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Physical Motivations of the Constitutive Relations for Ferroelectric Ceramics and the Existence of Butterfly and Hysteresis Loops

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ABSTRACT

The responses of ferroelectric ceramics can be quite complex depending on the physical processes to which they are subjected. Their mechanical, electromechanical and dielectric properties depend on domain switching, dipole dynamics and phase transformation which can be caused by external stimuli such as mechanical and electrical loadings, and temperature variations. A theory, taking into account the effects of domain switching and dipole dynamics, has been formulated, and in its present stage of development is sufficient to characterize various observable responses. Specifically, a special case of the theory predicts the nature of the butterfly and hysteresis loops. The butterfly and hysteresis loops are manifestations of the mechanical, electro-mechanical and dielectric responses due to domain switching produced by cyclic electric fields. Comparisons of the predictions of the theory with experimental results are made in a pseudo one dimensional context.

Basic Equations

Generally speaking there are three constitutive properties which must be taken into account in order to describe the responses of ferroelectric ceramics, viz. their mechanical, electro-mechanical and dielectric properties. These properties can also depend on domain switching, dipole dynamics and phase transformation which may occur due to external stimuli such as mechanical and electrical loadings, and temperature variations. Therefore, constitutive relations for ferroelectric ceramics can be quite complex depending on the physical processes to which they are subjected. Special cases can, of course, be postulated, and which are applicable to specific situations.

Let $\underset{\sim}{\mu}$ denote the electric dipole moment. We presume that its magnitude and direction depend on the mechanical strain $\underset{\sim}{S}$, the absolute temperature Θ and the external electric field $\underset{\sim}{E}$. We also introduce the vector $\underset{\sim}{N}$, defined by the relation

$$\underset{\sim}{N} = (\Sigma\underset{\sim}{\mu}\cdot\underset{\sim}{j})\underset{\sim}{j} \quad , \tag{1}$$

where $\underset{\sim}{j}$ is a unique unit vector such that if $\underset{\sim}{N}$ is not the zero vector then it must have maximum magnitude, and where the summation is carried out over each subpart of a ferroelectric specimen. The direction of $\underset{\sim}{j}$ defines the direction of polarization and the magnitude of $\underset{\sim}{N}$ gives the effective number of aligned unit cell dipoles in this direction. We further presume that the response of $\underset{\sim}{\mu}$ may be partitioned into its transient response $\underset{\sim}{\mu}_t$ and its instantaneous response $\underset{\sim}{\mu}_i$ so that

$$\underset{\sim}{\mu} = \underset{\sim}{\mu}_t + \underset{\sim}{\mu}_i \quad . \tag{2}$$

In the absence of phase transformation, the responses of a ferroelectric ceramic may be described by the constitutive relations[1]

$$\underset{\sim}{T} = \hat{\underset{\sim}{T}}(\underset{\sim}{S},\Theta,\underset{\sim}{E},\underset{\sim}{\mu}_t,\underset{\sim}{N}) \quad ,$$
$$\underset{\sim}{D} = \hat{\underset{\sim}{D}}(\underset{\sim}{S},\Theta,\underset{\sim}{E},\underset{\sim}{\mu}_t,\underset{\sim}{N}) \quad , \tag{3}$$

where $\underset{\sim}{T}$ is the stress and $\underset{\sim}{D}$ is the electric displacement, together with the rate laws

$$\dot{\underset{\sim}{\mu}} = \underset{\sim}{f}(\underset{\sim}{S},\Theta,\underset{\sim}{E},\underset{\sim}{\mu}_t,\underset{\sim}{N}) \quad ,$$
$$\dot{\underset{\sim}{N}} = \underset{\sim}{g}(\underset{\sim}{S},\Theta,\underset{\sim}{E},\underset{\sim}{\mu}_t,\underset{\sim}{N}) \quad . \tag{4}$$

In the following section we consider representations of a special case of (3) and (4) which leads to the hysteresis and butterfly loops.

