Micro-electromechanically Informed Phenomenological Constitutive Models for Ferroelectrics

Chad M. Landis∗, Jianxin Wang and Jianshun Sheng
Rice University, Department of Mechanical Engineering and Materials Science

ABSTRACT
Accurate phenomenological constitutive laws for ferroelectric ceramics that can be rapidly integrated are required for finite element models aiming to resolve the complex fields in ferroelectric devices. At best, phenomenological theories can provide a framework within which thermodynamic restrictions are satisfied and undetermined functions exist for “fitting” material behavior. The ultimate challenge in deriving a final constitutive law is to capture the physics of the material deformation and polarization processes within these undetermined functions. A number of micro-electromechanical models exist in the literature. These models are based on domain switching events at the domain/grain level and then are generalized to polycrystalline behavior by averaging over many different domain/grain orientations. In this work it will be shown how information obtained from these micro-electromechanical models can be incorporated directly into the undetermined functions of a phenomenological theory.

Keywords: ferroelectricity, constitutive behavior, phenomenology, micro-electromechanics

1. INTRODUCTION
The need for accurate yet simple constitutive laws for ferroelectric ceramics arises in a number of problems that require the resolution of the inhomogeneous electrical and mechanical fields in ferroelectric materials. Such problems range from the prediction of poling patterns around electrodes in ferroelectric actuator designs to the determination of switching zones near crack tips that govern failure in these materials. Due to the relative complexity of the constitutive response of ferroelectrics, these types of problems will most likely be solved by implementing the finite element method or some other numerical technique. Hence, it is desirable to keep the mathematical description of the constitutive response as simple as possible while maintaining the prominent physical features of the material behavior.

Along these lines, a phenomenological internal variable constitutive framework for the coupled multi-axial constitutive response of polycrystalline ferroelectrics has been developed by Cocks and McMeeking [1] and Landis [2]. As with any phenomenological constitutive framework, this theory sets up constraints that enforce the laws of thermodynamics and contains undetermined functions that can be tailored to predict specific material behavior. Such theories are usually sufficiently general as to admit a wide range of material response, and it is up to the practitioner to provide the appropriate inputs required to model a specific material. These inputs to the theory must come from at least two sources, experimental observations and considerations of the underlying crystal structure of the material. Before any theory can be considered viable for use in more detailed computations, it must be shown to be in at least qualitative agreement with experimental observations on electric displacement versus electric field hysteresis loops, electric field versus strain butterfly loops, strain and electric displacement versus stress during mechanical depolarization, and polarization rotation, [3,4]. Additionally, the geometric constraints on the possible remanent strain and remanent polarization states resulting from the underlying crystal structure must be enforced within any phenomenological model.

It is well established that the saturation behavior of ferroelectric ceramics arises due to the underlying crystal structure of the material, [5]. Furthermore, since the undetermined functions of a phenomenological constitutive theory cannot predict the remanent saturation states of the material a priori, the saturation conditions must be determined by some other means and entered into the model. Without such restrictions, phenomenological constitutive models will allow unrealistic combinations of remanent strain and polarization to arise. Due to the fact that the experimental determination of the saturation states in ferroelectrics would be difficult if not impossible, micro-electromechanical investigations of the possible remanent states in these materials are the most appropriate procedure to determine the saturation conditions.

∗ landis@rice.edu, phone 713-348-3609, fax 713-348-5423,
MEMS MS 321, Rice University PO Box 1892, Houston, TX 77251-1892
A number of micro-electromechanical methods exist that model the behavior of ferroelectric polycrystals as the averaged response of randomly oriented single crystal grains. In all cases the constitutive response of the single crystals is intended to model the domain switching mechanism that gives rise to remanent strain and polarization in these materials. Then, the polycrystalline averages range in sophistication from Taylor and Reuss-like models where interaction between crystals is neglected [6,7], to self consistent methods where grain to grain constraints are accounted for in an average sense [8,9], to finite element simulations of many cubic single crystals where interactions are fully accounted for [10,11]. In principle, any of these micro-electromechanical models can be applied to the task of determining the complete range of remanent strain and remanent polarization states that are attainable by a polycrystalline ferroelectric ceramic.

The remainder of this paper is organized as follows. Section 2 will review the salient features of the micro-electromechanical constitutive model of Huber et al. [9] that will be applied to determine the polycrystalline saturation states. Section 3 will present the methodology applied to determine the attainable remanent states and the results obtained. Section 4 will review the phenomenological constitutive framework of Landis [2] and demonstrate how the micro-electromechanical results can be implemented within the theory. Predictions of electromechanical constitutive response will be made in this section as well. Lastly, Section 5 will offer a discussion of the results and implications of the model for different crystal structures and textured polycrystals.

