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Electrostriction

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The form of the lowest-order electrostrictive effect in crystals is investigated using a nonlinear theory of the elastic dielectric, described in a previous publication. We find that the electrostrictive coefficients in the equation of state for the applied stress (a) has one form for a dielectric-vacuum interface and another for a dielectric-conductor interface, and (b) is different from the analogous coefficients in the equation of state for the electric field. These differences are shown to be numerically significant in the case of barium titanate.

I. INTRODUCTION

Electrostriction is the nonlinear coupling of the elastic and dielectric properties of an insulator. The standard[1] development of the theory of this effect is obtained by adopting the field equations and boundary conditions of the linear theory and adding nonlinear terms to the equation of state. Recent work[2–4] on the nonlinear theory of the elastic dielectric shows that this procedure is not generally valid. (The form of the nonlinear field equations and boundary conditions and the arguments in the "nonlinear" energy density cannot be obtained from an inspection or extrapolation of the results of the linear theory.) In the present paper we investigate the form of the lowest-order nonlinear equations of state based on the analysis of the elastic dielectric presented in I. We find that the electrostrictive coefficients in the equation of state for the applied stress (a) have one form at a dielectric-vacuum boundary and another at a dielectric-conductor boundary, and (b) differ from the analogous coefficients in the equation of state for the electric field. In the second part of the paper these results are applied to the case of barium titanate. We find here that these differences are important.

II. EQUATIONS OF STATE

A. Nonlinear Equation of State

The deformation and displacement of an elastic dielectric is completely described by two fields: (a) the set of position coordinates $X_K (K=1, 2, 3)$ specifying the positions of the volume elements of the body in some initial configuration, and (b) the analogous set of position coordinates $x_i (i=1, 2, 3)$ describing their positions in the final configuration of interest. We shall suppose that the components of each field are measured in the same rectangular coordinate system. For a continuous body there exists some functional relationship $x_i=x_i(X_K)$. We denote differentiation with respect to the initial position coordinates X_K in the following manner: $\partial f/\partial X_K=f_{;K}$.[5] The deformation gradients are $x_{i;K}$. The displacement suffered by the volume element initially at X_i is $x_i-X_i=u_i$; here u_i is the displacement vector and $u_{i;K}$ the displacement gradient. The strain tensor η_{KL} is defined $\eta_{KL}=\frac{1}{2}(x_{i;K}x_{i;L}-\delta_{KL})$, where in this and all later expressions the repetition of a subscript denotes a summation over the values 1, 2, 3. δ_{KL} is the Kronecker delta, $\delta_{KL}=1$, $K=L$; $\delta_{KL}=0$, $K\neq L$. From the definition of η_{KL}, we can easily show that

$$\eta_{KL}=\tfrac{1}{2}(u_{K;L}+u_{L;K}+u_{i;K}u_{i;L}). \tag{1}$$

In I we deduced the following relations:

(i) At the surface of the dielectric [see Eq. (33) in I]

$$t_i=\left(\frac{\partial\psi}{\partial x_{i;K}}\right)_D (x_{j;K}n_j) -\left[\frac{D_j^A D_j^A}{2\epsilon_0}-\psi+\tfrac{1}{2}(E_j^V+E_j^A)(D_j^V-D_j^A)\right]n_i; \tag{2}$$

(ii) within the dielectric [see Eq. (25) in I]

$$E_i=\frac{\partial\psi}{\partial D_i}, \tag{3}$$

where t_i is the applied mechanical stress, $\psi=[\psi(x_{i;K},D_i)]$ the dielectric energy density, n_i the unit vector parallel to the outward normal at the dielectric surface, E_i and D_i the electric field and the electric displacement field, and ϵ_0 the permitivity of free space. The dielectric and free-space values of the fields E_i, D_i are distinguished, where necessary, by the superscripts V and A, respectively. We shall refer to the quantity in the square brackets in Eq. (2) as the Maxwell stress. Since $x_{i;K}=u_{i;K}+\delta_{iK}$, we have from Eq. (2)

$$t_i=\left(\frac{\partial\psi}{\partial u_{i;K}}\right)_D (u_{j;K}+\delta_{jK})n_j -\left[\frac{D_j^A D_j^A}{2\epsilon_0}-\psi+\tfrac{1}{2}(E_j^V+E_j^A)(D_j^V-D_j^A)\right]n_i. \tag{4}$$

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[1] P. W. Forsburgh, Jr., in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXVI.

[2] R. A. Toupin, J. Rat. Mech. Anal. **5**, 849 (1956); Arch. Rat. Mech. Anal. **5**, 440 (1960).

