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Comments

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Homogeneous deformation theory for piezoelectric crystals using the Ewald transformation and relationships among electrostatic contributions to second- and third-order elastic constants

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In order to calculate the electrostatic contributions to the elastic constants of piezoelectric crystals, Fuller and Naimon [Phys. Rev. B 6, 3609 (1972)] used the conventional method of homogeneous deformation by evaluating the lattice sums using the Ewald transformation and omitting the zero-wave-vector term. This procedure, however, lacks justification, since it is well known that the conventional homogeneous deformation theory breaks down for piezoelectric crystals. We develop here the full theory for this case. (The use of a new technique for performing the Ewald transformation makes the treatment much simpler.) The theory verifies that the procedure of Fuller and Naimon will give the correct contribution to the elastic constants. We also explain why the zero-wave-vector term remained absent in their treatment. Moreover, we derive for an arbitrary crystal structure some relationships between the electrostatic contributions to the different second- and third-order elastic constants. In view of these relationships, one has to calculate a lesser number of electrostatic contributions for a given crystal structure, and some of the evaluations of Fuller and Naimon become redundant.

I. INTRODUCTION

Fuller and Naimon[1] (abbreviated as FN in this paper) in their detailed tabulation of electrostatic contributions to elastic constants, applied the method of homogeneous deformation to a number of metallic and ionic crystals. Their procedure was to use the Ewald theta transformation in the expression for the electrostatic energy of the deformed crystal, without considering the zero-wave-vector term. But some of the crystals concerned are piezoelectric in nature and it is well known that the standard method of homogeneous deformation breaks down for piezoelectric crystals (Ref. 2, Secs. 11 and 25). This failure is traced to the fact that some of the Coulomb sums occurring in the expression for the strain energy density become indeterminate in the limit of an infinite crystal, as they involve the macroscopic electric field which develops as a result of strain. Therefore, a rigorous demonstration of the logic underlying the procedure of FN has yet to be performed. For this purpose, one has to develop the full theory of homogeneous deformation for piezoelectric crystals, since it would not be possible to discuss the elastic and piezoelectric effects in isolation (Ref 2, p. 229). Born and Huang[2] were the first to build up a microscopic theory by going over to the long-wavelength approach and by separating out the macroscopic electric field from the indeterminate lattice sum. Recently, it has been shown[3,4] that the same separation can be achieved in the homogeneous deformation theory without using the theta transformation. In the present paper we show that, within the framework of homogeneous deformation theory, the separation can be achieved by using the theta transformation for evaluating the troublesome Coulomb sums. {Incidentally, we use a new technique[5] [see Eq. (9) below] for performing the theta transformation, which leads to the final result more easily than in the conventional approach.} We shall justify the procedure of FN by showing that the whole of the zero-wave-vector term is connected to the macroscopic electric field, as in the long-wavelength theory. Furthermore, we shall derive for an arbitrary crystal structure, some relationships between the electrostatic contributions to the different second- and third-order elastic constants, that were not noticed by FN. These relationships make some of the calculations of FN redundant.

We shall now present (Sec. II) the homogeneous deformation theory for second- and third-order elastic constants and then discuss (Sec. III) the relationships between the electrostatic contributions. In the concluding section, we explain why the term containing the electric field is absent in FN's treatment.

II. HOMOGENEOUS DEFORMATION THEORY

We consider a piezoelectric single crystal of finite but macroscopically large size, which has the shape of a parallelopiped, with each face perpendicular to a primitive translation vector, and with two parallel faces much larger than the other faces. This ensures that the macroscopic electric field and the macroscopic polarization developed in response to a homogeneous macroscopic strain are also homogeneous. Furthermore, we shall assume that all relevant physical properties satisfy periodic boundary conditions so that a quasicontinuous space of allowed wave vectors $\mathbf{q}$ exists. These wave vectors satisfy the well-known equality,[6]

$$\sum_{l}\exp(i\mathbf{q}\cdot\mathbf{r}_l)=N\sum_{\mathbf{G}}\delta_{\mathbf{q},\mathbf{G}} \ , \tag{1}$$

where $\mathbf{r}_l$ is the position of the lth lattice site, N the number of unit cells in the lattice, and $\mathbf{G}$ denotes a reciprocal lattice vector.

