Symmetric Constitutive Laws for Polycrystalline Ferroelectric Ceramics

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ABSTRACT
A class of fully coupled, symmetric, multi-axial, ferroelectric constitutive laws is presented. The foundation of the theory is an assumed form for the Helmholtz free energy of the material. Yield surfaces and associated flow rules are postulated in a modified stress and electric field space such that a positive dissipation rate during switching is guaranteed. The resulting tangent moduli relating increments of stress and electric field to increments of strain and electric displacement are symmetric since changes in the linear elastic, dielectric and piezoelectric properties of the material are included in the switching surface and flow law. Symmetry is further investigated with a simple one-dimensional loading situation comparing the thermodynamically consistent framework to a more ad hoc theory.

Keywords: Ferroelectrics, constitutive law, electromechanical coupling

1. INTRODUCTION
Descriptions of the multi-axial constitutive behavior of ferroelectric ceramics remain in their infancy. Phenomenological single crystal models based on gradual switching along transformation systems, Huber et al.¹, or complete switching of the entire crystallite, Hwang et al.², have been developed. These single crystal models have been applied as constitutive models for inclusions in self-consistent calculations to determine polycrystal behavior. While self-consistent models are able to adequately reproduce the multi-axial behavior of ferroelectrics, see Huber and Fleck³, they are unfortunately relatively slow to compute. Hence it is desirable to formulate a phenomenological constitutive law with fewer internal variables in order to decrease computation time.

A theory recently developed by the author employs the components of the remanent polarization vector and remanent strain tensor as the variables that characterize the internal state of the material, Landis⁴. The theory is cast within a thermodynamically consistent framework. Changes in the elastic, piezoelectric and dielectric properties that accompany changes in the internal variables are included in the theory. Switching surfaces and associated flow rules are postulated in a modified stress and electric field space such that positive dissipation rate is guaranteed. The theory is demonstrated for a simple material that does not strain remanently and is loaded mechanically and electrically along a single axis. A comparison to an ad hoc theory that yields asymmetric tangent moduli is presented.

2. THEORY
Details of the derivation of the constitutive equations along with functional forms for linear properties, switching surfaces and hardening moduli can be found in the author’s previous work, Landis⁴. The theory is concerned with isothermal deformation and polarization processes. Both deviatoric and volumetric remanent straining are allowed. Assuming linear piezoelectric response about some remanent state the constitutive law is given by

\[ \varepsilon_{ij} - \varepsilon'_{ij} = s_{ijkl}^{E} \sigma_{kl} + d_{kij} E_{k} \]  

\[ D_{i} - P'_{i} = d_{kij}^{E} \sigma_{kl} + \kappa_{ij}^{\sigma} E_{j} \]  

Where \( \varepsilon'_{ij} \) and \( P'_{i} \) are the remanent strain and polarization, \( s_{ijkl}^{E} \) is the fourth order tensor of elastic compliance measured at constant applied electric field, \( d_{kij} \) is the third order tensor of piezoelectricity and \( \kappa_{ij}^{\sigma} \) is the second order tensor of dielectric permittivity measured at constant applied stress. The goal of a rate independent constitutive law is to relate increments of stress and electric field to increments of strain and electric displacement such that

\[ \dot{\varepsilon}_{ij} = s_{ijkl}^{E} \dot{\sigma}_{kl} + d_{kij}^{E} \dot{E}_{k} \]
\[ \dot{D}_t = d_{ijkl}^t \sigma_{kl} + \kappa_{ij}^{\sigma^t} \dot{E}_j \] (4)

Or for a rate dependent constitutive law the following forms for the time rates are desired.

\[ \dot{\varepsilon}_{ij} = s_{ijkl}^E \sigma_{kl} + d_{ijkl} \dot{E}_k + \dot{\varepsilon}_{ij}^l \] (5)

\[ \dot{D}_t = d_{ijkl}^t \sigma_{kl} + \kappa_{ij}^{\sigma^t} \dot{E}_j + \dot{D}_t^l \] (6)

Where \( \dot{\varepsilon}_{ij}^l \) and \( \dot{D}_t^l \) are the inelastic contributions to the strain and electric displacement rates.