2. THE MICRO-ELECTROMECHANICAL MODEL

The model presented here for the constitutive response of ferroelectric polycrystals has been developed in detail by Huber et al. [9]. This constitutive law consists of two primary components, a constitutive law for single crystals and a self-consistent averaging technique to determine the polycrystalline response. The single crystal constitutive law accounts for domain switching between the crystallographic variants of the crystal in a manner analogous to continuum slip models for plasticity in metal single crystals. Then, the self-consistent averaging model proposed by Hill [12,13] and implemented by Hutchinson [14] for metal polycrystals is applied to determine the constitutive behavior of the polycrystal.

Figure 1. The six possible tetragonal variants in a single crystal. Here the 1,2, and 3 coordinate directions correspond to the (100) crystal directions.

Throughout this paper it is assumed that the underlying atomic structure of the single crystal is tetragonal. This assumption will of course limit the applicability of the results presented to tetragonal materials, however the models can be readily generalized to other crystal structures as well. In this work we are only concerned with the possible remanent states of the material and not the electromechanical loading required to generate them. Therefore, conceptual and computational simplicity within the single crystal constitutive model will be afforded if the linear elastic, piezoelectric
and dielectric response of a single variant is taken to be isotropic. This implies that within the model, the piezoelectric coefficients $d_{kij}$ all go to zero for a single domain single crystal.

The single crystal constitutive law is analogous to continuum slip plasticity models with the added effects of polarization and strain saturation. In order to derive the single crystal constitutive law it is assumed that the stress and electric field are uniform and both the total and remanent parts of the strain and electric displacement are the volume averages over the entire crystal. Note that by assuming the stress and electric field within the single crystal are uniform, we are neglecting electromechanical interactions between domains in the crystal. As illustrated in Figure 1, six tetragonal variants can exist in any single crystal. Hence, the remanent strain and polarization of the crystal are

$$e^{r}_{ij} = \sum_{I=1}^{6} c^{I} e^{r(I)}_{ij} \quad \text{and} \quad P^{r}_{i} = \sum_{I=1}^{6} c^{I} P^{r(I)}_{i}$$

where $c^{I}$ represents the volume concentration of the I-th variant. Also, the remanent strains and polarizations of each of the variants are given by

$$e^{r(1,2)}_{ij} = e_{0} \left( 3\delta_{ij} \delta_{j1} - \delta_{ij} \right)/2, \quad e^{r(3,4)}_{ij} = e_{0} \left( 3\delta_{ij} \delta_{j2} - \delta_{ij} \right)/2, \quad \text{and} \quad e^{r(5,6)}_{ij} = e_{0} \left( 3\delta_{ij} \delta_{j3} - \delta_{ij} \right)/2$$

$$P^{r(1)}_{i} = P_{0} \delta_{i1}, \quad P^{r(2)}_{i} = -P_{0} \delta_{i1}, \quad P^{r(3)}_{i} = P_{0} \delta_{i2}, \quad P^{r(4)}_{i} = -P_{0} \delta_{i2}, \quad P^{r(5)}_{i} = P_{0} \delta_{i3}, \quad \text{and} \quad P^{r(6)}_{i} = -P_{0} \delta_{i3}$$

where the 1,2 and 3 coordinate directions are parallel to the $\langle 100 \rangle$ crystal directions as drawn in Figure 1, $\delta_{ij}$ is the Kronecker delta, $e_{0}$ is the spontaneous strain of a single variant and can be given in terms of the lattice parameters as $e_{0} = 2(c-a)/(c+2a)$, and $P_{0}$ is the spontaneous polarization of a single variant. With these definitions of the remanent strains and polarizations for the individual variants, the remanent strain and polarization of the entire crystal will be zero if there are equal volume concentrations of each of the variants. Finally, under the assumption that the variants are elastically and electrically isotropic (non-piezoelectric), the total strain and electric displacement of the single crystal are

$$\varepsilon^{\prime}_{ij} = \frac{1}{2\mu} \sigma^{\prime}_{ij} - \frac{\nu}{2\mu(1+\nu)} \sigma_{kk} \delta_{ij} + e^{\prime}_{ij}$$

and

$$D_{i} = \kappa E_{i} + P^{r}_{i}$$

where $\mu$, $\nu$ and $\kappa$ are the isotropic shear modulus, Poisson’s ratio and dielectric permittivity respectively. Note that Eqs. (2.4) and (2.5) differ from those appearing in [9] due to the simplification that the linear properties of the variants are isotropic.