When the sample is subjected to a homogeneous stress, the kth particle in the lth lattice cell suffers a displacement

$$\mathbf{u}(lk)=\mathbf{r}(lk)-\mathbf{r}_0(lk)=\underline{\upsilon}\mathbf{r}_0(lk)+\mathbf{u}(k) \ , \tag{2}$$

where $\underline{\upsilon}$ is the homogeneous macroscopic strain tensor, $\mathbf{u}(k)$ the internal strain for ions of type k, and $\mathbf{r}(lk)$ and $\mathbf{r}_0(lk)$ the final and initial equilibrium positions, respectively. This deformation produces a Lagrangian strain

$$\underline{s}=\underline{\upsilon}+\tfrac{1}{2}\underline{\upsilon\upsilon} \ , \tag{3}$$

and a polarization

$$\mathbf{P}=(1/V)e_k\mathbf{u}(k) \ , \tag{4}$$

under the assumption that the ions are rigid, where e_k is the charge of the kth ion and V the volume of a unit cell in the deformed configuration. (Summation will always be implied over repeated Cartesian and other indices.)

We expand now the strain energy per unit undeformed volume about the initial configuration up to terms cubic in the macroscopic and internal strain as (see Sec. 11 of Ref. 2 and Refs. 4 and 7),

$$\begin{aligned}\mathscr{E}={}&\tfrac{1}{2}A\begin{pmatrix}k & k'\\ \alpha & \beta\end{pmatrix}u_\alpha(k)u_\beta(k')+A\begin{pmatrix}k & & \\ \alpha & \beta & \gamma\end{pmatrix}u_\alpha(k)s_{\beta\gamma}+\tfrac{1}{2}A(\alpha\beta\gamma\epsilon)s_{\alpha\beta}s_{\gamma\epsilon}+\tfrac{1}{6}B\begin{pmatrix}k & k' & k''\\ \alpha & \beta & \gamma\end{pmatrix}u_\alpha(k)u_\beta(k')u_\gamma(k'')\\ &+\tfrac{1}{2}B\begin{pmatrix}k & k' & & \\ \alpha & \beta & \gamma & \epsilon\end{pmatrix}u_\alpha(k)u_\beta(k')s_{\gamma\epsilon}+\tfrac{1}{2}B\begin{pmatrix}k & & & & \\ \alpha & \beta & \gamma & \epsilon & \zeta\end{pmatrix}u_\alpha(k)s_{\beta\gamma}s_{\epsilon\zeta}+\tfrac{1}{6}B(\alpha\beta\gamma\epsilon\zeta\eta)s_{\alpha\beta}s_{\gamma\epsilon}s_{\zeta\eta} \ ,\end{aligned} \tag{5}$$

where α, β, etc., denote Cartesian components and the coefficients A and B are certain lattice sums to be evaluated in the initial configuration. It can be seen[2–4] that the Coulomb parts of $A\left(\begin{smallmatrix}k & k'\\ \alpha & \beta\end{smallmatrix}\right)$ and $B\left(\begin{smallmatrix}k & k' & & \\ \alpha & \beta & \gamma & \epsilon\end{smallmatrix}\right)$, viz.,

$$A^C\begin{pmatrix}k & k'\\ \alpha & \beta\end{pmatrix}=(e_k/V_0)\left(\delta_{kk'}\sum_{l_0k_0}-\sum_{\substack{l_0\\ k_0=k'}}\right)[e_{k_0}(1/r_0^5)(3r_{0\alpha}r_{0\beta}-\delta_{\alpha\beta}r_0^2)] \tag{6a}$$