A Special Case

An interesting physical situation we have in mind is a specimen in isothermal, stress-free and uniaxial strain conditions subjected to a slowly varying unidirectional cyclic electric field of sufficient magnitude to cause domain switching.[1] Since dipole dynamics as described by $(4)_1$ occurs on a much faster time scale, we have $\underset{\sim}{\mu}_t = \underset{\sim}{0}$. We denote the direction of the electric field as X_3. Therefore,

$$\underset{\sim}{E} = (0,0,E) \quad ,$$
$$\underset{\sim}{N} = (0,0,N) \quad , \tag{5}$$

and the non-zero component of the strain is $S_{33} \equiv S$. It follows from (3), (4) and (5) that the stress component $T_{33} \equiv T$ and the electric displacement component $D_3 \equiv D$ are given by

$$T = \hat{T}(S,E,N) \quad ,$$
$$D = \hat{D}(S,E,N) \quad , \tag{6}$$

and the rate law $(4)_2$ becomes

$$\dot{N} = g(E,N) \quad . \tag{7}$$

The effective number of aligned dipoles N is also given by

$$N = N^{\parallel} + N^{\perp} \quad , \tag{8}$$

where $N^{\parallel}$ and $N^{\perp}$ denote, respectively, the effective number of aligned parallel and perpendicular dipoles. In addition, $N^{\parallel}$ and $N^{\perp}$ are given by

$$N^{\parallel} = N_s^{\parallel} + N_n^{\parallel}, \; N^{\perp} = N_s^{\perp} + N_n^{\perp} \quad , \tag{9}$$

[1]A domain is a region of the specimen containing several parallel dipoles.

where the subscripts s and n denote, respectively, the effective number of aligned permanently switchable and non-permanently switchable parallel or perpendicular dipoles.

We now consider the following specific representations of the constitutive relations (6):

$$T = (C+C'N)S-eNE+h^{\parallel}N^{\parallel}+h^{\perp}N^{\perp} \quad , \qquad D = eNS+(\varepsilon+\varepsilon'N)E+kN \quad . \tag{10}$$

In (10), C and ε are the elastic and dielectric constants of the virgin specimen. The term $C'N$ gives the change to C and $\varepsilon'N$ gives the change to ε due to domain switching. The coefficient eN with e>0 plays the role of the electro-mechanical coupling coefficient. Notice that the values of these terms depend on the effective number of aligned dipoles. The terms $h^{\parallel}N^{\parallel}$ and $h^{\perp}N^{\perp}$ give the additional stress and the term kN gives the additional electric displacement due to domain switching. In particular, we require that

$$\operatorname{sgn} h^{\parallel} = -\operatorname{sgn} N^{\parallel}, \quad \operatorname{sgn} h^{\perp} = -\operatorname{sgn} N^{\perp} \quad , \tag{11}$$

and k>0.

We presume that (7) has the specific representation

$$\dot{N}+\alpha(E)N = \beta(E) \quad . \tag{12}$$

This linear differential equation (12) describing the consequences of domain switching under the action of an externally applied electric field seems sufficient and reasonable. However, the dependences of the functions α and β on E, are quite complex. First, it is a simple matter to show that $1/\alpha(E)$ plays the role of switching time corresponding to each value of the field E. Since switching time must decrease with increasing magnitude of the electric field, we require α to be a positive even function of E which increases monotonically with increasing $|E|$ and $\alpha(0)=0$. Now suppose that a constant applied field has been maintained for a sufficiently long time so that domains have ceased switching. It follows directly from (12) that we have $N_e(E)=\beta(E)/\alpha(E)$. It is clear that $N_e(E)$ gives the total effective number of dipoles which may be aligned by the field E. Hence, we require β/α to be an odd function of E such that $\operatorname{sgn} \beta(E)/\alpha(E)=\operatorname{sgn} E$ and whose magnitude increases monotonically with increasing $|E|$ such that for sufficiently large $|E|$ the values of β/α are bounded. The properties of the function β may be deduced from those of α and β/α.