In order to determine how the volume concentrations of the variants can change with applied loading, we will first consider the free energy of the crystal. Under isothermal conditions, the Helmholtz free energy of the single crystal, $\Psi^{\text{sc}}$, is equal to the stored electromechanical energy of the crystal and is given as

$$\Psi^{\text{sc}}(\varepsilon, e^{\prime}, D, P^{r}) = \mu \left( \varepsilon_{ij} - e^{\prime}_{ij} \right) \left( \varepsilon_{ij} - e^{\prime}_{ij} \right) + \frac{\mu\nu}{1-2\nu} \left( \varepsilon_{kk} \right)^{2} + \frac{1}{2\kappa} \left( D_{i} - P^{r}_{i} \right) \left( D_{i} - P^{r}_{i} \right)$$

Note that isotropy of the linear properties and the deviatoric nature of the remanent strains ($e^{r}_{kk} = 0$) have been used to derive Eq. (2.6). The dissipation rate in the single crystal is given as the work rate due to applied stresses and electric fields minus the free energy rate. By applying the previously stated assumptions the dissipation rate can be shown to be
\[ \dot{\Psi}^sc = \sigma_{ij} \dot{e}_{ij} + E_i \dot{P}_i = \sum_{i=1}^{6} \epsilon^I_i \left( \sigma_{ij} e^{(1)\alpha} + E_i P_i^{(\alpha)} \right) \]  

(2.7)

Note, that thirty different switching transformations are possible, i.e. each of the six variants can switch to the other five. Furthermore, if a transformation is occurring, then the volume concentrations of the variants being switched to and from increase and decrease respectively at exactly the same rates. By applying these facts, it is then possible to rewrite the dissipation rate and define the transformation driving forces, \( G^\alpha \), as

\[ \dot{\Psi}^D = \sum_{\alpha=1}^{30} j^\alpha \left( \sigma_{ij} \Delta e^{(\alpha)\alpha} + E_i \Delta P_i^{(\alpha)\alpha} \right) \]  

(2.8)

Here, \( \alpha \) numbers the thirty possible transformation systems and the \( \Delta \) represents the difference in the following quantity between the variant being transformed to and that being transformed from. For example, take \( \alpha = 1 \) to represent the transformation from variant 1 to variant 3. Then, \( \Delta e^{(\alpha)\alpha} = 3 \epsilon_{00} (\delta_{12} \delta_{23} - \delta_{13} \delta_{21})/2 \) (note that this is a pure shear strain), \( \Delta P_i^{(\alpha)\alpha} = P_0 (\delta_{12} - \delta_{21}) \) and the volume concentration rates are \( \epsilon^{(1)\alpha} = -j^{(\alpha)\alpha} \) and \( \epsilon^{(3)\alpha} = j^{(\alpha)\alpha} \). Note that six of these transformation systems account for 180 degree switching, and the other twenty-four model 90 degree switching. Furthermore, due to the assumption of isotropic linear properties, the driving forces identified in Eq. (2.8) do not contain terms associated with changes in the linear properties as in [9], and are identical to the driving forces for switching employed in [6,7].

It is assumed that if a quantity of a given variant exists, i.e. \( c^1 > 0 \), then it is possible to incrementally switch that variant into one of the other five. Furthermore, this switching between variants is assumed to occur only if such a transformation results in a characteristic rate of non-negative dissipation. Specifically, a transformation system is potentially active if

\[ G^\alpha = G^\alpha_c \rightarrow j^\alpha \geq 0 \]  

(2.9)

and the transformation system is inactive if

\[ G^\alpha < G^\alpha_c \rightarrow j^\alpha = 0 \]  

(2.10)

If the volume fraction of a given variant vanishes, then the transformation systems that reduce the quantity of that variant cannot be activated. This feature enables the model to account for strain and polarization saturation at the single crystal level. Driving forces greater than the critical levels are not permissible except under saturation conditions. In the absence of hardening of the transformation systems, i.e. when the \( G^\alpha_c \) remain fixed during switching, the single crystal constitutive law requires the following inputs; the isotropic linear properties of a single tetragonal variant \( \mu, \nu \) and \( \kappa \), the critical driving forces to induce 180 and 90 degree transformations \( G_c^{180} \) and \( G_c^{90} \), the lattice parameters of a tetragonal variant that determine \( \epsilon_0 \), and the spontaneous polarization of a single variant \( P_0 \). Ultimately, the possible saturation states of the material will only depend on \( \epsilon_0 \) and \( P_0 \).

From Equations (2.1)-(2.10) it is a mathematical exercise to determine the transformation rates, \( j^\alpha \), in terms of the applied strain and electric displacement rates, and then forms for the single crystal tangent moduli follow. This procedure will not be given here, but it is presented clearly in Reference [9].

Using the single crystal constitutive law described above, a self-consistent model is applied to compute the overall electromechanical behavior of a polycrystal. For conceptual simplicity the polycrystal is viewed as an infinite collection of randomly oriented single crystals subjected to homogenous states of stress, electric field, strain and electric displacement. The Cartesian components of the macroscopic field increments of the polycrystal are taken to be the volume averages of the Cartesian components of the corresponding increments in the single crystals. Each individual single crystal region is modeled as a spherical inclusion embedded in an infinite effective medium matrix. The tangent moduli of the effective medium are taken to be those of the polycrystal. Since neighboring grains are not modeled
explicitly, the constraint interactions between grains are not determined directly in this model. Instead, each grain is constrained by the effective medium matrix, and in this sense the model accounts for grain-to-grain constraints in an averaged sense. Ultimately, the electromechanical state in each single grain will depend on the applied loading history and the orientation of the crystal. For more details of both the single crystal constitutive law and the self-consistent averaging method the reader is referred to Reference [9]. The most significant feature of the self-consistent model for the polycrystal is that, given the current state of the material, it provides incremental constitutive relations of the form