and

$$\begin{aligned}B^C\begin{pmatrix}k & k' & & \\ \alpha & \beta & \gamma & \epsilon\end{pmatrix}={}&(e_k/V_0)\left(\delta_{kk'}\sum_{l_0k_0}-\sum_{\substack{l_0\\ k_0=k'}}\right)e_{k_0}[(3/r_0^5)(\delta_{\alpha\beta}r_{0\gamma}r_{0\epsilon}+\tfrac{1}{2}\delta_{\alpha\gamma}r_{0\beta}r_{0\epsilon}+\tfrac{1}{2}\delta_{\alpha\epsilon}r_{0\beta}r_{0\gamma}\\ &+\tfrac{1}{2}\delta_{\beta\gamma}r_{0\alpha}r_{0\epsilon}+\tfrac{1}{2}\delta_{\beta\epsilon}r_{0\alpha}r_{0\gamma})-(15/r_0^7)r_{0\alpha}r_{0\beta}r_{0\gamma}r_{0\epsilon}] \ ,\end{aligned} \tag{6b}$$

are both indeterminate in the limit of an infinite crystal and are, therefore, surface dependent. [$\mathbf{r}_0=\mathbf{r}_0(l_0k_0)-\mathbf{r}_0(lk)$ and V_0 is the volume of a unit cell in undeformed configuration.] To proceed further we have to separate from these coefficients, the part that involves macroscopic electric field. FN in their treatment overlook this point and hence their subsequent development lacks justification.

We consider a hypothetical configuration $\mathscr{H}$, where the particles have suffered only the macroscopic strain $\underline{\upsilon}$ but no internal strain,

$$\mathbf{R}(lk)=\mathbf{r}_0(lk)+\underline{\upsilon}\mathbf{r}_0(lk) \ . \tag{7}$$

The coefficient of Eq. (6a) evaluated at $\mathscr{H}$ can be written as

$$A^C_{\mathscr{H}}\begin{pmatrix}k & k'\\ \alpha & \beta\end{pmatrix}=(e_k/V)\left(\delta_{kk'}\sum_{l_0k_0}-\sum_{\substack{l_0\\ k_0=k'}}\right)e_{k_0}\left(\frac{\partial^2}{\partial r_\alpha\partial r_\beta}\frac{1}{r}\right)_{\mathbf{r}=\mathbf{R}} \ , \tag{8}$$

where $\mathbf{R}=\mathbf{R}(l_0k_0)-\mathbf{R}(lk)$. To transform this Coulomb sum we start with the Fourier transform relationship

$$\frac{1}{r}\operatorname{erf}(r\sigma)=\frac{1}{2\pi^2}\int\frac{1}{q^2}\exp\left(i\mathbf{q}\cdot\mathbf{r}-\frac{q^2}{4\sigma^2}\right)d\mathbf{q} \ . \tag{9}$$

To prove it, one may calculate the inverse Fourier integral

$$\int\frac{1}{r}\operatorname{erf}(r\sigma)\exp(-i\mathbf{q}\cdot\mathbf{r})d\mathbf{r}$$

by first performing the angular integration and then using a standard formula.[8] Here, erf x is the error function and σ is an arbitrary real parameter. We write now $(1/r)$ in Eq. (8) as $(1/r)\mathrm{erf}(r\sigma)+(1/r)\mathrm{erfc}(r\sigma)$, use Eqs. (9) and (1) in order, and convert the integration over $\mathbf{q}$ to summation, to obtain finally,

$$A^{C}_{\mathscr{X}}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}=\mathscr{L}_{D,\mathscr{X}}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}+\mathscr{L}_{R,\mathscr{X}}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}+(4\pi/V^2)e_k e_{k'}\lim_{\mathbf{q}\to 0}(q_\alpha q_\beta/q^2)\ , \tag{10}$$

where

$$\mathscr{L}_{D,\mathscr{X}}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}=(e_k/V)\left[\delta_{kk'}\sum_{l_0 k_0}-\sum_{\substack{l_0\\ k_0=k'}}\right]e_{k_0}\{R_\alpha R_\beta f(R,\sigma)-\tfrac{1}{3}\delta_{\alpha\beta}R^2[f(R,\sigma)-(4\sigma^3/\sqrt{\pi}R^2)\exp(-R^2\sigma^2)]\}\ , \tag{10a}$$

and

$$\mathscr{L}_{R,\mathscr{X}}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}=(4\pi/V^2)e_k\sum_{\mathbf{G}}(G_\alpha G_\beta/G^2)f(\mathbf{G},\mathbf{R},\sigma)\ , \tag{10b}$$

with

$$f(R,\sigma)=(3/R^5)\mathrm{erfc}(R\sigma)+(6\sigma/\sqrt{\pi}R^4)(1+\tfrac{2}{3}R^2\sigma^2)\exp(-R^2\sigma^2)\ ,$$

and

$$f(\mathbf{G},\mathbf{R},\sigma)=\left[e_{k'}\exp(i\mathbf{G}\cdot\mathbf{R}_{k'k})-\delta_{kk'}\sum_{k_0}e_{k_0}\exp(i\mathbf{G}\cdot\mathbf{R}_{k_0 k})\right]\exp(-G^2/4\sigma^2)\ .$$

