated that this assumption violates the invariance of the stored energy to rigid rotations. Toupin also raises the following interesting point: If the electric field and polarization are not parallel to each other, the Maxwell stress tensor in the dielectric medium is not symmetric. Hence, if the medium is to be in static equilibrium there must be an additional stress system whose antisymmetric part is equal and opposite to the antisymmetric part of the Maxwell stress tensor. One can call these additional stresses, local stresses. Toupin then states that the local stresses are to be compared with the stress tensor of elasticity theory. The calculation presented in Sec. II will show that Maxwell stresses and local stresses can be identified and that both are in static equilibrium with each other. The stress tensor, with inclusion of the Maxwell stresses, can therefore be written as a polynomial in the electric field and elements of infinitesimal strain measure.

It might appear, at first, that to calculate an effect quadratic in the macroscopic field one would need to work within the framework of the theory of finite elasticity. This, however, is not necessary since even though

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[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

[2] W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 1.

[3] W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1961), Vol. 10, p. 401.

[4] A. F. Devonshire, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 85.

[5] M. E. Drougard, R. Landauer, and D. R. Young, Phys. Rev. **98**, 1010 (1955); S. Triebwasser, J. Phys. Chem. Solids **3**, 53 (1957); E. Stern and A. Lurio, Phys. Rev. **123**, 117 (1961).

[6] P. W. Anderson, in *Fizika Dielektrikov*, edited by G. I. Skanavi (Akad. Nauk SSSR, Fisicheskii Institut im. P. N. Lebedeva, Moscow, 1960), in Russian.

[7] R. A. Toupin, J. Rational Mech. and Anal. **5**, 849 (1956).

the macroscopic field depends on the ionic displacements, it also depends on the geometry of the sample through the depolarization factor and, therefore, the field and displacement are independent quantities. One can, therefore, work to any given order in each independently.

## II. ELECTROSTRICTIVE CONSTANTS

Expressions for the electrostrictive constants are obtained after a comparison has been made between the macroscopic and microscopic theories. In this section we will, therefore, consider the elastic equation of motion for an electrostrictive medium and the microscopic lattice equations of motion. These equations will be put into a form which will facilitate their comparison. The elastic equation of motion is

$$\rho\ddot{u}_\alpha=\sum_\nu(\partial S_{\alpha\nu}/\partial X_\nu), \tag{1}$$

where $\rho$ is the mass density of the medium, $u_\alpha$ is the $\alpha$th component of the displacement in the medium, $S_{\alpha\nu}$ is the $\alpha\nu$th component of the stress tensor, and $X_\nu$ is the $\nu$th component of a general point in the medium.

The constitutive relation between stress, strain, and field is

$$S_{\alpha\nu}=\sum_{\delta,\Delta} C_{\alpha\nu,\delta\Delta}s_{\delta\Delta}+\sum_{\delta,\Delta} d_{\alpha\nu,\delta\Delta}E_\delta E_\Delta. \tag{2}$$

We assume that the piezoelectric effect is absent, since the crystal is assumed to possess a center of symmetry. The $C_{\alpha\nu,\delta\Delta}$ and $d_{\alpha\nu,\delta\Delta}$ are the elastic constants and electrostrictive constants, respectively. $E_\delta$ is the $\delta$th component of the macroscopic field. $s_{\delta\Delta}$ is the $\delta\Delta$th component of the strain tensor which is related to the displacement gradients as follows:

$$s_{\delta\Delta}=\frac{1}{2}\left(\frac{\partial u_\delta}{\partial X_\Delta}+\frac{\partial u_\Delta}{\partial X_\delta}\right). \tag{3}$$

Substituting Eq. (2) and Eq. (3) into Eq. (1), we obtain

$$\rho\ddot{u}_\alpha=\sum_{\nu,\delta,\Delta} C_{\alpha\nu,\delta\Delta}\frac{\partial^2 u_\delta}{\partial X_\nu\partial X_\Delta}+2\sum_{\nu,\delta,\Delta} d_{\alpha\nu,\delta\Delta}E_\Delta\frac{\partial E_\delta}{\partial X_\nu}. \tag{4}$$

The symmetry of the elastic and electrostrictive constants have been used to obtain this result. The displacements and macroscopic field are now Fourier analyzed:

$$u_\alpha=\int d\mathbf{y}\, u_{\alpha\mathbf{y}}e^{2\pi i\mathbf{y}\cdot\mathbf{r}}, \tag{5}$$

$$E_\delta=\int d\mathbf{y}\, E_{\delta\mathbf{y}}e^{2\pi i\mathbf{y}\cdot\mathbf{r}}. \tag{6}$$

If Eqs. (5) and (6) are substituted into Eq. (4), and the usual manipulations performed to obtain uncoupled motion in the harmonic approximation, one obtains

$$\rho\ddot{u}_{\alpha\mathbf{y}}=4\pi^2\sum_{\nu,\delta,\Delta} C_{\alpha\nu,\delta\Delta}y_\nu y_\Delta u_{\delta\mathbf{y}}+4\pi i\sum_{\nu,\delta,\Delta} d_{\alpha\nu,\delta\Delta}\times\int\int d\mathbf{y}'\, d\mathbf{y}''\, E_{\delta\mathbf{y}''}E_{\Delta\mathbf{y}'}y_\nu'\delta(\mathbf{y}''+\mathbf{y}'-\mathbf{y}). \tag{7}$$

$\delta(\mathbf{y})$ is the Dirac delta function. It is seen from Eq. (7) that modes of wave vector $\mathbf{y}$ are no longer uncoupled. Different modes are coupled due to the presence of the electrostrictive term. Expressions for the electrostrictive constants will be obtained from a comparison of Eq. (7) with the microscopic equations of motion. Therefore, we turn to an examination of the microscopic equations of motion. In what follows, the rigid-ion model is used for simplicity. The generalization to more sophisticated models within the adiabatic approximation should be straightforward.