$$\dot{\sigma}^{pc}_{ij} = c^{i}_{ijkl} \dot{\varepsilon}^{pc}_{kl} - h^{i}_{kj} \dot{D}^{pc}_{k}$$

and

$$\dot{E}^{pc}_{i} = -h^{i}_{ij} \varepsilon^{pc}_{ij} + \beta^{i}_{ij} \dot{D}^{pc}_{j}$$

where $c^{i}_{ijkl}$, $h^{i}_{ki}$ and $\beta^{i}_{ij}$ are the tangent electromechanical moduli of the polycrystal and $\dot{\sigma}^{pc}_{ij}$, $\dot{E}^{pc}_{i}$, $\dot{\varepsilon}^{pc}_{ij}$ and $\dot{D}^{pc}_{i}$ are the components of the increments of the stress, electric field, strain and electric displacement of the polycrystal.

### 3. POSSIBLE REMANENT STATES

Due to the isotropy of the single crystals, the remanent strain and polarization of the polycrystal are simply the volume average of the remanent strain and polarization of the single crystals. Furthermore, the linear elastic and dielectric properties of the polycrystal are simply those of the single crystals as well. In order to probe for the possible remanent states of the polycrystalline material we would like to be able to control the increments of the remanent quantities, $\dot{\varepsilon}^{pc}_{ij}$, $\dot{E}^{pc}_{i}$ and $\dot{D}^{pc}_{i}$, given the increments of remanent strain and remanent polarization that are desired, the following equations can be manipulated to determine the increments of total strain and electric displacement.

$$\dot{\sigma}^{pc}_{ij} = 2\mu \left[ \dot{\varepsilon}^{pc}_{ij} - \varepsilon^{pc}_{ij} \varepsilon^{pc}_{kl} \delta_{kl} \right] = c^{i}_{ijkl} \dot{\varepsilon}^{pc}_{kl} - h^{i}_{kj} \dot{D}^{pc}_{k}$$

$$\dot{E}^{pc}_{i} = \frac{1}{\kappa} \left[ D^{pc}_{i} - \dot{P}^{pc}_{i} \right] = -h^{i}_{ij} \dot{\varepsilon}^{pc}_{ij} + \beta^{i}_{ij} \dot{D}^{pc}_{j}$$

Equations (3.1) and (3.2) represent nine equations for the nine unknown polycrystalline strain and electric displacement increments, $\dot{\varepsilon}^{pc}_{ij}$ and $\dot{D}^{pc}_{i}$, given the specified increments of the remanent quantities, $\dot{\varepsilon}^{pc}_{ij}$, $D^{pc}_{i}$, and the tangent moduli supplied by the self-consistent averaging model, $c^{i}_{ijkl}$, $h^{i}_{ki}$ and $\beta^{i}_{ij}$. Through the solution of these equations, any remanent strain and polarization path up to saturation can be traversed within the self-consistent model. In the following, it will be shown how this procedure is applied to find the full multi-axial set of remanent strain saturation states, and the uniaxial set of remanent polarization saturation states.

The goal of this first investigation is to map out the saturation conditions for remanent strain states between axisymmetric extension, through pure shear remanent strain, and on to axisymmetric contraction. To do this the following remanent strain invariants are introduced

$$J^*_2 = \left( \frac{2}{3} \varepsilon^{*}_{ij} \varepsilon^{*}_{ij} \right)^{1/2}$$

and

$$J^*_3 = \left( \frac{4}{3} \varepsilon^{*}_{ij} \varepsilon^{*}_{jk} \varepsilon^{*}_{ki} \right)^{1/3}$$

Here $\varepsilon^{*}_{ij}$ is the remanent strain deviator, $\varepsilon^{*}_{ij} = \varepsilon^{pc}_{ij} - \delta_{ij} \varepsilon^{pc}_{kk} / 3$. With the definition of these two invariants, a full range of remanent strain saturation states can be probed by allowing the ratio of $J^*_3 / J^*_2$ to vary from $-1$ (axisymmetric contraction) to 0 (pure shear) to 1 (axisymmetric extension). If we consider any volume conserving remanent strain in the principal directions, then the remanent strain tensor and $J^*_3 / J^*_2$ can be written as
\[
\varepsilon^r = \begin{pmatrix}
\varepsilon^r & 0 & 0 \\
0 & b\varepsilon^r & 0 \\
0 & 0 & -(1+b)\varepsilon^r
\end{pmatrix}
\quad \text{and} \quad
\frac{J^3_2}{J^2_2} = \frac{-\sqrt[3]{(b+b^2)^{1/3}}}{4^{1/6}\sqrt{1+b+b^2}}\text{sgn}(\varepsilon^r)
\] (3.4)

where \(b\) can be any arbitrary constant. In other words, every multi-axial volume conserving remanent strain state can be described by the ratio of these two invariants, and this ratio will always lie in the range \(-1 \leq \frac{J^3_2}{J^2_2} \leq 1\).