In the above, the summations exclude $\mathbf{R}=0$ and $\mathbf{G}=0$ terms, erfc x is the complementary error function, $\mathbf{G}$ a reciprocal lattice vector in the configuration $\mathscr{X}$, and $\mathbf{R}_{kk'}=\mathbf{R}(lk)-\mathbf{R}(lk')$.

To interpret the last term in Eq. (10) which has no unique limit, we note that the macroscopic electric field $\mathbf{E}$ in the specimen is the field due to a homogeneous polarization $\mathbf{P}$ given by Eq. (4). This field may be regarded as the $\mathbf{q}\to 0$ limit of the field due to a continuous dipole distribution given by

$$\mathbf{p}(\boldsymbol{\rho})=\mathbf{P}\exp(i\mathbf{q}\cdot\boldsymbol{\rho})\ , \tag{11}$$

where $\boldsymbol{\rho}$ varies continuously over the space occupied by the sample. One obtains therefore,[9]

$$E_\alpha=-\lim_{\mathbf{q}\to 0}4\pi(q_\alpha q_\beta/q^2)P_\beta\ , \tag{12}$$

so that Eq. (10) can be rewritten as

$$A^{C}_{\mathscr{X}}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}u_\beta(k')=\left[\mathscr{L}_{D,\mathscr{X}}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}+\mathscr{L}_{R,\mathscr{X}}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}\right]u_\beta(k')-(e_k/V)E_\alpha\ . \tag{13}$$

We now expand every term of this equation about the initial configuration in powers of Lagrangian strain, using Eqs. (3), (6a), (7), (10a), and (10b), and retain terms up to the first power in $\underline{s}$. This gives

$$\begin{aligned}A^{C}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}u_\beta(k')+B^{C}\begin{bmatrix}k & k' & & \\ \alpha & \beta & \gamma & \epsilon\end{bmatrix}u_\beta(k')s_{\gamma\epsilon}&=\left[\mathscr{L}_{D}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}+\mathscr{L}_{R}\begin{bmatrix}k & k'\\ \alpha & \beta\end{bmatrix}\right]u_\beta(k')\\ &\quad+\left[\mathscr{L}_{D}\begin{bmatrix}k & k' & & \\ \alpha & \beta & \gamma & \epsilon\end{bmatrix}+\mathscr{L}_{R}\begin{bmatrix}k & k' & & \\ \alpha & \beta & \gamma & \epsilon\end{bmatrix}\right]u_\beta(k')s_{\gamma\epsilon}-(e_k/V_0)E_\alpha\ .\end{aligned} \tag{14}$$

Here, all the coefficients and summations are to be evaluated in undeformed configuration, $B^{C}(\begin{smallmatrix}k & k' & & \\ \alpha & \beta & \gamma & \epsilon\end{smallmatrix})$ is as defined in Eq. (6b), $\mathscr{L}_D(\begin{smallmatrix}k & k'\\ \alpha & \beta\end{smallmatrix})$ and $\mathscr{L}_R(\begin{smallmatrix}k & k'\\ \alpha & \beta\end{smallmatrix})$ are given by Eqs. (10a) and (10b) with volume V replaced by V_0, all the $\mathbf{R}$ by $\mathbf{r}_0$ and $\mathbf{G}$ by $\mathbf{G}_0$ (the reciprocal lattice vectors corresponding to an undeformed lattice), and