[3] A. C. Eringen, Int. J. Eng. Sci. **1**, 127 (1965).

[4] J. Grindlay, Phys. Rev. **149**, 637 (1966), referred to in the text as I.

[5] In I we used the semicolon notation for differentiation with respect to both X_K *and* x_i.

We set

$$\left(\frac{\partial\psi}{\partial u_{i;K}}\right)_D (u_{j;K}+\delta_{jK})-\left[\frac{D_j{}^A D_j{}^A}{2\epsilon_0}-\psi+\tfrac{1}{2}(E_j{}^V+E_j{}^A)\times(D_j{}^V-D_j{}^A)\right]\delta_{ij}=T_{ji}. \quad (5)$$

The field T_{ji} is defined only on the surface of the dielectric and has the following properties: (a) $T_{ji}n_j=t_i$; (b) at any point on the surface at which the normal is parallel to one of the coordinate axes, x_k say, $n_j=\delta_{kj}$ and hence $T_{ki}=t_i$, i.e., T_{kk} is a normal stress and $T_{ki}(i\neq k)$ a shear stress. Thus T_{ji} possesses some of the properties of the stress-tensor field of the standard linear theory. However, in general $T_{ji}\neq T_{ij}$.

Equations (3) and (5) can be regarded as equations of state, in the sense that they relate the applied stress and the electric field to the displacement gradients and the displacement field (D_i). However, the latter relation, Eq. (5), differs considerably in form from the usual stress-strain relation characteristic of the linear theory. It is the object of this paper to examine these differences and to determine under what circumstances they could be significant in the special case of the crystal barium titanate. We shall base our analysis on an approximation scheme suggested by the nonlinear behavior of real crystals, principally barium titanate. It appears that a good first-order nonlinear approximation to the equations of state is one in which (a) the applied stress components are represented by the sum of two polynomials, one of order unity in the displacement gradients $u_{K;L}$ and the other of order two in the components D_i, and (b) the electric-field components are represented by the sum of three polynomials one of order unity in $u_{K;L}$, one bilinear in $u_{K;L}$ and D_i and one of arbitrary order in D_i. (See, for example, Jona and Shirane.[6])

Approximation

We assume that the energy density $\psi(x_{i;K},D_i)$ can be represented by a polynomial in the arguments $x_{i;K}$, D_i. Then the demands of invariance with respect to changes of axes (see I) lead to the result that the polynomial representation for ψ is reducible to a polynomial in the ten arguments η_{KL}, $\Pi_K=x_{i;K}D_i$, and $a=D_iD_i$.

From an inspection of Eqs. (3) and (5) and the definitions of η_{KL}, Π_K, and a we can verify that we get the polynomial representation for T_{ji} and E_i described at the end of the previous section from the following polynomial representation for ψ:[7]

$$\psi=\tfrac{1}{2}H_{KLMN}{}^1\eta_{KL}\eta_{MN}+H_{KLM}{}^2\eta_{KL}\Pi_M+\tfrac{1}{2}H_{KL}{}^3\Pi_K\Pi_L+H^4a+H_{KLMN}{}^5\eta_{KL}\Pi_M\Pi_N+H_{KL}{}^6\eta_{KL}a+g(\Pi_K,a), \quad (6)$$

where g is a polynomial containing terms of order two and higher in a and of order three and higher in Π_K. The $H_{KLM\cdots}{}^\alpha$'s are tensors characteristic of the dielectric of interest. Since they are coefficients in a polynomial, each one is invariant under certain interchanges of subscripts; for example, $H_{KL}{}^3=H_{LK}{}^3$. In addition, the $H_{KLMN\cdots}{}^\alpha$ are invariant under the operations of the material symmetry group of the dielectric.[2] While the tensor η_{KL} is symmetric, it is convenient in algebraic manipulations to use the convention that η_{KL} and η_{LK} are treated as independent variables. In the first-order nonlinear approximation described above we have from Eqs. (3) and (6)

$$E_M=H^2{}_{KLM}u_{KL}+(H_{MN}{}^3+2H^4\delta_{MN})D_N+2[H_{KLMN}{}^5+H_{KL}{}^6\delta_{MN}+\tfrac{1}{2}(H_{ML}{}^3\delta_{NK}+H_{LN}{}^3\delta_{MK})]u_{KL}D_N+\frac{dg^0}{dD_M}, \quad (7)$$

$$\frac{\partial\psi}{\partial x_{K;J}}x_{L;J}=H_{KLMN}{}^1u_{MN}+H_{KLM}{}^2D_M+[H_{KLMN}{}^5+H_{KL}{}^6\delta_{MN}\ \tfrac{1}{2}(H_{ML}{}^3\delta_{NK}+H_{LN}{}^3\delta_{MK})]D_MD_N, \quad (8)$$

where we have dropped the semicolon notation, i.e., $u_{K;L}\rightarrow u_{KL}$ and $g^0=g(\Pi_K,a)\,|\,u_{KL}\equiv 0$.