In order to map out the full set of strain saturation conditions, a specific ratio of \(\frac{J^3_2}{J^2_2}\) is specified and the magnitude of the applied loading is increased until changes in the remanent state become negligible. Figure 1a illustrates the type of stress versus remanent strain response that occurs during such a simulation, and Figure 1b plots the effective remanent strain saturation state as a function of the ratio \(\frac{J^3_2}{J^2_2}\).

![Figure 2](image)

**Figure 2.** (a) The effective stress versus the \(J^2_2\) remanent strain invariant for a range of the ratio \(\frac{J^3_2}{J^2_2}\). Pure axisymmetric contraction corresponds to \(\frac{J^3_2}{J^2_2} = -1\), pure shear remanent strain is at \(\frac{J^3_2}{J^2_2} = 0\), and axisymmetric extension is \(\frac{J^3_2}{J^2_2} = 1\). The saturation levels of \(J^2_2\) correspond to the asymptotic values as the effective stress goes to infinity. The critical shear stress \(\tau_0\) is the shear stress when 90 degree switching occurs in a single crystal such that \(G_c^{90} = 3\tau_0\varepsilon_0\). (b) The asymptotic or saturation levels of \(J^2_2\) as a function of \(\frac{J^3_2}{J^2_2}\). Remanent strain states below the curve are possible in the material, but those states above the curve are unattainable.

Given that Figure 2b illustrates the full multi-axial range of remanent strain states that are possible in a polycrystalline ferroelectric material with underlying tetragonal crystal structure, we now turn to the determination of the possible remanent polarization states. It is noted that the saturation level of the remanent polarization is dependent on the remanent strain state. For example, consider only axisymmetric states of remanent strain and remanent polarization aligned along the same axis. If the remanent strain is tensile then the magnitude of the remanent polarization that is possible is maximized. However, if the remanent strain is compressive, then there is not “enough room” for the full remanent polarization to fit into this remanent strain state. To illustrate this point in a quantitative manner, the following computations were performed. First, the self-consistent model material is loaded by either a uniaxial tensile or compressive stress in order to achieve an axisymmetric remanent strain state. Next, electric field and mechanical stress are applied in the appropriate proportions by manipulating Equations (3.1) and (3.2) such that the remanent strain state remains constant while the remanent polarization state is increased to saturation. Again, all loading and change in remanency occur along the same axis.
Figure 3 plots the saturation levels of polarization $P_{\text{sat}}$ versus the magnitude or the uniaxial remanent strain $\varepsilon'$. Note that the range on the uniaxial remanent strain is $-0.40\varepsilon_0 \leq \varepsilon' \leq 0.55\varepsilon_0$ and the remanent polarization can be in two directions such that $-P_{\text{sat}} \leq P' \leq P_{\text{sat}}$. It is worth noting that a few points appearing on Figures 2b and 3 are in agreement with results reported from other micro-electromechanical computations. First, the magnitudes of the saturation levels of remanent strain in tension and compression quoted in Reference [5,15] are $\varepsilon_t = 0.552\varepsilon_0$ and $\varepsilon_c = 0.4035\varepsilon_0$. Also, the maximum tensile remanent strain and the maximum remanent polarization for a polycrystal from Reference [7] are $\varepsilon_t = 0.5514\varepsilon_0$ and $P_{\text{sat}}^{\max} = 0.831P_0$. The results presented here suggest that $\varepsilon_t = 0.55\varepsilon_0$, $\varepsilon_c = 0.40\varepsilon_0$ and $P_{\text{sat}}^{\max} = 0.83P_0$. Hence, the results presented here are in excellent agreement with other micro-electromechanical models. This is to be expected since the saturation states of the material should only depend on the geometry of the underlying crystal structure and not on the specific details of the micro-model. Hence, any of these other micro-electromechanical models could be used to generate the results presented in Figures 2b and 3. Finally, one last result presented in Figure 3 demonstrates that the maximum amount of remanent polarization that can be achieved when the uniaxial remanent strain is at its maximum compressive level is approximately one quarter of its maximum level. Specifically, $P_{\text{sat}}(\varepsilon' = -0.40\varepsilon_0) = 0.21P_0$.