The lattice equation of motion in the notation of Born and Huang is

$$m_k\ddot{u}_\alpha\binom{l}{k}=-\sum_{l',k',\beta}\phi_{\alpha\beta}\binom{l\ l'}{k\ k'}u_\beta\binom{l'}{k'}+q_k\epsilon_\alpha-\tfrac{1}{2}\sum_{l',k',\beta;l'',k'',\gamma}\phi_{\alpha\beta\gamma}\binom{l\ l'\ l''}{k\ k'\ k''}u_\beta\binom{l'}{k'}u_\gamma\binom{l''}{k''}. \tag{8}$$

$m_k$ is the mass of the $k$th type atom and $u_\alpha(_k^l)$ is the $\alpha$th component of the displacement of the $k$th type atom in the $l$th cell. The $\phi_{\alpha\beta}$ and $\phi_{\alpha\beta\gamma}$ are second- and third-order coupling coefficients, respectively, $q_k$ is the ionic charge of the $k$th type atom, and $\epsilon_\alpha$ is the $\alpha$th component of the macroscopic field. The harmonic interaction has been split up into a short- and long-range part, as discussed by Born and Huang. The macroscopic field $\epsilon$, therefore, includes contributions from the long-range interaction between ions, and $\phi_{\alpha\beta}$ is determined by the short-range interactions between ions.

After application of

$$w_\alpha\binom{l}{k}=\frac{1}{\sqrt{N}}\sum_{\mathbf{y}} w_\alpha(k\,|\,\mathbf{y})\exp\left[2\pi i\mathbf{y}\cdot\mathbf{x}\binom{l}{k}\right] \tag{9}$$

with

$$w_\alpha\binom{l}{k}=(m_k)^{1/2}u_\alpha\binom{l}{k}, \tag{10}$$

the equation of motion Eq. (8) can be written in the following form:

$$\ddot{w}_\alpha(k\,|\,\mathbf{y})=-\sum_{m,k',\beta}D_{\alpha\beta}\binom{-m}{k\quad k'}\exp\left[2\pi i\mathbf{y}\cdot\mathbf{x}\binom{m\ 0}{k'\ k}\right]w_\beta(k'\,|\,\mathbf{y})+\frac{q_k}{(m_k)^{1/2}}\epsilon_\alpha(\mathbf{y})-\frac{1}{2\sqrt{N}}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{m,k',\beta;n,k'',\gamma}D_{\alpha\beta\gamma}\binom{0\ m\ n}{k\ k'\ k''}w_\beta(k'\,|\,\mathbf{y}')w_\gamma(k''\,|\,\mathbf{y}'')\exp\left\{2\pi i\left[\mathbf{y}'\cdot\mathbf{x}\binom{m\ 0}{k'\ k}+\mathbf{y}''\cdot\mathbf{x}\binom{n\ 0}{k''\ k}\right]\right\}\times\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y}), \tag{11}$$

where we have set

$$D_{\alpha\beta}\binom{l\ l'}{k\ k'}=(m_k m_{k'})^{-1/2}\phi_{\alpha\beta}\binom{l\ l'}{k\ k'}, \tag{12}$$

$$D_{\alpha\beta\gamma}\binom{l\ l'\ l''}{k\ k'\ k''}=(m_k m_{k'} m_{k''})^{-1/2}\phi_{\alpha\beta\gamma}\binom{l\ l'\ l''}{k\ k'\ k''}, \tag{13}$$

$$\epsilon_\alpha(\mathbf{y})=-\frac{4\pi}{v_a}\left(\frac{y_\alpha}{|\mathbf{y}|}\right)\sum_\beta\left(\frac{y_\beta}{|\mathbf{y}|}\right)\sum_{k'}\frac{q_{k'}}{(m_{k'})^{1/2}} \times w_\beta\binom{k'|\mathbf{y}}{j}, \tag{14}$$

$$\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y})=1 \quad \text{for } \mathbf{y}'+\mathbf{y}''-\mathbf{y}=0 \text{ or a reciprocal lattice vector,}$$
$$=0 \quad \text{all other values of } \mathbf{y}', \mathbf{y}'', \text{ and } \mathbf{y}. \tag{15}$$

One method of identifying the electrostrictive coefficients in Eq. (7) with the microscopic parameters of Eq. (11) is the following: Let us assume that, up to time zero, the nonlinear interactions in both of these equations are not present. At time zero they are instantaneously switched on. The displacements are set equal to unperturbed displacements plus small corrections due to the presence of the nonlinear interactions. We will treat Eq. (11) first. Set

$$w_\alpha(k|\mathbf{y})=w_{0\alpha}(k|\mathbf{y})+v_\alpha(k|\mathbf{y}). \tag{16}$$

Subscript zero refers to the displacements in the absence of the third-order anharmonic coupling parameter. For an infinitesimal time after the anharmonic interaction has been turned on, we may write[8]

$$\ddot{w}_{0\alpha}(k|\mathbf{y})=-\sum_{m,k',\beta}D_{\alpha\beta}\binom{-m}{k\quad k'}\exp\left[2\pi i\mathbf{y}\cdot\mathbf{x}\binom{m\ 0}{k'\ k}\right] \times w_{0\beta}(k'|\mathbf{y})+\frac{q_k}{(m_k)^{1/2}}\epsilon_\alpha(\mathbf{y}), \tag{17}$$

$$\ddot{v}_\alpha(k|\mathbf{y})=-\frac{1}{2\sqrt{N}}\sum_{\mathbf{y}'\mathbf{y}''}\sum_{mk'\beta;nk''\gamma}D_{\alpha\beta\gamma}\binom{0\ m\ n}{k\ k'\ k''} \times w_{0\beta}(k'|\mathbf{y}')w_{0\gamma}(k''|\mathbf{y}'') \times\exp\left\{2\pi i\left[\mathbf{y}'\cdot\mathbf{x}\binom{m\ 0}{k'\ k}+\mathbf{y}''\cdot\mathbf{x}\binom{n\ 0}{k''\ k}\right]\right\} \times\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y}). \tag{18}$$