Consider the Maxwell stress. From the boundary conditions $e_{ijk}(E_j{}^A-E_j{}^V)n_k=0$ and $(D_i{}^A-D_i{}^V)n_i=0$, (where e_{ijk} is the Levi-Civita density), the free-space relationship $D_i{}^A=\epsilon_0E_i{}^A$, and (7), we can express the nine components $D_i{}^A$, $E_i{}^A$, $E_i{}^V$ in terms of the components $D_i{}^V$ and u_{KL}. Thus the leading term in the Maxwell stress is a quadratic function of u_{KL} and $D_i{}^V$. However, within our approximation scheme we neglect all but the quadratic terms in $D_i{}^V$ and hence we set

$$\left[\frac{D_j{}^AD_j{}^A}{2\epsilon_0}-\psi+\tfrac{1}{2}(E_j{}^V+E_j{}^A)(D_j{}^V-D_j{}^A)\right]=J_{MN}D_M{}^VD_N{}^V, \quad (9)$$

where the J_{MN} are functions of the $H_{KLM\cdots}{}^\alpha$'s. We shall

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[6] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., Oxford, England, 1962).

[7] No terms linear in η_{KL} and Π_K appear in this representation because we assume that in the initial configuration or state the electric field, the displacement field (**D**), and the applied stress field are identically zero. In the case of crystals in a ferroelectric phase the state satisfying these conditions is unstable. [See L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon Press, Inc., Oxford, England, 1960), Chap. 2.] However, we know of no physical reasons against the use of such states as initial states.

derive an explicit expression for J_{MN} in the following section.

Combining Eqs. (5), (8), and (9), we get

$$\begin{aligned} T_{KL}=H_{KLMN}{}^1u_{MN}+H_{KLM}{}^2D_M{}^V &\\ +[H_{KLMN}{}^5+H_{KL}{}^6\delta_{MN} &\\ +\tfrac{1}{2}(H_{ML}{}^3\delta_{NK}+H_{LN}{}^3\delta_{MK}) &\\ -J_{MN}\delta_{KL}]D_M{}^VD_N{}^V. &\quad (10)\end{aligned}$$

From Eqs. (7) and (10) we identify the quantities $H_{KLMN}{}^1$, $H_{KLM}{}^2$, and $(H_{MN}{}^3+2H^4\delta_{MN})$ as the elastic compliance, the piezoelectric coefficient, and the dielectric permeability, respectively. The quantities in the square brackets in these equations play the role of electrostrictive coefficients. However, they differ in two respects from their counterparts in the standard theory. First of all, these quantities, by inspection, are not symmetric under an interchange of the subscripts K and L; hence (i) $T_{KL}\neq T_{LK}$ and (ii) the electric field components are functions of the displacement gradient tensor u_{KL} and not merely the symmetric tensor $\frac{1}{2}(u_{KL}+u_{LK})$, the so-called infinitesimal strain. Secondly, the electrostrictive coefficients appearing in the relation for T_{KL} differ from the electrostrictive coefficients in the relation for E_M. The difference is $J_{MN}\delta_{KL}$.

Maxwell Stress

We now determine expressions for the J_{MN} in terms of the coefficients $H_{KL}{}^3$ and H^4. Consider a point on the surface of the dielectric. For simplicity let the normal to this point be parallel to the x_1 axis. From the boundary conditions for D_i, E_i we have $D_1{}^A=D_1{}^V$, $E_2{}^A=E_2{}^V$, and $E_3{}^A=E_3{}^V$. Since $D_i{}^A=\epsilon_0E_i{}^A$, then $E_1{}^A=D_1{}^V/\epsilon_0$, $D_2{}^A=\epsilon_0E_2{}^V$, and $D_3{}^A=\epsilon_0E_3{}^V$. To calculate J_{MN} we need only consider $E_M{}^V$ as a linear function of $D_M{}^V$ (see above), that is $E_M{}^V=(H_{MN}{}^3+2H^4\delta_{MN})D_N{}^V$: See Eq. (7). Setting $(H_{MN}{}^3+2H^4\delta_{MN})=\kappa_{MN}$ and combining the results listed above, we get