As we have remarked, the effective number of aligned dipoles is given by

$$N = N_s^{\parallel}+N_s^{\perp}+N_n^{\parallel}+N_n^{\perp} \quad . \tag{13}$$

We may assume that the switching responses of these four classes of domains are uncoupled and that we may prescribe separate rate laws for $N_s^{\parallel}$, $N_s^{\perp}$, $N_n^{\parallel}$ and $N_n^{\perp}$. To this end, we define the functions β_s and β_n of E via the relations

$$\beta_s(E) = s\beta(E), \ \beta_n(E) = n\beta(E) \quad , \tag{14}$$

where s and n are positive numbers such that s+n = 1 and

$$\beta(E) = \beta_s(E)+\beta_n(E) \quad . \tag{15}$$

We also introduce the functions N_{se} and N_{ne}, defined by the relations

$$N_{se}(E) = \beta_s(E)/\alpha(E) = sN_e(E), \qquad N_{ne}(E) = \beta_n(E)/\alpha(E) = nN_e(E), \tag{16}$$

so that

$$N_e(E) = N_{se}(E) + N_{ne}(E). \tag{17}$$

$N_{se}(E)$ and $N_{ne}(E)$ give, respectively, the total effective number of permanently switchable and non-permanently switchable dipoles which may be aligned by the field E.

We now specify the following rate laws for $N_s^{\parallel}$, $N_s^{\perp}$, $N_n^{\parallel}$ and $N_n^{\perp}$:

(i) If at any time t

$$\operatorname{sgn} N_s^{\parallel}(t) = \operatorname{sgn} N_{se}(E) \text{ and } |N_s^{\parallel}(t)| \geq |(1-\delta)N_{se}(E)|, \tag{18}$$

then

$$\dot{N}_s^{\parallel} = 0 \quad ; \tag{19}$$

otherwise $N_s^{\parallel}$ obeys the rate law

$$\dot{N}_s^{\parallel}+\alpha^{\parallel}(E)N_s^{\parallel} = \alpha^{\parallel}(E)(1-\delta)N_{se}(E) \quad . \tag{20}$$

(ii) If at any time t

$$\operatorname{sgn} N_s^{\perp}(t)=\operatorname{sgn} N_{se}(E) \text{ and } |N_s^{\perp}(t)| \geq |\delta N_{se}(E)|, \tag{21}$$

then

$$\dot{N}_s^{\perp} = 0 \quad ; \tag{22}$$

otherwise $N_s^{\perp}$ obeys the rate law

$$\dot{N}_s^{\perp}+\alpha^{\perp}(E)N_s^{\perp} = \alpha^{\perp}(E)\delta N_{se}(E) \quad . \tag{23}$$

(iii) If at any time t

$$\operatorname{sgn} N_n^{\parallel}(t)=\operatorname{sgn} N_{ne}(E) \text{ and } |N_n^{\parallel}(t)| \geq |\tfrac{1}{3}N_{ne}(E)|, \tag{24}$$

then

$$\dot{N}_n^{\parallel}+\alpha N_n^{\parallel} = 0 \quad ; \tag{25}$$

otherwise $N_n^{\parallel}$ obeys the rate law

$$\dot{N}_n^{\parallel}+q^{\parallel}\alpha^{\parallel}(E)N_n^{\parallel} = \tfrac{1}{3}q^{\parallel}\alpha^{\parallel}(E)N_{ne}(E) \quad . \tag{26}$$

(iv) If at any time t

$$\operatorname{sgn} N_n^{\perp}(t)=\operatorname{sgn} N_{ne}(E) \text{ and } |N_n^{\perp}(t)| \geq |\tfrac{2}{3}N_{ne}(E)|, \tag{27}$$

then

$$\dot{N}_n^{\perp}+\alpha_n N^{\perp} = 0 \tag{28}$$

otherwise $N_n^{\perp}$ obeys the rate law

$$\dot{N}_n^{\perp}+q^{\perp}\alpha^{\perp}(E)N_n^{\perp} = \tfrac{2}{3}q^{\perp}\alpha^{\perp}(E)N_{ne}(E) \quad . \tag{29}$$