In a fashion similar to Cocks and McMeeking, the Helmholtz free energy for the material is introduced as

\[ \Psi = \Psi^s(e_{ij}, D_i, P_i^r) + \Psi^r(e_{ij}^l, P_i^r) \] (7)

The reversible or stored part of the free energy is \( \Psi^s \). \( \Psi^r \) represents an additional contribution to the free energy associated only with the internal state of the material. Assuming linear piezoelectric response the first term in (7) is written as

\[ \Psi^s = \frac{1}{2} c_{ijkl}^D (e_{ij} - e_{ij}^l) (e_{kl} - e_{kl}^l) - h_{ijkl} (D_k - P_k^r) (D_i - P_i^r) + \frac{1}{2} \beta_{ij}^p (D_i - P_i^r) (P_j - P_j^r) \] (8)

Note that \( c_{ijkl}^D, h_{ijkl} \) and \( \beta_{ij}^p \) can depend on \( e_{ij}^l \) and \( P_i^r \). The stress and electric field can be derived from the Helmholtz free energy as

\[ \sigma_{ij} = \frac{\partial \Psi}{\partial e_{ij}} = \frac{\partial \Psi^s}{\partial e_{ij}} = c_{ijkl}^D (e_{kl} - e_{kl}^l) - h_{ijkl} (D_k - P_k^r) \] (9)

\[ E_i = \frac{\partial \Psi}{\partial D_i} = \frac{\partial \Psi^r}{\partial D_i} = -h_{ijkl} (e_{kl} - e_{kl}^l) + \beta_{ij}^p (D_j - P_j^r) \] (10)

Inversion of (1) and (2) can be used to relate \( c_{ijkl}^E, h_{ijkl} \) and \( \beta_{ij}^p \) to \( s_{ijkl}^E, d_{ijkl} \) and \( \kappa_{ij}^{\sigma^t} \). Derivatives of \( \Psi^r \) with respect to \( e_{ij}^l \) and \( P_i^r \) are

\[ \frac{\partial \Psi^s}{\partial e_{ij}^l} = -\sigma^l_j - \frac{1}{2} \frac{\partial s_{pqrs}^E}{\partial e_{ij}^l} \sigma^l_p \sigma^l_r - \frac{1}{2} \frac{\partial d_{pqrs}^E}{\partial e_{ij}^l} E_q \sigma^l_r - \frac{1}{2} \frac{\partial \kappa_{pq}^{\sigma^t}}{\partial e_{ij}^l} E_p E_q = -\sigma^l_j - \sigma^l_j \] (11)

\[ \frac{\partial \Psi^s}{\partial P_i^r} = -E_i - \frac{1}{2} \frac{\partial s_{pqrs}^E}{\partial P_i^r} \sigma^l_p \sigma^l_r - \frac{1}{2} \frac{\partial d_{pqrs}^E}{\partial P_i^r} E_q \sigma^l_r - \frac{1}{2} \frac{\partial \kappa_{pq}^{\sigma^t}}{\partial P_i^r} E_p E_q = -E_i - E_i \] (12)

Note that (11) and (12) have been used to define \( \bar{\sigma}_{ij} \) and \( \bar{E}_i \). Also a Legendre transformation has been used to obtain (11) and (12). The back stress, \( \sigma_{ij}^B \), and back electric field, \( E_i^B \), are conjugate to \( e_{ij}^l \) and \( P_i^r \) such that

\[ \sigma_{ij}^B = \frac{\partial \Psi^r}{\partial e_{ij}^l} \] (13)

and

\[ E_i^B = \frac{\partial \Psi^r}{\partial P_i^r} \] (14)
The second law of thermodynamics implies that the dissipation rate, $\dot{\Lambda}$, for the material is non-negative, i.e.