The macroscopic equation [Eq. (7)] can be treated in a similar fashion. The displacement $u_{\alpha\mathbf{y}}$ is set equal to an unperturbed part plus a small correction,

$$u_{\alpha\mathbf{y}}=u_{0\alpha\mathbf{y}}+v_{\alpha\mathbf{y}}. \tag{19}$$

In the same spirit in which Eqs. (17) and (18) have been written, we write

$$\rho\ddot{u}_{0\alpha\mathbf{y}}=-4\pi^2\sum_{\nu,\delta,\Delta}C_{\alpha\nu,\delta\Delta}y_\nu y_\Delta u_{\delta\mathbf{y}}, \tag{20}$$

$$\rho\ddot{v}_{\alpha\mathbf{y}}=4\pi i\sum_{\nu,\delta,\Delta}d_{\alpha\nu,\delta\Delta}\int\int d\mathbf{y}'d\mathbf{y}''\,E_{\delta\mathbf{y}''}E_{\Delta\mathbf{y}'}y_\nu' \times\delta(\mathbf{y}''+\mathbf{y}'-\mathbf{y}). \tag{21}$$

Equations (17) and (20) are just the equations that Born and Huang use to obtain expressions for the elastic constants. Had we included the piezoelectric terms in Eq. (20), these equations could be used to determine expressions for the piezoelectric coefficients also. To obtain expressions for the electrostrictive coefficients we must compare Eq. (18) with (21). Before this comparison is possible however, Eq. (18) must be written in the limit of long waves; the quadratic dependence on the macroscopic field must be exhibited; the center-of-mass motion for the unit cell must be obtained. In what follows we describe in some detail how this is done.

To obtain the motion of the center of mass of the unit cell we multiply both sides of Eq. (18) by $(m_k)^{1/2}$, sum over the contents of the unit cell, and divide by the sum of the masses in the unit cell.

$$\ddot{v}_\alpha(\mathbf{y})\equiv\frac{\sum_k(m_k)^{1/2}\ddot{v}_\alpha(k|\mathbf{y})}{\sum_k m_k} =-\frac{1}{2\sqrt{N}}\frac{1}{\sum_k m_k}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{mk'\beta;nk''\gamma;k}(m_k)^{1/2} \times D_{\alpha\beta\gamma}\binom{0\ m\ n}{k\ k'\ k''}w_{0\beta}(k'|\mathbf{y}')w_{0\gamma}(k''|\mathbf{y}'') \times\exp\left\{2\pi i\left[\mathbf{y}'\cdot\mathbf{x}\binom{m\ 0}{k'\ k}+\mathbf{y}''\cdot\mathbf{x}\binom{n\ 0}{k''\ k}\right]\right\} \times\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y}). \tag{22}$$

For wavelengths large compared with the atomic interaction distance, the exponential in Eq. (22) is expanded:

$$\exp\left\{2\pi i\left[\mathbf{y}'\cdot\mathbf{x}\binom{m\ 0}{k'\ k}+\mathbf{y}''\cdot\mathbf{x}\binom{n\ 0}{k''\ k}\right]\right\} =1+2\pi i\left[\mathbf{y}'\cdot\mathbf{x}\binom{m\ 0}{k'\ k}+\mathbf{y}''\cdot\mathbf{x}\binom{n\ 0}{k''\ k}\right]+\cdots. \tag{23}$$

The first term in this expansion appearing on the right

[8] This procedure is not valid for a material which lacks a center of symmetry. Since the displacements will consist partly of contributions that are quadratic in the field, there will be a contribution to $\ddot{v}_\alpha(k|\mathbf{y})$ from the first term on the right in Eq. (11).

of Eq. (22) is

$$-\frac{1}{2\sqrt{N}}\frac{1}{\sum_k m_k}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{mk'\beta;nk''\gamma;k}(m_k)^{1/2}D_{\alpha\beta\gamma}\binom{0\ m\ n}{k\ k'\ k''}\times w_{0\beta}(k'|\mathbf{y}')w_{0\gamma}(k''|\mathbf{y}'')\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y}), \quad (24)$$

and this term vanishes due to the following translational invariance condition:

$$\sum_{m,k}\phi_{\alpha\beta\gamma}\binom{0\ m\ n}{k\ k'\ k''}=0. \quad (25)$$

Contributions to Eq. (22) from the next term in the expansion do not vanish, and we therefore write

$$\ddot{v}_\alpha(\mathbf{y})=-\frac{\pi i}{\sqrt{N}}\frac{1}{\sum_k m_k}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{mk'\beta;nk''\gamma;k}(m_k)^{1/2}\times D_{\alpha\beta\gamma}\binom{0\ m\ n}{k\ k'\ k''}w_{0\beta}(k'|\mathbf{y}')w_{0\gamma}(k''|\mathbf{y}'')\times\left[\mathbf{y}'\cdot\mathbf{x}\binom{m\ 0}{k'\ k}+\mathbf{y}''\cdot\mathbf{x}\binom{n\ 0}{k''\ k}\right]\times\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y}). \quad (26)$$

If the following interchanges are performed in the term arising from the second quantity in the square brackets:

$$\mathbf{y}'\rightleftharpoons\mathbf{y}'',\quad m\rightleftharpoons n,\quad k'\rightleftharpoons k'',\quad \beta\rightleftharpoons\gamma,$$

we can write

$$\ddot{v}_\alpha(\mathbf{y})=-\frac{2\pi i}{\sqrt{N}}\frac{1}{\sum_k m_k}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{mk'\beta;nk''\gamma;k}(m_k)^{1/2}\times D_{\alpha\beta\gamma}\binom{0\ m\ n}{k\ k'\ k''}w_{0\beta}(k'|\mathbf{y}')w_{0\gamma}(k''|\mathbf{y}'')\mathbf{y}'\cdot\mathbf{x}\binom{m\ 0}{k'\ k}\times\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y}). \quad (27)$$