In the preceding equations δ is some number between 0 and 2/3 (for a thoroughly poled specimen $\delta = 0$, and for a virgin specimen $\delta = 2/3$), $q^{\parallel}$ and $q^{\perp}$ are constants, $\alpha^{\parallel}$ and $\alpha^{\perp}$ (also $q^{\parallel}\alpha^{\parallel}$ and $q^{\perp}\alpha^{\perp}$) give the switching times of the parallel and perpendicular domains, and $\alpha_n^{\parallel}$ and $\alpha_n^{\perp}$ give the decay times of the non-permanently switchable parallel and perpendicular domains.

A thoroughly poled state is that for which

$$T=0, \ S=S_p, \ E=0, \ D=D_p, \ N=N_s^{\parallel}+N_s^{\perp}=N_p \quad . \tag{30}$$

For convenience, we may normalize N with respect to the poled state, viz,

$$N_p = \pm 1 \quad . \tag{31}$$

The stress free condition yields via $(10)_1$ the result

$$S = \frac{eNE - h^{\parallel}N^{\parallel} - h^{\perp}N^{\perp}}{C + C'N} \quad . \tag{32}$$

Substituting (32) into $(10)_2$, we have

$$D = \left(\varepsilon + \varepsilon' N + \frac{e^2N^2}{C+C'N}\right) E - \frac{eN(h^{\parallel}N^{\parallel} + h^{\perp}N^{\perp})}{C+C'N} + kN. \tag{33}$$

The mechanical and dielectric responses of a ferroelectric ceramic during the course of domain switching under the action of an external electric field from the virgin state are, therefore, given by (32) and (33) together with the solutions of the rate laws (18) through (29). The results are valid under isothermal, stress-free and uniaxial strain conditions. Results concerning butterfly and hysteresis loops are given in the papers by Chen and Tucker[2], and Chen and Madsen[3]. They determine the material properties and compare their numerical results to experimental results concerning the ferroelectric ceramics PZT65/35 and PLZT7/65/35 in a pseudo one dimensional context. These comparisons suggest that the proposed theory does have merit because it predicts the fine details of the butterfly and hysteresis loops, see, for instance, Fig. 1 and Fig. 2.

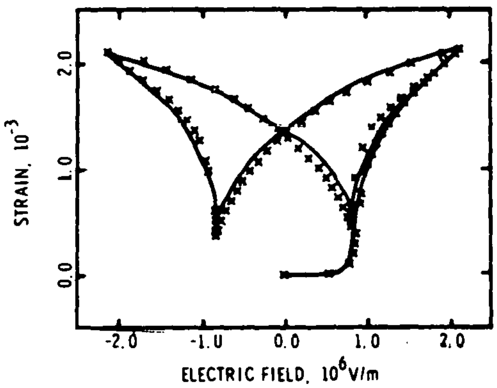

Fig. 1 Calculated butterfly loop (solid line) and experimental butterfly loop (x) for PZT65/35.

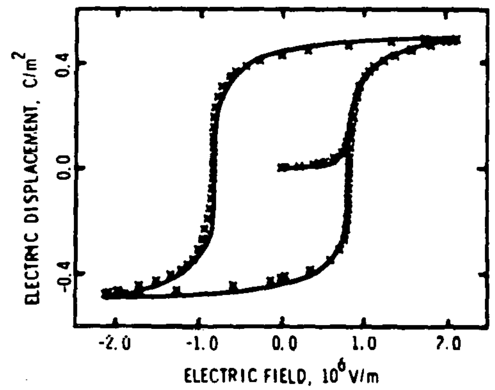

Fig. 2 Calculated hysteresis loop (solid line) and experimental hysteresis loop (x) for PZT65/35.

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