$$\dot{\Lambda} = \sigma_{ij} \dot{\varepsilon}_{ij} + E_i \dot{D} - \Psi$$

where

$$\dot{\sigma}_{ij} = \sigma_{ij} - \sigma^B_{ij} + \sigma$$

and

$$\dot{E}_i = E_i - E^B_i + \dot{E}_i$$

For the rate independent case the inequality of Equation (15) and additionally the electromechanical form of the postulate of maximum plastic dissipation will be satisfied for any convex yield surface, $\Phi$, containing the origin in $\{\dot{\sigma}_{ij}, \dot{E}_i\}$ space with an associated normality condition for the flow rule. During switching the condition

$$\Phi(\dot{\sigma}_{ij}, \dot{E}_i, \varepsilon^r_i, P'_i) = 0$$

must be satisfied. The increments of remanent strain and polarization are normal to the switching surface such that

$$\dot{\varepsilon}^r_i = \lambda \frac{\partial \Phi}{\partial \dot{\sigma}_{ij}} = \lambda \dot{E}_i$$

and

$$\dot{P}'_i = \lambda \frac{\partial \Phi}{\partial E'_i} = \lambda \dot{P}$$

Note that $\dot{\varepsilon}_i$ and $\dot{P}_i$ are defined in equations (19) and (20). The plastic multiplier $\lambda$ is greater than zero during a switching increment and equal to zero during an increment of linear response. During switching the consistency condition requires that

$$\Phi = \dot{\varepsilon}_i \dot{\sigma}_{ij} + \dot{P}_i \dot{E}_i + \frac{\partial \Phi}{\partial \varepsilon^r_i} \dot{\varepsilon}^r_i + \frac{\partial \Phi}{\partial P'_i} \dot{P}'_i = 0$$

After some algebraic manipulation the incremental form of the constitutive law in a form similar to Equations (3) and (4) is

$$\dot{\varepsilon}^r_i = \left( s_{ijkl}^E + \frac{1}{D} \dot{\varepsilon}^r_i \dot{\varepsilon}^r_k \right) \sigma_{kl} + \left( d_{ijkl} + \frac{1}{D} \dot{P}_k \dot{\varepsilon}^r_i \right) E_k$$

$$\dot{P}'_i = \left( d_{ijkl} + \frac{1}{D} \dot{P}_k \dot{\varepsilon}^r_k \right) \sigma_{kl} + \left( \kappa^p_{ij} + \frac{1}{D} \dot{P}_j \dot{P}'_i \right) E_j$$

where

$$D = \left( H_{ijkl} - U_{ijkl}^m \right) \dot{\varepsilon}^r_i \dot{\varepsilon}^r_k + 2 \left( H_{ijkl} - U_{ijkl}^m \right) \dot{P}_k \dot{\varepsilon}^r_i + \left( H_{ijkl} - U_{ijkl}^m \right) \dot{P}_j \dot{P}'_i$$

$$U_{ijkl}^m = \frac{1}{2} \frac{\partial^2 s_{pqrs}^E}{\partial \varepsilon^r_i \partial \varepsilon^r_k} \sigma_{pq} \sigma_{rs} + \frac{\partial^2 d_{pqrs}^E}{\partial \varepsilon^r_i \partial \varepsilon^r_k} E_q \sigma_{rs} + \frac{1}{2} \frac{\partial^2 \kappa^p_{pqrs}^E}{\partial \varepsilon^r_i \partial \varepsilon^r_k} E_p E_q$$

$$U_{ijkl}^m = \frac{1}{2} \frac{\partial^2 s_{pqrs}^E}{\partial P'_k \partial \varepsilon^r_i} \sigma_{pq} \sigma_{rs} + \frac{\partial^2 d_{pqrs}^E}{\partial P'_k \partial \varepsilon^r_i} E_q \sigma_{rs} + \frac{1}{2} \frac{\partial^2 \kappa^p_{pqrs}^E}{\partial P'_k \partial \varepsilon^r_i} E_p E_q$$
Note here that \( A_{ijkl}^{E} \neq A_{klij}^{E} \), \( A_{kjij}^{E} \neq A_{kijj}^{E} \) and \( A_{ij}^{PP} \neq A_{ji}^{PP} \).