![Figure 3. The saturation curve for states of remanent polarization as a function of remanent strain. Note that the uniaxial remanent strain ranges from $-0.40\varepsilon_0 \leq \varepsilon' \leq 0.55\varepsilon_0$ corresponding to the saturation states for $J_2^1/J_2^1 = -1$ and $J_2^3/J_2^3 = 1$. This saturation curve is for remanent polarization states aligned along the remanent strain axis. Furthermore, $P_{\text{sat}}$ represents the magnitude of the maximum remanent strain such that the remanent polarization aligned with the strain axis can take on values $-P_{\text{sat}} \leq P' \leq P_{\text{sat}}$.](image)

**4. THE PHENOMENOLOGICAL MODEL**

The goal of any phenomenological internal variable constitutive theory is to provide a relatively simple framework within which the laws of thermodynamics are satisfied and a wide range of material behaviors can be represented. The micro-electromechanical model described in the previous section cannot be considered simple because the number of internal variables, i.e. the volume concentrations of each variant type in each single crystal grain, is too large. The phenomenological framework developed in References [1] and [2] postulates that the minimum number of internal variables required to model fully coupled ferroelectric material behavior is nine (eight if the remanent strain is volume conserving), specifically the Cartesian components of the remanent strain and remanent polarization. The most general form of the framework will not be presented here and the reader is referred to Reference [2] for all of the details. Instead, only the specific form of the theory used to model the PLZT material investigated by Lynch [3] will be given here.

First, it is assumed that the Helmholtz free energy of the polycrystal is given as
where the linear elastic, piezoelectric and dielectric properties of the polycrystal, $c^D_{ijkl}$, $h_{ijkl}$ and $\beta_{ij}$ can each depend on the remanent state of the material. The theory is greatly simplified if the following forms are taken for the inverse properties,

$$s_{ijkl} = \frac{1}{4\mu} (\delta_{ik}\delta_{jr} + \delta_{ij}\delta_{rk}) - \frac{v}{2\mu(1+v)} \delta_{ij}\delta_{kl}$$

(4.2)

$$\kappa_{ij} = \kappa \delta_{ij}$$

(4.3)

$$d_{ij} = \frac{d_{33}}{4} \frac{P_r}{P_{max}} (3n_i\delta_{jk} + 3n_j\delta_{ik} - 2n_k\delta_{ij})$$

(4.4)

where

$$P' = \sqrt{P_i' P_i'} \text{ and } n_j = P_i' / P'$$

(4.5)

Here, $d_{33}$ is the piezoelectric coefficient when the material reaches its maximum remanent polarization $P_{max} = 0.83P_0$. Note that this form for the piezoelectric coefficients has $d_{31} = -d_{33}/2$ and $d_{15} = 3d_{33}/2$. This is a reasonable assumption based on measured values in polycrystals, and this assumption can be relaxed at the added expense of complexity within the theory. Note that the “remanent potential” $\Psi'$ only depends on the remanent state of the material and is intended to account for the free energy associated with the changes in stored energy due to intergranular constraints that generate internal residual stresses and electric fields.

It is assumed that there exists some region in stress and electric field space within which the material responds in a linear elastic, piezoelectric and dielectric manner about the current state of remanent strain and remanent polarization. The surface bounding this region will be called the switching surface. In Reference [2], it was shown that the second law of thermodynamics and the postulate of maximum dissipation are satisfied if the switching surface is convex and encloses the origin in a modified stress and electric field space, and that the increments of remanent strain and remanent polarization are normal to the switching surface during changes in remanency. The specific form of the switching surface used here is

$$\Phi = \frac{3\hat{s}_{ij}\hat{s}_{ij}}{2\sigma_0^2} + \frac{\hat{E}_{i} \hat{E}_i}{E_0^2} + \frac{\beta}{2\sigma_0^2 P_{max}} \left( \hat{E}_i P_j' + \hat{E}_j P_i' - \frac{2}{3} \hat{E}_k P_k' \delta_{ij} \right) - 1 = 0$$

(4.6)

where the modified stress and electric field are

$$\hat{\sigma}_{ij} = \sigma_{ij} - \frac{\partial \Psi'}{\partial \epsilon_{ij}} \text{ with } \hat{s}_{ij} = \hat{\sigma}_{ij} - \frac{\sigma_{0k}}{3} \delta_{ij}, \text{ and } \hat{E}_i = E_i - \frac{\partial \Psi'}{\partial P_i'} + \frac{\partial d_{ijkl}}{\partial P_i'} E_j \sigma_{kl}$$

(4.7)

Then, during switching the remanent strain and remanent polarization increments are given by

$$\dot{\epsilon}_{ij}' = \lambda \frac{\partial \Phi}{\partial \dot{\sigma}_{ij}} = \lambda \left[ \frac{3\hat{s}_{ij}}{\sigma_0^2} + \frac{\beta}{2\sigma_0^2 P_{max}} \left( \hat{E}_i P_j' + \hat{E}_j P_i' - \frac{2}{3} \hat{E}_k P_k' \delta_{ij} \right) \right]$$

(4.8)

and

$$\dot{P}_i' = \lambda \frac{\partial \Phi}{\partial E_i} = \lambda \left[ \frac{2\hat{E}_i}{E_0^2} + \frac{\beta \hat{s}_{ij} P_j'}{\sigma_0 E_0 P_{max}} \right]$$