$$\begin{aligned}\mathscr{L}_{D}\begin{bmatrix}k & k' & & \\ \alpha & \beta & \gamma & \epsilon\end{bmatrix}=(e_k/V_0)\left[\delta_{kk'}\sum_{l_0 k_0}-\sum_{\substack{l_0\\ k_0=k'}}\right]e_{k_0}\{&(\delta_{\alpha\beta}r_{0\gamma}r_{0\epsilon}+\tfrac{1}{2}\delta_{\alpha\gamma}r_{0\beta}r_{0\epsilon}+\tfrac{1}{2}\delta_{\alpha\epsilon}r_{0\beta}r_{0\gamma}+\tfrac{1}{2}\delta_{\beta\gamma}r_{0\alpha}r_{0\epsilon}+\tfrac{1}{2}\delta_{\beta\epsilon}r_{0\alpha}r_{0\gamma})f(r_0,\sigma)\\ &-r_{0\alpha}r_{0\beta}r_{0\gamma}r_{0\epsilon}[(5/r_0^2)f(r_0,\sigma)+(8\sigma^5/\sqrt{\pi}r_0^2)\exp(-r_0^2\sigma^2)]\}\ ,\end{aligned} \tag{15a}$$

$$\begin{aligned}\mathscr{L}_{R}\begin{bmatrix}k & k' & & \\ \alpha & \beta & \gamma & \epsilon\end{bmatrix}=(4\pi e_k/V_0^2)\sum_{\mathbf{G}_0}\{&G_{0\alpha}G_{0\beta}G_{0\gamma}G_{0\epsilon}[(2/G_0^2)+(1/2\sigma^2)]-\delta_{\gamma\epsilon}G_{0\alpha}G_{0\beta}-\tfrac{1}{2}\delta_{\alpha\gamma}G_{0\beta}G_{0\epsilon}-\tfrac{1}{2}\delta_{\alpha\epsilon}G_{0\beta}G_{0\gamma}\\ &-\tfrac{1}{2}\delta_{\beta\gamma}G_{0\alpha}G_{0\epsilon}-\tfrac{1}{2}\delta_{\beta\epsilon}G_{0\alpha}G_{0\gamma}\}(1/G_0^2)f(\mathbf{G}_0,\mathbf{r}_0,\sigma)\ .\end{aligned} \tag{15b}$$

It is interesting to recast Eq. (14) in a different form for the special case of bulk strain $s_{\gamma\epsilon}=\delta_{\gamma\epsilon}s$. Thus, we consider a sample which has the shape of a sphere in the initial (and hence the final) configuration with center at the site (lk) and radius ξ, and denote the corresponding coefficients by A_ξ^C and B_ξ^C. We note that the lattice sums $\mathscr{L}_D$ and $\mathscr{L}_R$, being convergent, are independent of the shape of the sample, but the macroscopic field becomes $-(4\pi/3)\mathbf{P}$. This gives an expression for

$$\left[\mathscr{L}_D\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}+\mathscr{L}_R\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}\right]u_\beta(k')+\sum_\gamma\left[\mathscr{L}_D\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \gamma \end{bmatrix}+\mathscr{L}_R\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \gamma \end{bmatrix}\right]su_\beta(k')$$

in terms of $\mathbf{P}$, A_ξ^C, and B_ξ^C, so that Eq. (14) can be written with the help of Eq. (4) as

$$A^C\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}u_\beta(k')+\sum_\gamma B^C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \gamma \end{bmatrix}su_\beta(k')=\left[A_\xi^C\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}-(4\pi/3)(e_ke_{k'}/V_0^2)\delta_{\alpha\beta}\right]u_\beta(k')$$
$$+\sum_\gamma\left[B_\xi^C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \gamma \end{bmatrix}+(4\pi/3)(e_ke_{k'}/V_0^2)\delta_{\alpha\beta}\right]su_\beta(k')-(e_k/V_0)E_\alpha\ . \quad (16)$$

We point out here that FN have also derived expressions similar to those in Eqs. (10a), (10b), (15a), and (15b), with the difference that they used in place of internal strain, the quantity $\mathbf{u}(k)+\underline{\nu}\mathbf{u}(k)$. The present derivation shows how easily such expressions can be obtained by using Eq. (9) in lieu of the usual Ewald transformation.

