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Non-linear constitutive modeling of ferroelectrics

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Abstract

Due to the large coupling between their electrical and mechanical properties, ferroelectric ceramics are increasingly being implemented in novel devices. This review reports on recent advances in the development of predictive constitutive models for the coupled and non-linear electromechanical behavior of ferroelectrics. Such constitutive models are required to analyze the performance of ferroelectric devices and to model the failure processes in these devices and materials. The topics covered in this review include micro-electromechanical constitutive models, macroscopic phenomenological modeling for polycrystals, and the implementation of these non-linear constitutive models.

1. Introduction

Ferroelectric ceramics are presently being used in a broad range of applications including sonar, MEMS devices, fuel injectors for high efficiency-low emission diesel engines, actuators for active control of helicopter rotor blades and underwater vehicle control surfaces, and ultrasonic rotary inchworm motors with high power and torque densities. Recent work on rapid prototyping and stereolithography techniques has led to the ability to "print" layers of ferroelectric and layers of metal electrode material to produce complex structures in the green state that can later be co-fired. This new technology for producing complex ferroelectric ceramic–metal electrode structures is enabling the development of a broad range of novel actuators at low cost. Accurate modeling tools are required for the reliable design and optimized performance of these devices.

By definition, an electromechanical device or material converts and input of electrical energy to an output of mechanical energy (actuating application) or and input of mechanical energy to an output of electrical energy (sensing application). Hence, there exists a fundamental coupling between the electrical and mechanical fields in these materials, and constitutive models for electromechanics must provide relationships between the stress, strain, electric field and electric polarization/electric displacement in these materials. Within a device of arbitrary geometric design, the electrical and mechanical fields in the body will vary from point to point, and the distributions of these fields are governed by the fundamental physical laws of mechanical equilibrium, geometric compatibility of strains and displacements, Gauss' law for conservation of charge, and Maxwell's law that states that the electric field must be curl-free under quasi-static conditions.

If written out explicitly these physical laws represent 13 equations for 22 independent field variables. In order to close this system of equations and allow for their solution, nine more constitutive equations are required. The electromechanical constitutive response is of course dependent on the material and will differ between say glass and lead–zirconate–titanate (PZT). This review is concerned with the response of ferroelectrics and hence it is informative to illustrate the mechanisms responsible for the behavior of most ferroelectric materials of technological interest. Fig. 1 illustrates the perovskite crystal structure of many ferroelectric ceramics including barium titanate, lead titanate and PZT. Note that only the tetragonal crystal structure is pictured and discussed here, however other crystal structures such as orthorhombic and rhombohedral exist as well. Above the Curie temperature, the material is in the paraelectric state and the structure of the unit cell is cubic and centro-symmetric. As the material is cooled to below T_c it undergoes a phase transformation from cubic to

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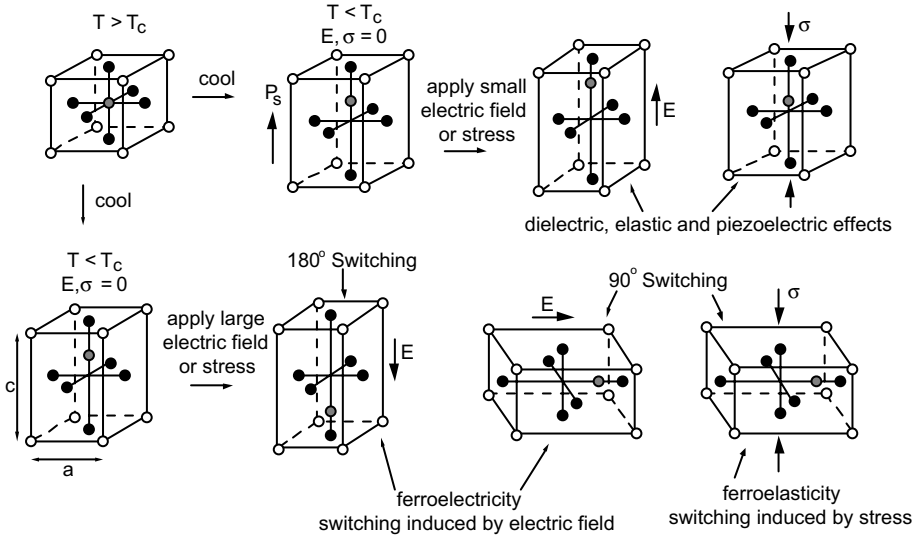

Fig. 1. The perovskite crystal structure common to many ferroelectric ceramics. For PZT the white ions at the corners are lead ions with a +2 charge, the black ions on the faces are oxygen ions (−2 charge) and the central ion is titanium or zirconium (+4 charge). The top set of figures illustrates the phase change through the Curie temperature, the spontaneous polarization, and the linear response of the crystal. The bottom set of figures illustrates the spontaneous shape change of the crystal, and 180° and 90° switching due to applied electric field or stress. The magnitudes of the ion displacements have been exaggerated for clarity.