(4.9)
Use of the consistency condition during switching, i.e. $\dot{\Phi} = 0$, can be used to determine the switching multiplier $\lambda$ and the associated tangent moduli for the material. Details of these derivations are given in Reference [2]. Now, to have a final material specific form of the theory, the remanent potential $\Psi'_{\text{f}}$ must also be specified. For the results to be presented in this section, $\Psi'$ is split into a mechanical part $\Psi'_{\text{m}}$ that enforces the strain saturation conditions, an electrical part $\Psi'_{\text{e}}$ that enforces the polarization saturation conditions, and a coupled electromechanical part $\Psi'_{\text{em}}$ that is required to obtain reasonable agreement with experimental observations. The forms for each of these potentials are given as follows.

\begin{equation}
\Psi' = \Psi'_{\text{m}} + \Psi'_{\text{e}} + \Psi'_{\text{em}}
\end{equation}

\begin{equation}
\frac{d\Psi'_{\text{m}}}{d\varepsilon^*} = H_0^m \left[ \frac{1}{1 - \varepsilon^*/\varepsilon_c} \right]^{m^*} - 1
\end{equation}

where

\begin{equation}
\varepsilon^* = (1 - w)J_2^e + w\bar{\varepsilon},
\end{equation}

\begin{equation}
\bar{\varepsilon} = J_2^e f\left( \frac{J_3^e}{J_2^e} \right),
\end{equation}

\begin{equation}
w(\bar{\varepsilon}) = 504 \left[ \frac{1}{4} \left( \frac{\bar{\varepsilon}}{\varepsilon_c} \right)^4 - \left( \frac{\bar{\varepsilon}}{\varepsilon_c} \right)^5 + \frac{5}{3} \left( \frac{\bar{\varepsilon}}{\varepsilon_c} \right)^6 - \frac{10}{7} \left( \frac{\bar{\varepsilon}}{\varepsilon_c} \right)^7 + \frac{5}{8} \left( \frac{\bar{\varepsilon}}{\varepsilon_c} \right)^8 - \frac{1}{9} \left( \frac{\bar{\varepsilon}}{\varepsilon_c} \right)^9 \right]
\end{equation}

and

\begin{equation}
f\left( \frac{J_3^e}{J_2^e} \right) = -0.0965 \left( \frac{J_3^e}{J_2^e} \right)^3 + 0.01 \left( \frac{J_3^e}{J_2^e} \right)^6 + 0.8935, \text{ for } \left( \frac{J_3^e}{J_2^e} \right) < 0
\end{equation}

\begin{equation}
f\left( \frac{J_3^e}{J_2^e} \right) = -0.1075 \left( \frac{J_3^e}{J_2^e} \right)^3 - 0.027 \left( \frac{J_3^e}{J_2^e} \right)^6 - 0.028 \left( \frac{J_3^e}{J_2^e} \right)^{21} + 0.8935, \text{ for } \left( \frac{J_3^e}{J_2^e} \right) \geq 0.
\end{equation}

Then,

\begin{equation}
\Psi'_{\text{e}} = \frac{H_0^e P_{\text{max}}^2}{(m^* - 1)(m^* - 2)} \left( \frac{1}{1 - P'/P_{\text{sat}}} \right)^{m^* - 2} - \frac{H_0^e P_{\text{max}}}{(m^* - 1)} P'
\end{equation}

where

\begin{equation}
P_{\text{sat}} = \frac{P_{\text{max}} - P_{\text{min}}}{\varepsilon_t + \varepsilon_c} + P_{\text{min}}, \text{ with } P_{\text{max}} = 0.83P_0 \text{ and } P_{\text{min}} = P_{\text{max}}/4
\end{equation}

and finally,

\begin{equation}
\Psi'_{\text{em}} = \frac{H_0^{\text{em}}}{(m^{\text{em}} + 1)(m^{\text{em}} + 2)} \left( \frac{P_{\text{max}}}{P_{\text{max}} - \varepsilon_t} \right)^{m^{\text{em}} + 2}.
\end{equation}

The mechanical part of the remanent potential in Equation (4.11) enforces the remanent strain saturation conditions by forcing the potential to go to infinity as the newly defined remanent strain variable $\varepsilon^*$ approaches the magnitude of the compressive strain saturation level $\varepsilon_c$. Note that only the first derivative is given since the actual potential is not required for any computations. Details of the reasons for the use of the weighting function $w$ have to do with maintaining smoothness of the ferroelastic hysteresis loops and can be found in Reference [16]. The primary result taken from the micro-electromechanical simulations presented in Figure 2b is the functional fit $f\left( \frac{J_3^e}{J_2^e} \right)$ of Equations (4.15) and (4.16). This function is able to reproduce the numerical results of Figure 2b to within 0.15% as $\varepsilon^*$ approaches $\varepsilon_c$.