Let us next decompose the displacements into the normal modes:

$$w_{0\alpha}(k|\mathbf{y})=\sum_j\epsilon_\alpha\left(k\middle|\begin{matrix}\mathbf{y}\\ j\end{matrix}\right)Q\binom{\mathbf{y}}{j}. \quad (28)$$

The equations of motion for the $Q(_j^{\mathbf{y}})$ are

$$\ddot{Q}\binom{\mathbf{y}}{j}+\omega^2\binom{\mathbf{y}}{j}Q\binom{\mathbf{y}}{j}=\sum_{k,\alpha}\epsilon_\alpha^*\left(k\middle|\begin{matrix}\mathbf{y}\\ j\end{matrix}\right)\frac{q_k}{(m_k)^{1/2}}\epsilon_\alpha(\mathbf{y}). \quad (29)$$

We can write

$$Q\binom{\mathbf{y}}{j}=q\binom{\mathbf{y}}{j}+\sum_{k,\alpha}\epsilon_\alpha^*\left(k\middle|\begin{matrix}\mathbf{y}\\ j\end{matrix}\right)\frac{q_k}{(m_k)^{1/2}}\epsilon_\alpha(\mathbf{y})/\omega^2\binom{\mathbf{y}}{j}, \quad (30)$$

where $q(_j^{\mathbf{y}})$ is the solution of

$$\ddot{q}\binom{\mathbf{y}}{j}+\omega^2\binom{\mathbf{y}}{j}q\binom{\mathbf{y}}{j}=0. \quad (31)$$

Substituting (28) and (30) into (27), we obtain

$$\ddot{v}_\alpha(\mathbf{y})=-\frac{2\pi i}{\sqrt{N}}\frac{1}{\sum_k m_k}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{i',i''}\sum_{mk'\beta;nk''\gamma}\sum_{k''',\delta;k^{\mathrm{iv}},\Delta}D_{\alpha\beta\gamma}\binom{0\ m\ n}{k\ k'\ k''}\frac{\epsilon_\delta^*\left(k'''\middle|\begin{matrix}0\\ j'\end{matrix}\right)\epsilon_\beta\left(k'\middle|\begin{matrix}0\\ j'\end{matrix}\right)}{\omega^2\binom{0}{j'}}\frac{\epsilon_\Delta^*\left(k^{\mathrm{iv}}\middle|\begin{matrix}0\\ j''\end{matrix}\right)\epsilon_\gamma\left(k''\middle|\begin{matrix}0\\ j''\end{matrix}\right)}{\omega^2\binom{0}{j''}}\times\frac{(m_k)^{1/2}q_{k'''}q_{k^{\mathrm{iv}}}}{(m_{k'''}m_{k^{\mathrm{iv}}})^{1/2}}\mathbf{y}'\cdot\mathbf{x}\binom{m\ 0}{k'\ k}\epsilon_\delta(\mathbf{y}')\epsilon_\Delta(\mathbf{y}'')\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y}). \quad (32)$$

Finally, the Kronecker delta function goes over to a Dirac delta function in the limit of infinite periodicity volume:

$$\Delta(\mathbf{y})\rightarrow(1/Nv_a)\delta(\mathbf{y});\quad \sum_{\mathbf{y}}\rightarrow Nv_a\int d\mathbf{y}.$$

We obtain

$$\ddot{v}_{\alpha\mathbf{y}}=-\frac{2\pi i}{\rho v_a}\int\int d\mathbf{y}'d\mathbf{y}''\sum_{i',i''}\sum_{mk'\beta;nk''\gamma;k}\sum_{k''',\delta;k^{\mathrm{iv}},\Delta}D_{\alpha\beta\gamma}\binom{0\ m\ n}{k\ k'\ k''}\frac{\epsilon_\delta^*\left(k'''\middle|\begin{matrix}0\\ j'\end{matrix}\right)\epsilon_\beta\left(k'\middle|\begin{matrix}0\\ j'\end{matrix}\right)}{\omega^2\binom{0}{j'}}\frac{\epsilon_\Delta^*\left(k^{\mathrm{iv}}\middle|\begin{matrix}0\\ j''\end{matrix}\right)\epsilon_\gamma\left(k''\middle|\begin{matrix}0\\ j''\end{matrix}\right)}{\omega^2\binom{0}{j''}}\times\left(\frac{m_k}{m_{k'''}m_{k^{\mathrm{iv}}}}\right)^{1/2}q_{k'''}q_{k^{\mathrm{iv}}}\mathbf{y}'\cdot\mathbf{x}\binom{m\ 0}{k'\ k}E_{\delta\mathbf{y}'}E_{\Delta\mathbf{y}''}\delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y}), \quad (33)$$

where use has been made of

$$v_{\alpha\mathbf{y}}=\sqrt{N}v_a v_\alpha(\mathbf{y}),\quad E_{\alpha\mathbf{y}}=\sqrt{N}v_a\epsilon_\alpha(\mathbf{y}). \quad (34)$$

Equation (33) can now be compared directly with Eq. (21) and the following expression obtained for the electrostrictive coefficients:

$$d_{\alpha\nu,\delta\Delta}=\frac{1}{2v_a}\sum_{j',j''}\sum_{mk'\beta;nk''\gamma;k}\sum_{k''';k^{\mathrm{iv}}}D_{\alpha\beta\gamma}\begin{pmatrix}0 & m & n\\ k & k' & k''\end{pmatrix}\frac{\epsilon_\delta^*\begin{pmatrix}k''' & 0\\ & j'\end{pmatrix}\epsilon_\beta\begin{pmatrix}k' & 0\\ & j'\end{pmatrix}}{\omega^2\begin{pmatrix}0\\ j'\end{pmatrix}}\frac{\epsilon_\Delta^*\begin{pmatrix}k^{\mathrm{iv}} & 0\\ & j''\end{pmatrix}\epsilon_\gamma\begin{pmatrix}k'' & 0\\ & j''\end{pmatrix}}{\omega^2\begin{pmatrix}0\\ j''\end{pmatrix}}$$
$$\times\left(\frac{m_k}{m_{k'''}m_{k^{\mathrm{iv}}}}\right)^{1/2}q_{k'''}q_{k^{\mathrm{iv}}}x_\nu\begin{pmatrix}0 & m\\ k & k'\end{pmatrix}. \quad (35)$$

These coefficients are subject to the following symmetry relations[9]:

$$d_{\alpha\nu,\delta\Delta}=d_{\nu\alpha,\delta\Delta}=d_{\alpha\nu,\Delta\delta}\,, \quad (36)$$

and, in general, there are thirty-six independent constants.