Equations (14) and (16) achieve separation of macroscopic electric field from the indeterminate coefficients $A^C\binom{k\ k'}{\alpha\ \beta}$ and $B^C\binom{k\ k'}{\alpha\ \beta\ \gamma\ \epsilon}$. We have shown elsewhere[3,4] that from these separation equations one may obtain the expressions for second- and third-order elastic and other constants, by minimizing the strain energy density $\mathscr{E}$ with respect to internal strain. Closely following that derivation, it is found that in the expression for elastic constant, no contribution comes from the term involving $\mathbf{E}$ in Eqs. (14) and (16). One concludes, therefore, that, although Coulomb contributions towards the coefficients $A\binom{k\ k'}{\alpha\ \beta}$ and $B\binom{k\ k'}{\alpha\ \beta\ \gamma\ \epsilon}$ are actually undefined (for an infinite sample), one can obtain the Coulomb terms [$C\binom{k\ k'}{\alpha\ \beta}$ and $C\binom{k\ k'}{\alpha\ \beta\ \gamma\ \epsilon}$ say,] that arise from these coefficients in the expression for Brugger second- and third-order elastic constants, by omitting the term involving macroscopic electric field, i.e., the $\mathbf{q}\rightarrow 0$ limit, from the Ewald expansion, Eq. (10). This is exactly the method which FN have followed and the present theory thus justifies their procedure. We find furthermore that

$$C\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}=\mathscr{L}_D\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}+\mathscr{L}_R\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix} \quad (17a)$$

$$=A_\xi^C\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}-(4\pi/3)(e_ke_{k'}/V_0^2)\delta_{\alpha\beta}\ , \quad (17b)$$

$$C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \epsilon \end{bmatrix}=\mathscr{L}_D\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \epsilon \end{bmatrix}+\mathscr{L}_R\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \epsilon \end{bmatrix}\ , \quad (18a)$$

and

$$\sum_\gamma C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \gamma \end{bmatrix}=\sum_\gamma B_\xi^C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \gamma \end{bmatrix}+4\pi(e_ke_{k'}/V_0^2)\delta_{\alpha\beta}\ . \quad (18b)$$

III. INTERRELATIONS BETWEEN ELECTROSTATIC CONTRIBUTIONS

We shall now derive certain relationships among the electrostatic contributions $C\binom{k\ k'}{\alpha\ \beta}$ and $C\binom{k\ k'}{\alpha\ \beta\ \gamma\ \epsilon}$ for an arbitrary crystal structure. First, we note from Eq. (6a) that $\sum_\alpha A^C\binom{k\ k'}{\alpha\ \alpha}$ is zero, whatever the shape of the sample. Equation (17b), therefore, gives

$$\sum_\alpha C\begin{bmatrix} k & k' \\ \alpha & \alpha \end{bmatrix}=-4\pi(e_ke_{k'}/V_0^2)\ . \quad (19)$$

Similarly, Eq. (6b) gives

$$\sum_\gamma B^C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \gamma \end{bmatrix}=-3A^C\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}\ ,$$

so that from Eqs. (17b) and (18b) we have

$$\sum_\gamma C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \gamma \end{bmatrix}=-3C\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}\ . \quad (20)$$

Lastly, from Eqs. (17a) and (18a) one can verify, with the help of Eqs. (10a), (10b), (15a), and (15b), that

$$C\begin{bmatrix} k & k' & & \\ \alpha & \alpha & \beta & \beta \end{bmatrix}-C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \alpha & \beta \end{bmatrix}=\frac{1}{2}\left[C\begin{bmatrix} k & k' \\ \beta & \beta \end{bmatrix}-C\begin{bmatrix} k & k' \\ \alpha & \alpha \end{bmatrix}\right]\ , \quad (21)$$

$$C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \gamma & \epsilon \end{bmatrix}=C\begin{bmatrix} k & k' & & \\ \beta & \alpha & \gamma & \epsilon \end{bmatrix}\ , \quad (22)$$

and

$$C\begin{bmatrix} k & k' & & \\ \alpha & \alpha & \alpha & \beta \end{bmatrix}-C\begin{bmatrix} k & k' & & \\ \alpha & \beta & \alpha & \alpha \end{bmatrix}=C\begin{bmatrix} k & k' \\ \alpha & \beta \end{bmatrix}\ . \quad (23)$$