Note that the tangent moduli in Equations (22) and (23), including the electromechanical cross terms, are symmetric. This feature would not have appeared if changes in the linear properties were not accounted for in the description of the switching surface and flow rule. A simple one-dimensional model will be presented in the next section to further illustrate this point.

For the rate dependent case \( \Phi(\dot{\sigma}_{ij}, \dot{E}_{ij}, P_{ij}) \) no longer represents a switching surface but rather a rate potential that remanent or inelastic strain and electric displacement rates can be derived from. The remanent rates are

\[
\dot{\varepsilon}_{ij} = \frac{\partial \Phi}{\partial \dot{\sigma}_{ij}}
\]

(37)

and

\[
\dot{P}_{ij} = \frac{\partial \Phi}{\partial \dot{E}_{ij}}
\]

(38)

and the inelastic rates can be shown to be

\[
\dot{\varepsilon}_{ij} = \frac{\partial \Phi}{\partial \sigma_{ij}}
\]

(39)

and
\[ \dot{D}_i = \frac{\partial \Phi}{\partial E_i} \]  

Hence the rate form of the constitutive equations become

\[ \dot{\varepsilon}_{ij} = s_{ijkl} \dot{\sigma}_{kl} + d_{ijkl} \dot{E}_k + \frac{\partial \Phi}{\partial E_{ij}} \]  

\[ \dot{\sigma}_{ij} = d_{ijkl} \dot{\sigma}_{kl} + \kappa_{ij} \dot{E}_j + \frac{\partial \Phi}{\partial E_{ij}} \]  

In general the combinations of invariants used to describe the shape of the switching surface for the rate independent case will be similar to those used to describe the rate potential for the rate dependent case. In fact, under certain limiting conditions, the rate dependent form will approach the rate independent case.

### 3. SYMMETRY

Consider the simple situation of a material that can obtain remanent polarization and piezoelectricity but does not accumulate remanent strain. Furthermore consider only one-dimensional loading situations where both stress and electric field are applied along the same axis. Finally, assume that the piezoelectric properties of the material are proportional to the remanent polarization and the elastic compliance and dielectric permittivity do not depend on the remanent polarization. Equations (1) and (2) become

\[ \varepsilon = s^E \sigma + \frac{d_0 P^r}{P_0} E \]  

\[ D = \frac{d_0 P^r}{P_0} \sigma + \kappa^\sigma E + P^r \]  

where \( P_0 \) is the saturation level of remanent polarization and \( d_0 \) is the piezoelectric coefficient when the material attains polarization saturation. The incremental forms of these constitutive relations is

\[ \dot{\varepsilon} = s^E \dot{\sigma} + \frac{d_0 P^r}{P_0} \dot{E} + \frac{d_0 E}{P_0} \dot{P}^r \]  

\[ \dot{D} = \frac{d_0 P^r}{P_0} \dot{\sigma} + \kappa^\sigma \dot{E} + \left(1 + \frac{d_0 \sigma}{P_0}\right) \dot{P}^r \]  

Next, assume that in the absence of applied stress an electric displacement versus electric field curve is measured. If polarization switching commences at an applied electric field level of \( E_0 \) this suggests that the one-dimensional switching condition could be

\[ \Phi = \left(E - E^B\right)^2 - E_0^2 = 0 \]  

where the back electric field, \( E^B \), is a function of the remanent polarization such that hardening is accounted for appropriately. Differentiation of (47) can be used to show that

\[ \dot{E} = \frac{dE^B}{dP^r} \dot{P}^r = H \dot{P}^r \]  

during switching. The hardening parameter \( H \), which is a function of \( P^r \), can readily be determined from the electric displacement versus electric field curve. Now (45) and (46) can be rewritten in a form like (3) and (4) as
\[ \dot{\varepsilon} = s^E \dot{\sigma} + \left( \frac{d_\sigma P'}{P_0} + \frac{d_\sigma E}{H P_0} \right) \dot{E} \]  