As we have mentioned in the Introduction, Toupin[7] has pointed out the following interesting fact: If the electric field and polarization in a medium are not parallel to each other, the Maxwell stress tensor in the dielectric medium is not symmetric. Hence, if the medium is to be in static equilibrium there must be an additional stress system whose antisymmetric part is equal and opposite to the antisymmetric part of the Maxwell stress tensor. The previous calculation should include the Maxwell stresses since we have been working to terms second order in the field. The Maxwell stress tensor is bilinear in the electric field and polarization. Since the induced polarization is proportional to the field however, the Maxwell stress tensor is essentially quadratic in the electric field variables. The symmetry of the electrostrictive coefficients Eq. (36) however, always leads to symmetric stresses in the medium. This guarantees the rotational invariance of the energy function of the medium. It is, therefore, apparent that in the calculation just described, Maxwell stresses and local stresses have been lumped together. This will be shown in what follows.

The third-order coupling parameter appearing in Eq. (18) can be written as the sum of two terms:

$$D_{\alpha\beta\gamma}\begin{pmatrix}0 & m & n\\ k & k' & k''\end{pmatrix}=D_{\alpha\beta\gamma}{}^{N}\begin{pmatrix}0 & m & n\\ k & k' & k''\end{pmatrix}+D_{\alpha\beta\gamma}{}^{C}\begin{pmatrix}0 & m & n\\ k & k' & k''\end{pmatrix}. \quad (37)$$

Superscript $N$ indicates the short-range non-Coulomb contribution to the third-order coupling parameter. This term can include the effects of covalency, and general $n$-body interactions. Superscript $C$ refers to two-body Coulomb interactions and, therefore, $k$, $k'$, and $k''$ must each be equal to one of two types of ions for $D_{\alpha\beta\gamma}{}^{C}(k^0k'^{m}k''^{n})$ to be nonvanishing. Let us restrict attention to the Coulomb term and write the equation of motion Eq. (18) for this term:

$$\ddot{v}_\alpha(k|\mathbf{y})=-\frac{1}{2\sqrt{N}}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{\beta;n,k'',\gamma}D_{\alpha\beta\gamma}{}^{C}\begin{pmatrix}0 & 0 & n\\ k & k & k''\end{pmatrix}w_{0\beta}(k|\mathbf{y}')w_{0\gamma}(k''|\mathbf{y}'')\exp\left[2\pi i\mathbf{y}''\cdot\mathbf{x}\begin{pmatrix}n & 0\\ k'' & k\end{pmatrix}\right]\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y})$$
$$-\frac{1}{2\sqrt{N}}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{\gamma;m,k',\beta}D_{\alpha\beta\gamma}{}^{C}\begin{pmatrix}0 & m & 0\\ k & k' & k\end{pmatrix}w_{0\beta}(k'|\mathbf{y}')w_{0\gamma}(k|\mathbf{y}'')\exp\left[2\pi i\mathbf{y}'\cdot\mathbf{x}\begin{pmatrix}m & 0\\ k' & k\end{pmatrix}\right]\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y})+\cdots. \quad (38)$$

The two terms appearing in Eq. (38) can be combined if the following relations are used to rewrite the first term:

$$\mathbf{y}'\rightleftharpoons\mathbf{y}'',\quad \beta\rightleftharpoons\gamma,\quad n\rightarrow m,\quad k''\rightarrow k',\quad D_{\alpha\beta\gamma}{}^{C}\begin{pmatrix}0 & 0 & n\\ k & k & k''\end{pmatrix}=D_{\alpha\beta\gamma}{}^{C}\begin{pmatrix}0 & n & 0\\ k & k'' & k\end{pmatrix}, \quad (39)$$

and we obtain

$$\ddot{v}_\alpha(k|\mathbf{y})=-\frac{1}{\sqrt{N}}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{\gamma;m,k',\beta}D_{\alpha\beta\gamma}{}^{C}\begin{pmatrix}0 & m & 0\\ k & k' & k\end{pmatrix}w_{0\beta}(k'|\mathbf{y}')w_{0\gamma}(k|\mathbf{y}'')\exp\left[2\pi i\mathbf{y}'\cdot\mathbf{x}\begin{pmatrix}m & 0\\ k' & k\end{pmatrix}\right]\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y})+\cdots. \quad (40)$$

[9] See Appendix.

Using Eq. (13) we can write

$$D_{\alpha\beta\gamma}{}^{c}\begin{pmatrix}0 & m & 0\\ k & k' & k\end{pmatrix}=\frac{1}{m_k m_{k'}{}^{1/2}}\phi_{\alpha\beta\gamma}{}^{c}\begin{pmatrix}0 & m & 0\\ k & k' & k\end{pmatrix}, \tag{41}$$

with

$$\phi_{\alpha\beta\gamma}{}^{c}\begin{pmatrix}0 & m & 0\\ k & k' & k\end{pmatrix}=-q_k q_{k'}\frac{\partial^3}{\partial x_\alpha\begin{pmatrix}0\\ k\end{pmatrix}\partial x_\beta\begin{pmatrix}0\\ k\end{pmatrix}\partial x_\gamma\begin{pmatrix}0\\ k\end{pmatrix}}\left\{\frac{1}{\left|\mathbf{x}\begin{pmatrix}m\\ k'\end{pmatrix}-\mathbf{x}\begin{pmatrix}0\\ k\end{pmatrix}\right|}\right\}. \tag{42}$$