In view of these hitherto unnoticed interrelationships [Eqs. (19)–(23)] one now needs to evaluate a lesser number of Coulomb contributions while calculating the elastic constants for a given crystal structure. Thus, in the tabulation by FN for cubic zinc-blende, WC-type (ionic hexagonal close packed), and wurtzite structures, a total of 29 evaluations become redundant. For example, for cubic zinc-blende structure, one obtains by invoking cubic symmetry in Eq. (19),

$$C\begin{bmatrix} k & k \\ \alpha & \alpha \end{bmatrix}=-(4\pi/3)(e_k^2/V_0^2),\quad \alpha=1,2,3\ , \quad (24)$$

and we have evaluated this Coulomb contribution *purely from analytic considerations.*

Besides, we have verified that the results obtained by FN, after proper conversion as regards definition, etc., satisfy Eqs. (19)–(23), in every case; this, incidentally, serves as a check for their numerical results.

To conclude, we point out that Eqs. (19) and (20) are also derivable (by using Ewald transformation), from the expressions for $\mathcal{L}_D$, $\mathcal{L}_R$ in Eqs. (10a), (10b), (15a), and (15b). Hence, Eqs. (19)–(23) can also be obtained from the expressions given by FN, but that derivation will be more lengthy.

IV. FULLER AND NAIMON'S PROCEDURE

It is physically obvious that the electrostatic energy of a strained piezoelectric crystal should involve a macroscopic electric field. We shall now discuss why such a term did not appear in the treatment of FN. Their procedure was to write down the expression for electrostatic energy per unit initial volume in strained configuration as

$$U_{ii}' = \frac{1}{2V_0\lambda} \sum_{l_0 k_0 k} \frac{e_k e_{k_0}}{(r/\lambda)} ,$$

[where $\lambda = (V_0/n)^{1/3}$, n being the number of ions per unit cell] and then substitute in it the definition of the Γ function to obtain

$$U_{ii}' = \frac{1}{2V_0\lambda} \sum_{l_0 k_0 k} e_k e_{k_0} \left(\int_0^\sigma + \int_\sigma^\infty \right) dt\, t^{-1/2} \exp\left(-\frac{\pi r^2 t}{\lambda^2} \right) . \tag{25}$$

Then they interchange the order of summation and integration and this is the step which is objectionable, because the summand is indeterminate and the lattice periodicity is lost due to surface sensitivity [see Eqs. (6a) and (6b)]. Therefore, Ewald transformation is not applicable as such and, in view of the basic idea involved therein (Ref. 2, p. 250), the correct procedure would be rather to perform Fourier transformation *of the integral* $\int_0^\sigma dt\, t^{-1/2} \exp(-\pi r^2 t/\lambda^2)$. It is clear that, in the zero-wave-vector term obtained by this procedure, the order of the $\mathbf{q} \rightarrow 0$ limit and integration over t will be the reverse of that in FN's expression. Thus, U_{ii}' will now contain the term

$$-\frac{\lambda^2}{2V_0 V} \sum_{k_0 k} e_k e_{k_0} \lim_{\mathbf{q} \rightarrow 0} \int_0^\sigma dt\, t^{-2} \exp\left(i\mathbf{q} \cdot \mathbf{r}_{k_0 k} - \frac{\lambda^2 q^2}{4\pi t} \right) ,$$

which becomes, on account of the charge neutrality condition,

$$(\pi / V_0 V) \left(\lim_{\mathbf{q} \rightarrow 0} q_\alpha q_\beta / q^2 \right) \sum_{k_0 k} e_k e_{k_0} r_{k_0 k \alpha} r_{k_0 k \beta} .$$

We conclude, therefore, that, to FN's expression for electrostatic energy [Eq. (8) therein], one should add the above correction term which, as seen from Eq. (12), will involve macroscopic electric field.

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[9] See Born and Huang, Ref. 2, p. 249. Although their derivation does not take into account surface charges and therefore breaks down in general, for $\mathbf{q} = 0$, it does hold true in our case, on account of the chosen shape of our sample.