Next, the electrical part of the potential given in Equation (4.17) enforces the polarization saturation conditions by causing the remanent potential to go to infinity as the magnitude of the remanent polarization $P'$ approaches $P_{\text{sat}}$. 
Furthermore, notice that $P_{\text{sat}}$ depends on the remanent strain state, and that the invariant $\epsilon'_{ij}n_{i}n_{j}$ has been used as a multiaxial generalization of the uniaxial results of Figure 3. The appropriateness of this generalization can only be verified by more detailed micro-electromechanical simulations. However, this generalization will not effect results generated for uniaxial situations where the applied stress and electric field are aligned along the same axis. Lastly, in order to maintain simplicity, the saturation curve of Figure 3 has been approximated as a straight line in Equation (4.18).

Finally, the coupled potential $\Psi^{em}$ along with the $\beta$ term appearing in the switching surface have been included in the theory in order to achieve the best possible agreement with experimental observations. Extensive investigations have been carried out in search for functional forms of $\Psi$ with $H_{0}^{em} = 0$ and $\Phi$ with $\beta = 0$. However, the results from these cases have not yet been able to reproduce the wide range of experimental observations presented in References [3] and [4]. It is possible that micro-electromechanical investigations may provide insight into these features of the model. However, such investigations will require the determination of the driving forces for changes in remanency and the assumption of isotropic linear properties for the single crystals as in Equations (2.4) and (2.5) will not be valid.

Figures 4a-4e illustrate the uniaxial predictions of the micro-electromechanically informed phenomenological model presented in this section for (a) the electric displacement versus electric field hysteresis loop, (b) the strain versus electric field butterfly loop, (c) the electric displacement versus stress during mechanical depolarization, (d) the strain versus stress during mechanical depolarization and (e) the ferroelastic stress versus strain hysteresis. Overall, the qualitative agreement of these predicted loops with the experimental observations of Lynch [3] is excellent. From these curves there are a few observations worth noting. On Figures 4a and 4b, reverse switching due to Bauschinger effects is occurring when $E = 0$ after the reversal of the electric field. This implies that the slopes of the hysteresis and butterfly loops at $E = 0$ are not indicative of the linear dielectric and piezoelectric coefficients of the material. Instead, the slopes of these loops just after the reversal of the electric field are the best measures of these linear properties. A similar argument can be made for the piezoelectric and elastic properties at the beginning of the mechanical depolarization in Figures 4c and 4d. The Young’s modulus of the material should be taken from the unloading portion of the stress versus strain during depolarization curve. Finally, notice the anisotropy in the achievable tensile and compressive strains during purely ferroelastic stress-strain response, i.e. larger strain magnitudes occur in tension than in compression.

5. DISCUSSION

In this paper, micro-electromechanical simulations have been carried out to determine the possible states of remanent strain and remanent polarization in ferroelectric polycrystals composed of single crystals with tetragonal crystal structure. These simulations were used to map out the entire multi-axial range of remanent strain states as well as the uniaxial polarization states. It was quantitatively shown how the remanent polarization saturation limit depends on the level of remanent strain in the material. The saturation information obtained from the micro-electromechanical simulations was then fed into a phenomenological framework in order to ensure that the phenomenological model could not produce unattainable combinations of remanent strain and remanent polarization. The predictions of the phenomenological model are found to be in excellent qualitative accord with experimental observations of polycrystalline material behavior.

The results generated with the micro-electromechanical model are specific to untextured polycrystals with tetragonal crystal structure. However, similar simulations could be carried out for different crystal structures, e.g. orthorhombic or rhombohedral, or for textured polycrystals. Different crystal structures would effect the descriptions of the variant strains and polarizations of Equations (2.2) and (2.3), and polycrystalline texture would change the self-consistent averaging technique by altering the volume concentrations of the different orientations of the single crystals. In either of these situations, or a combination of the two, micro-electromechanical simulations can be used to map out the remanent strain and polarization states that are possible in a given ferroelectric polycrystalline material.
Figure 4. (a) The electric displacement versus electric field hysteresis loop. (b) The strain versus electric field butterfly loop. (c) The electric displacement versus stress during mechanical depolarization. (d) The strain versus stress during mechanical depolarization. (e) The ferroelastic stress versus strain hysteresis loop. All curves represent uniaxial electromechanically coupled behavior. The model parameters used to generate these curves are $\sigma_0 = 27.5$ MPa, $E_0 = 0.36$ MV/m, $P_{\text{max}} = 0.26$ C/m$^2$, $\varepsilon_c = 0.12\%$, $\beta = 2.85$, $\kappa = 3 \times 10^{-8}$ C/(m·V), $\mu = 30.8$ GPa, $\nu = 0.25$, $d_{33} = 8 \times 10^{-10}$ m/V, $m^m = 0.5$, $H_0^m = 13.75$ MPa, $m^e = 2.01$, $H_0^e = 3000$ (m·V)/C, $m^{em} = 2$ and $H_0^{em} = 0.5$ MJ.
REFERENCES