Since we want to calculate the motion of the center of mass of the unit cell, one must multiply both sides of Eq. (40) by $m_k{}^{1/2}$, sum over $k$, and then divide by the sum of the masses in the unit cell. We obtain the following equation:

$$\ddot{v}_\alpha(\mathbf{y})=-\frac{8\pi^2 i}{v_a\sqrt{N}}\frac{1}{\sum_k m_k}\sum_{\mathbf{y}',\mathbf{y}''}\sum_{k,k';\beta,\gamma}\frac{q_k q_{k'}}{(m_k m_{k'})^{1/2}}\frac{y_\alpha' y_\beta' y_\gamma'}{|\mathbf{y}'|^2}w_{0\beta}(k'|\mathbf{y}')w_{0\gamma}(k|\mathbf{y}'')\Delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y})+\cdots, \tag{43}$$

after substitution of Eq. (42) into Eq. (40) and the use of

$$\frac{\partial^3}{\partial x_\alpha\begin{pmatrix}0\\ k\end{pmatrix}\partial x_\beta\begin{pmatrix}0\\ k\end{pmatrix}\partial x_\gamma\begin{pmatrix}0\\ k\end{pmatrix}}\sum_m\left[\frac{\exp\left[2\pi i\mathbf{y}'\cdot\mathbf{x}\begin{pmatrix}m & 0\\ k' & k\end{pmatrix}\right]}{\left|\mathbf{x}\begin{pmatrix}m\\ k'\end{pmatrix}-\mathbf{x}\begin{pmatrix}0\\ k\end{pmatrix}\right|}\right]\exp\left[2\pi i\mathbf{y}'\cdot\mathbf{x}\begin{pmatrix}0\\ k\end{pmatrix}\right]\doteq-\frac{8\pi^2 i}{v_a}\frac{y_\alpha' y_\beta' y_\gamma'}{|\mathbf{y}'|^2}\exp\left[2\pi i\mathbf{y}'\cdot\mathbf{x}\begin{pmatrix}0\\ k\end{pmatrix}\right]. \tag{44}$$

The dot over the equality sign in Eq. (44) indicates that we have only exhibited the macroscopic-field term on the right-hand side of this equation. The inner-field term, which we neglect, may be grouped with the short-range forces. If we perform the sum over $\beta$, $k'$, and $k$ in Eq. (43), and let the periodicity volume become infinite, we obtain

$$\rho\ddot{v}_{\alpha y}=2\pi i v_a\sqrt{N}\sum_\gamma\int\int d\mathbf{y}'d\mathbf{y}''\,E_{\alpha y'}P_{\gamma y''}y_{\gamma'}\times\delta(\mathbf{y}'+\mathbf{y}''-\mathbf{y})+\cdots. \tag{45}$$

This term on the right of Eq. (45) is just the Maxwell stress term that appears in the equation of motion. One can show this in the following way. The elastic equation of motion can be written

$$\rho\ddot{u}_\alpha=\sum_\gamma\frac{\partial S_{\alpha\gamma}}{\partial X_\gamma}=\sum_\gamma P_\gamma\frac{\partial E_\alpha}{\partial X_\gamma}+\cdots. \tag{46}$$

Components of the Maxwell stress tensor are given by

$$S_{\alpha\gamma}{}^{M}=E_\alpha P_\gamma. \tag{47}$$

Using the following Fourier decomposition of electric field and polarization

$$\begin{aligned}E_\alpha&=v_a\sqrt{N}\int_{-\infty}^{\infty}E_{\alpha\mathbf{y}}\exp(2\pi i\mathbf{y}\cdot\mathbf{r})d\mathbf{y};\\ P_\gamma&=v_a\sqrt{N}\int_{-\infty}^{\infty}P_{\gamma\mathbf{y}}\exp(2\pi i\mathbf{y}\cdot\mathbf{r})d\mathbf{y},\end{aligned} \tag{48}$$

it can be shown that the Maxwell stress term exhibited explicitly in Eq. (46) is identical with the term in Eq. (45). Hence, we have shown that the microscopic lattice equations of motion that have been used to obtain expressions for the electrostrictive constants, contain the Maxwell stress terms.

## III. ELECTROSTRICTION OF FERROELECTRIC MATERIALS

The piezoelectric and electrostrictive behavior of ferroelectric materials has been treated extensively in the past.[10] Many of the measurements have been made on materials in the polarized phase. In this phase the materials are piezoelectric, exhibiting a linear relation between stress and applied field. The interpretation of measurements in the polarized phase is complicated by the presence of ferroelectric domains. In the unpolarized or cubic phase the material is electrostrictive, i.e., there is a quadratic dependence of the stress on electric field. Devonshire's[4] treatment of the electromechanical properties of $BaTiO_3$ assumes that the piezoelectric coefficients in the polarized phase are related simply to the electrostrictive coefficients in the unpolarized phase. Verification of Devonshire's theory has formed the basis for much of the work on electrostriction. To

[10] W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics* (D. Van Nostrand, Inc., Princeton, New Jersey, 1950); M. E. Caspari and W. J. Merz, Phys. Rev. **80**, 1082 (1950); H. F. Kay, in Rept. Progr. Phys. **23**, 230 (1955); P. W. Forsbergh, Jr., in the *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956); E. J. Huibregtse, W. H. Bessey, and M. E. Drougard, J. Appl. Phys. **30**, 899 (1959).

the extent that the Devonshire theory is valid, the theory presented in this paper should form a basis for understanding the microscopic origin of the piezoelectric and electrostrictive behavior of $BaTiO_3$ and related isomorphs. In any event, the microscopic theory presented in Sec. II should be valid for application in the unpolarized phase of these materials.