$$\begin{aligned} J_{MN}D_M{}^VD_N{}^V=\frac{(D_1{}^V)^2}{2\epsilon_0}-\frac{\kappa_{MN}D_M{}^VD_N{}^V}{2} &\\ -\frac{\epsilon_0}{2}[\kappa_{2M}\kappa_{2N}+\kappa_{3M}\kappa_{3N}]D_M{}^VD_N{}^V &\\ +[\kappa_{2M}D_2D_M+\kappa_{3M}D_3D_M], &\end{aligned}$$

and hence

$$\begin{aligned} J_{11}=\frac{1}{2}\left[\frac{1}{\epsilon_0}-\kappa_{11}-\epsilon_0(\kappa_{12}{}^2+\kappa_{13}{}^2)\right] &\\ J_{12}=-\tfrac{1}{2}\epsilon_0[\kappa_{12}\kappa_{22}+\kappa_{13}\kappa_{23}], &\quad (11)\\ J_{22}=\tfrac{1}{2}[\kappa_{22}-\epsilon_0(\kappa_{22}{}^2+\kappa_{23}{}^2)] &\\ J_{23}=\tfrac{1}{2}[\kappa_{23}-\epsilon_0\kappa_{23}(\kappa_{22}+\kappa_{32})]. &\end{aligned}$$

J_{33}, J_{13} can be generated from J_{22}, J_{12} by replacing 2 with 3.

III. BARIUM TITANATE

O_h Material Symmetry

When the material symmetry group of the dielectric is the crystallographic point group O_h, the $H_{KLM\cdots}{}^\alpha$ appearing in Eq. (6) have the properties listed below.[8] The axes used here are the standard cubic crystallographic axes:

(i) $H_{1111}{}^1=H_{2222}{}^1=H_{3333}{}^1$; $H_{1122}{}^1=H_{2233}{}^1=H_{3311}{}^1$; $H_{2323}{}^1=H_{3131}{}^1=H_{1212}{}^1$.

The remaining $H_{KLMN}{}^1$'s are identically zero.

(ii) $H_{KLM}{}^2=0$ all K, L, M;

(iii) $H_{11}{}^3=H_{22}{}^3=H_{33}{}^3$; $H_{12}{}^3=H_{23}{}^3=H_{31}{}^3\equiv 0$; $H_{11}{}^6=H_{22}{}^6=H_{33}{}^6$; $H_{12}{}^6=H_{23}{}^6=H_{31}{}^6\equiv 0$;

(iv) $H_{1111}{}^5=H_{2222}{}^5=H_{3333}{}^5$; $H_{1122}{}^5=H_{1133}{}^5=H_{2233}{}^5=H_{3322}{}^5=H_{3311}{}^5=H_{2211}{}^5$; $H_{2323}{}^5=H_{1313}{}^5=H_{1212}{}^5$.

The remaining $H_{KLMN}{}^5$'s are identically zero.

Using these results we find that Eqs. (7) and (10) take the form

$$\begin{aligned} E_1=\kappa D_1+2q_{11}u_{11}D_1+2q_{12}(u_{22}+u_{33})D_1 &\\ +q_{44}[D_2(u_{12}+u_{21})+D_3(u_{13}+u_{31})], &\quad (12)\end{aligned}$$

$$\begin{aligned} T_{11}=c_{11}{}^Du_{11}+c_{12}{}^D(u_{22}+u_{33})+q_{11}(D_1{}^V)^2 &\\ +q_{12},[(D_2{}^V)^2+(D_3{}^V)^2]-J_{MN}D_M{}^VD_N{}^V, &\quad (13)\end{aligned}$$

$$T_{12}=c_{44}{}^D(u_{12}+u_{21})+q_{44}D_1{}^VD_2{}^V, \quad \text{etc.}, \qquad (14)$$

where

$$c_{11}{}^D=H_{1111}{}^1,\quad c_{12}{}^D=H_{1122}{}^1,\quad c_{44}{}^D=H_{1212}{}^1,$$

$$\kappa=H_{11}{}^3+2H^4,$$

$$q_{11}=(H_{1111}{}^5+H_{11}{}^3+H_{11}{}^6),\quad q_{12}=(H_{1122}{}^5+H_{11}{}^6),$$

$$q_{44}=(H_{1212}{}^5+H_{11}{}^3).$$

Thus for O_h symmetry $T_{KL}=T_{LK}$ and the components E_M are functions only of the symmetric part of the tensor u_{KL}.