(49)

\[ \dot{D} = \frac{d_\sigma P'}{P_0} \dot{\sigma} + \left( \kappa^\sigma + \frac{1}{H} \frac{d_\sigma \sigma}{H P_0} \right) \dot{E} \]  

(50)

However, notice that the tangent coupling terms are not equal; the constitutive law is not symmetric. If symmetry is desired, what went wrong? The short answer is that the dissipative effects due to changes in the piezoelectric properties were not included in the switching criterion. The theory of Section 2 suggests the following switching condition.

\[ \Phi = \left( E + \frac{d_0}{P_0} \sigma E - E^B \right)^2 - E_0^2 = 0 \]  

(51)

The consistency condition for (51) then implies that

\[ \dot{P}' = \frac{1}{H} \left( 1 + \frac{d_0}{P_0} \sigma \right) \dot{E} + \frac{1}{H} \left( \frac{d_0}{P_0} E \right) \dot{\sigma} \]  

(52)

which leads to the rate form of the constitutive law.

\[ \dot{\varepsilon} = \left[ s^E + \frac{1}{H} \left( \frac{d_\sigma E}{P_0} \right)^2 \right] \dot{\sigma} + \left[ \frac{d_\sigma P'}{P_0} + \frac{1}{H} \frac{d_\sigma E}{P_0} \left( 1 + \frac{d_\sigma \sigma}{P_0} \right) \right] \dot{E} \]  

(53)

\[ \dot{D} = \left[ \frac{d_\sigma P'}{P_0} + \frac{1}{H} \frac{d_\sigma E}{P_0} \left( 1 + \frac{d_\sigma \sigma}{P_0} \right) \right] \dot{\sigma} + \left[ \kappa^\sigma + \frac{1}{H} \left( 1 + \frac{d_\sigma \sigma}{P_0} \right)^2 \right] \dot{E} \]  

(54)

Note that in the absence of an applied stress Equations (49) and (50) are identical to Equations (53) and (54). Therefore simple hysteresis and butterfly loop measurements are not sufficient to determine if the thermodynamically consistent framework is more viable than the ad hoc approach.

Figures 1, 2 and 3 show hysteresis and butterfly loops derived from both the thermodynamically consistent and ad hoc theories presented in this section. The hardening parameter \( H \) as a function of \( P' \) was chosen to create sensible hysteresis curves and was taken to be identical for both theories. The bold lines on all figures represent behavior under no applied stress. Figure 1 contains plots of hysteresis loops derived from the thermodynamically consistent theory. Notice that the loops are wider when there is an applied compressive stress and narrower under an applied tensile stress. Figure 2 contains the corresponding hysteresis loops from the ad hoc theory. In the ad hoc theory applied stress has no effect on the width of the loops. Figure 3 plots the butterfly loops derived from both theories. The variable plotted on the \( y \)-axis has been chosen such that the elastic part of the strain due to the applied stress is subtracted off causing all of the loops to coincide at zero applied electric field. Note that the thin lines are for the thermodynamically consistent theory only. When plotted in this fashion, stress has absolutely no effect on the shapes of the butterfly loops in the ad hoc theory and the loops for all stress levels correspond to the bold line.
Figure 1. Hysteresis loops from the thermodynamically consistent theory.

Figure 2. Hysteresis loops from the ad hoc theory.

Figure 3. Butterfly loops from both theories. Note that butterfly loops from the ad hoc theory do not depend on stress when plotted in this fashion.
REFERENCES