Measurements on single-crystal barium titanate[11] and strontium titanate[12] have been made above the Curie temperature as a function of temperature. Over the range of measurement, these materials are paraelectric having a large dielectric constant which obeys a Curie-Weiss law. The measured temperature variation of the electrostrictive coefficients $d$, is given by

$$d\sim 1/(T-T_c)^2. \tag{49}$$

$T_c$ is the Curie temperature obtained from high-temperature dielectric measurements. This temperature variation is in agreement with the result predicted from Devonshire's phenomenological theory. That this temperature variation also results from the microscopic expressions obtained, is shown in the following way: The frequency of the low-lying "ferroelectric mode" of $SrTiO_3$ has an observed temperature dependence given by[13]

$$\omega\begin{pmatrix}0\\F\end{pmatrix}\sim(T-T_c)^{1/2}. \tag{50}$$

Such a temperature-dependent mode should also be present in $BaTiO_3$ and its isomorphs.[6,14] This is the mode which dominates the low-frequency dielectric behavior. This mode should also dominate the electrostrictive behavior due to its relatively low frequency and large oscillator strength.[15] Therefore, in the expression for the electrostrictive coefficients, Eq. (35), contributions are neglected from all optical modes other than the soft ferroelectric mode. The result can be written

$$d_{\alpha\nu,\delta\Delta}=\frac{1}{v_a}\sum_{mk'\beta;nk''\gamma}\sum_{k\ k'''\ ;k^{\mathrm{iv}}} D_{\alpha\beta\gamma}\begin{pmatrix}0\ m\ n\\ k\ k'\ k''\end{pmatrix} \times\frac{\epsilon_\delta^*\left(k'''\middle|\begin{matrix}0\\F\end{matrix}\right)\epsilon_\beta\left(k'\middle|\begin{matrix}0\\F\end{matrix}\right)\epsilon_\Delta^*\left(k^{\mathrm{iv}}\middle|\begin{matrix}0\\F\end{matrix}\right)\epsilon_\gamma\left(k''\middle|\begin{matrix}0\\F\end{matrix}\right)}{\omega^4\begin{pmatrix}0\\F\end{pmatrix}} \times\left(\frac{m_k}{m_{k'''}m_{k^{\mathrm{iv}}}}\right)^{1/2} q_{k'''}q_{k^{\mathrm{iv}}}X_\nu\begin{pmatrix}0\ m\\ k\ k'\end{pmatrix}\sim\frac{1}{(T-T_c)^2}. \tag{51}$$

The temperature dependence of the soft-mode frequency [Eq. (50)], therefore, leads to the observed temperature dependence of the electrostrictive coefficients.

Since we have written the electrostrictive coefficients in terms of the microscopic parameters of the lattice, let us see whether these parameters can be reasonably chosen to reproduce the measured value. An estimate for the room-temperature value of $d_{11,11}$ is obtained from the data of Winter and Rupprecht,[13] in the following manner:

$$d_{11,11}\approx C_{11,11}g_{11,11}=9.53\times10^{-7}\frac{\text{Newton}}{(\text{Volt})^2}. \tag{52}$$

This coefficient is written (with neglect of anharmonic shear interactions),

$$d_{11,11}=\frac{1}{v_a}\sum_{m,k';n,k''}\sum_{k\ k'''\ ;k^{\mathrm{iv}}} D_{111}\begin{pmatrix}0\ m\ n\\ k\ k'\ k''\end{pmatrix} \times\frac{\epsilon(k''')\epsilon(k')\epsilon(k^{\mathrm{iv}})\epsilon(k'')}{\omega^4\begin{pmatrix}0\\F\end{pmatrix}}\frac{1}{\sqrt{m}}q_{k'''}q_{k^{\mathrm{iv}}}X\begin{pmatrix}0\ m\\ k\ k'\end{pmatrix}. \tag{53}$$

This expression can be evaluated simply with use of the linear chain model of a ferroelectric.[16] For the chain model, we have

$$\begin{aligned}&\epsilon(1)=-1/\sqrt{2}, \quad q_1=-ne/b;\\ &\epsilon(2)=1/\sqrt{2}, \quad q_2=ne/b.\end{aligned} \tag{54}$$

$n$ is the number of electronic charges on the ions; $e$ the electronic charge; $b$ is a constant which includes effects of electronic polarizability and makes the $q_1$ and $q_2$ essentially effective charges. Two unit cells of the chain model are shown in Fig. 1. After the sums have been performed in Eq. (53) we obtain the relatively simple expression for $d_{11,11}$,

$$d_{11,11}=\frac{4\alpha(ne/b)^2d}{m^2\omega^4\begin{pmatrix}0\\F\end{pmatrix}v_a}. \tag{55}$$

$\alpha$ is a third-order coupling coefficient. $d$ is a lattice parameter shown in Fig. 1.

Values have been substituted for all of these quanti-

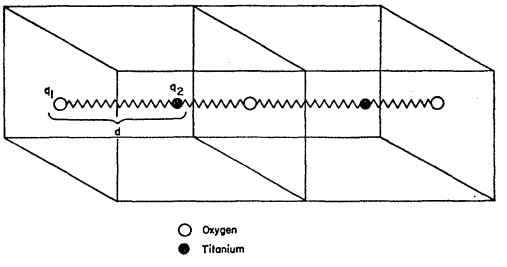


FIG. 1. Two unit cells of the chain model.

[11] G. Schmidt, Naturwiss. **45**, 8 (1958).
[12] W. H. Winter and G. Rupprecht, Bull. Am. Phys. Soc. **7**, 438 (1962).
[13] A. S. Barker, Jr. and M. Tinkham, Phys. Rev. **125**, 1527 (1962); R. A. Cowley, Phys. Rev. Letters **9**, 159 (1962).
[14] W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol. **9**, p. 387; R. Landauer, H. Juretschke, and P. Sorokin (unpublished).
[15] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. **126**, 1710 (1962).
[16] B. D. Silverman, Phys. Rev. **125**, 1921 (1962).

ties (except $n$) in a manner discussed previously.[16] The value of $n$ was then adjusted so that the value of (55) was equal to the observed value (52). In this fashion one obtains the reasonable value of $n=2$ electronic charges per ion.