For this material group $\kappa_{ij}=\kappa\delta_{ij}$, and hence

$$J_{11}=\frac{1}{2}\left(\frac{1}{\epsilon_0}-\kappa\right);\quad J_{22}=J_{33}=\tfrac{1}{2}(\kappa-\epsilon_0\kappa^2);$$

$$J_{12}=J_{23}=J_{31}=0.$$

We recall that the expressions for J_{MN} in Eq. (11) hold for a surface point at which the normal lies parallel to the x_1 axis. Hence on substituting the above results into Eq. (12), we find that at such a point the normal stress

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[8] Most of these results were obtained from tables; see, for example, H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 12. $H_{KLMN}{}^5$ is not tabulated and we applied the "direct-inspection method" [F. G. Fumi, Acta Cryst. 5, 44 (1952)] using the generators of O_h [R. R. Birss, *Reports on Progress in Physics* (The Institute of Physics and The Physical Society, London, 1963), Vol. 24] to obtain the results listed above.

satisfies the relation

$$T_{11}=c_{11}{}^{D}u_{11}+c_{12}{}^{D}(u_{22}+u_{33})+\frac{1}{2}\left[2q_{11}+\left(\kappa-\frac{1}{\epsilon_0}\right)\right](D_1{}^V)^2 + \tfrac{1}{2}[2q_{12}+(\epsilon_0\kappa^2-\kappa)][(D_2{}^V)^2+(D_3{}^V)^2]. \quad (15)$$

We have previously[9] considered the electrostrictive properties of a thin dielectric slab with O_h symmetry, placed between tightly fitting plates of a condenser.[10] In the present notation, the results obtained were

$$T_{11}=c_{11}{}^{D}u_{11}+c_{12}{}^{D}(u_{22}+u_{33}) + \tfrac{1}{2}[2q_{12}-\kappa+\epsilon_0\kappa^2](D_3{}^V)^2 \quad (16)$$

at a dielectric-vacuum boundary with $D_1{}^V=D_2{}^V=0$, and

$$T_{11}=c_{11}{}^{D}u_{11}+c_{12}{}^{D}(u_{22}+u_{33})+\tfrac{1}{2}[2q_{11}+\kappa](D_1{}^V)^2 \quad (17)$$

at a dielectric-conductor boundary with $D_1{}^V=D_2{}^V=0$. Equation (16) is a special case of (15). From (15) and (17), we conclude that the electrostrictive coefficients appearing in the relation satisfied by the applied normal stress vary, having one form for a dielectric-vacuum boundary and another for a dielectric-conductor boundary. It is clear that these conclusions also apply in the general case in which the surface normal does not lie parallel to the x_1 axis. The form of the coefficients in the general case can be obtained using the standard analysis associated with changes of coordinate axes.

Barium Titanate

In the case of zero applied stress,[11] the equation of state for the applied stress provides a relationship between the spontaneous strain and the spontaneous polarization in terms of the linear and the electrostrictive coefficients. In Ref. 9 we used this fact to calculate the electrostrictive coefficients for barium titanate at room temperature. We found that $q_{11}=-1.5\times10^{10}$ mks and $q_{12}=0.15\times10^{10}$ mks. These results are in reasonable agreement with the values obtained from other data.[6] For comparison we note that $1/\epsilon_0=11\times10^{10}$ mks and $\kappa=6.6\times10^5(T-T_0)$ mks, where $T_0=110°\mathrm{C}$.[11] Hence we may conclude that for barium titanate at room temperatures the Maxwell stress is significant at a dielectric-vacuum interface and not at a dielectric-conductor interface.

Since $1/\epsilon_0$ plays a numerically significant role in the electrostrictive properties at a dielectric-vacuum interface and does not appear in the case of a dielectric-conductor interface, the form of the relationship between the spontaneous strain and the spontaneous polarization depends critically on the nature of the boundaries of the dielectric specimen of interest. Because of this and because Kay and Vousden[12] do not describe the nature of the boundaries of the specimen used in their experimental determination of the spontaneous strains, we must regard the values for q_{11}, q_{12}, deduced in Ref. 9 from these strain values, as merely an order of magnitude estimate.

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[9] J. Grindlay, in *Proceedings of the International Meeting on Ferroelectricity* (Institute of Physics of the Czechoslovak Academy of Sciences, Prague, 1966), Vol. 1, p. 433.

[10] The analysis presented in I does not apply to the case in which the dielectric is in contact with a conductor.

[11] M. E. Drougard and D. R. Young, Phys. Rev. **94**, 1561 (1954).

[12] H. F. Kay and P. Vousden, Phil. Mag. **40**, 1019 (1949).