## APPENDIX

In this section we sketch how the symmetry relations [Eq. (36)] are obtained. The symmetry of the electrostrictive coefficient [Eq. (35)] upon the following interchange:

$$\delta \rightleftharpoons \Delta \tag{56}$$

is obtained simply by making the following interchanges:

$$k''' \rightleftharpoons k^{\mathrm{iv}},\quad k' \rightleftharpoons k'',\quad \beta \rightleftharpoons \gamma,\quad j' \rightleftharpoons j'',\quad m \rightleftharpoons n, \tag{57}$$

and by using the translational invariance condition [Eq. (25)].

The symmetry of the electrostrictive coefficient upon the interchange

$$\alpha \rightleftharpoons \nu, \tag{58}$$

is somewhat more involved. Upon interchange of $\alpha$ and $\nu$ in Eq. (35), we obtain

$$d_{\nu\alpha,\delta\Delta}=\frac{1}{2v_a}\sum_{j',j''}\sum_{mk'\beta;nk''\gamma;k}\sum_{k''';k^{\mathrm{iv}}} D_{\nu\beta\gamma}\begin{pmatrix}0 & m & n\\ k & k' & k''\end{pmatrix}\frac{\epsilon_\delta^*\begin{pmatrix}k''' & 0\\ & j'\end{pmatrix}\epsilon_\beta\begin{pmatrix}k' & 0\\ & j'\end{pmatrix}}{\omega^2\begin{pmatrix}0\\ j'\end{pmatrix}}\frac{\epsilon_\Delta^*\begin{pmatrix}k^{\mathrm{iv}} & 0\\ & j''\end{pmatrix}\epsilon_\gamma\begin{pmatrix}k'' & 0\\ & j''\end{pmatrix}}{\omega^2\begin{pmatrix}0\\ j''\end{pmatrix}}$$
$$\times\left(\frac{m_k}{m_{k'''}m_{k^{\mathrm{iv}}}}\right)^{1/2} q_{k'''}q_{k^{\mathrm{iv}}}x_\alpha\begin{pmatrix}0 & m\\ k & k'\end{pmatrix}. \tag{59}$$

The rotational invariance condition connecting third-order and second-order coupling parameters can be written[17]

$$\sum_{m,k}\phi_{\nu\beta\gamma}\begin{pmatrix}0 & m & n\\ k & k' & k''\end{pmatrix}x_\alpha\begin{pmatrix}0 & m\\ k & k'\end{pmatrix}+\phi_{\nu\gamma}\begin{pmatrix}0 & n\\ k' & k''\end{pmatrix}\delta_{\beta\alpha}+\phi_{\beta\nu}\begin{pmatrix}0 & n\\ k' & k''\end{pmatrix}\delta_{\gamma\alpha}$$
$$=\sum_{m,k}\phi_{\alpha\beta\gamma}\begin{pmatrix}0 & m & n\\ k & k' & k''\end{pmatrix}x_\nu\begin{pmatrix}0 & m\\ k & k'\end{pmatrix}+\Phi_{\alpha\gamma}\begin{pmatrix}0 & n\\ k' & k''\end{pmatrix}\delta_{\beta\nu}+\phi_{\beta\alpha}\begin{pmatrix}0 & n\\ k' & k''\end{pmatrix}\delta_{\gamma\nu}. \tag{60}$$

Using Eqs. (35), (59), and (60), and the defining Eqs. (12) and (13), one can write

$$d_{\nu\alpha,\delta\Delta}-d_{\alpha\nu,\delta\Delta}=\frac{1}{2v_a}\sum_{j',j''}\sum_{k',\beta;nk''\gamma}\sum_{k''';k^{\mathrm{iv}}}\left[D_{\alpha\gamma}\begin{pmatrix}0 & n\\ k' & k''\end{pmatrix}\delta_{\beta\nu}+D_{\beta\alpha}\begin{pmatrix}0 & n\\ k' & k''\end{pmatrix}\delta_{\gamma\nu}-D_{\nu\gamma}\begin{pmatrix}0 & n\\ k' & k''\end{pmatrix}\delta_{\beta\alpha}-D_{\beta\nu}\begin{pmatrix}0 & n\\ k' & k''\end{pmatrix}\delta_{\gamma\alpha}\right]$$
$$\times\frac{q_{k'''}q_{k^{\mathrm{iv}}}}{m_{k'''}m_{k^{\mathrm{iv}}}}\frac{\epsilon_\delta^*\begin{pmatrix}k''' & 0\\ & y'\end{pmatrix}\epsilon_\beta\begin{pmatrix}k' & 0\\ & j'\end{pmatrix}}{\omega^2\begin{pmatrix}0\\ j'\end{pmatrix}}\frac{\epsilon_\Delta^*\begin{pmatrix}k^{\mathrm{iv}} & 0\\ & j''\end{pmatrix}\epsilon_\gamma\begin{pmatrix}k'' & 0\\ & j''\end{pmatrix}}{\omega^2\begin{pmatrix}0\\ j''\end{pmatrix}}. \tag{61}$$

If the contribution to the macroscopic field is separated from the contributions to the inner and non-Coulomb field in the second-order coupling parameter,

$$\phi_{\gamma u}\begin{pmatrix}l\\ k & k'\end{pmatrix}=4\pi q_k q_{k'}\frac{y_\gamma y_u}{|\mathbf{y}|^2}+\phi'_{\gamma u}\begin{pmatrix}l\\ k & k'\end{pmatrix}. \tag{62}$$

or

$$D_{\gamma u}\begin{pmatrix}l\\ k & k'\end{pmatrix}=4\pi\frac{q_k q_{k'}}{(m_k m_{k'})^{1/2}}\frac{y_\gamma y_u}{|\mathbf{y}|^2}+D'_{\gamma u}\begin{pmatrix}l\\ k & k'\end{pmatrix}. \tag{63}$$

It can be shown that the term on the right of Eq. (61) vanishes, thereby proving the validity of Eq. (36).

[17] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 275.