tetragonal. Notice that the previously centered titanium ion has been displaced towards one face of the tetragonal cell. The direction of this ion displacement is also the direction of the spontaneous polarization of the material, P_s, and is aligned with the long c-axis of the tetragonal cell. Below T_c the material is both piezoelectric and ferroelectric, and the piezoelectric properties of the crystal are aligned with the spontaneous polarization direction. The piezoelectric, dielectric and elastic response of the material is illustrated on the first line of Fig. 1. Note that the position of the central titanium ion is related to the polarization of the material and the shape of the unit cell is related to the strain. The ferroelectric response of the material is illustrated on the second line of Fig. 1. In this figure ferroelastic switching has been differentiated from ferroelectric switching, however it is common practice to refer to all of these effects as ferroelectric switching or ferroelectricity. Note that a change in spontaneous strain, i.e. the orientation of the c-axis, accompanies the spontaneous polarization change during 90° switching but not during 180° switching.

Fig. 1 is a schematic of the constitutive response of many ferroelectric ceramics. The material behavior illustrated in this figure can be divided into two types: (a) Linear piezoelectric response which is characterized by the reversible and essentially time-independent displacements of the ions of the unit cell. (b) Non-linear ferroelectric response which is characterized by the irreversible "switching" of the spontaneous polarization direction of the unit cell and, for the case of non-180° switching, the reorientation of the c-axis of the unit cell. Switching of many unit cells occurs in an incremental fashion through the motion of domain walls and is a rate-dependent process. The initial step that most researchers in the field have taken is to represent these two separate parts of the strain and electric displacement mathematically as

$$\varepsilon_{ij} = s^E_{ijkl}\sigma_{kl} + d_{kij}E_k + \varepsilon^r_{ij}, \tag{1.1}$$

$$D_i = d_{ikl}\sigma_{kl} + \kappa^\sigma_{ij}E_j + P^r_i. \tag{1.2}$$

Here, ε^r_{ij} and P^r_i are the Cartesian components of the irreversible or "remanent" strain and polarization. Then s^E_{ijkl}, d_{kij} and κ^σ_{ij} represent the components of the elastic compliance, piezoelectric and dielectric permittivity tensors. These tensors relate the stress and electric field loading to the linear reversible parts of the strain and electric displacement configuration. For a region within a single ferroelectric domain the components of these tensors are constant and homogeneous. However, when averaged over multiple domains or grains, the components of these tensors can and do change as the remanent state of the material evolves. The role of non-linear constitutive models for ferroelectrics is to provide the history of the remanent strain and remanent polarization given the history of the applied stress and electric field. To address this task it is first important to decide the physical features of interest in a given problem. Is it important to resolve the electromechanical fields in individual domains or is it sufficient to treat material points as collections of grains? If fields in individual domains are important, then the actual geometry of the domain walls must be given and allowed to evolve.

However, if averages over many domains or many grains can supply sufficient information, then appropriate thermodynamic variables describing the internal state of the material must be selected and allowed to evolve. Ultimately, tracking the motion of domain walls or the evolution of internal thermodynamic variables allows for a mathematical description of the remanent strain and polarization in ferroelectrics. The remainder of this article will review recent work on the mathematical modeling of the averaged or phenomenological constitutive behavior of ferroelectric ceramics.

2. Micro-electromechanical models

The micro-electromechanical constitutive models reviewed here are in fact phenomenological. However, they are fundamentally different from the phenomenological constitutive laws discussed in the next section because they are constructed directly with the mechanism of domain switching as the motivation. The two primary components of micro-electromechanical constitutive laws for domain switching include a kinematic description of the remanent strain and remanent polarization and a switching criterion.

For the first set of models [*1,2–6,*7,8,9,*10], the kinematic description of a single crystal region is trivial because these theories assume that any given single crystal is also a single domain; there are essentially no domain walls. Hence, the remanent strain and remanent polarization of the single crystal are simply the spontaneous strain and spontaneous polarization of the unit cell of the material. Within these types of models if any part of the single crystal switches then all of the crystal switches. Hence, for a tetragonal material, any given single crystal region can exist in only one of six possible remanent states. The next component of the constitutive description is then to describe under what conditions the crystal will switch from one domain variant type to another. Consider the three domain variants illustrated in Fig. 2. For each variant the Cartesian components of the spontaneous strain and polarization are listed. Note that for small differences in the lattice parameters the spontaneous strain can be given as $\varepsilon_0 = 2(c-a)/(c+2a)$. Switching between variants can only occur if the free energy of the system decreases during the switching process. Hwang et al. [*1] argued that switching occurs if the work done by the applied stress and applied electric field achieves a critical level,

$$\sigma_{ij}\Delta\varepsilon^r_{ij} + E_i\Delta P^r_i \geqslant G_c. \tag{2.1}$$

Here $\Delta\varepsilon^r_{ij}$ and ΔP^r_i represent the components of the changes, final minus initial, in the spontaneous or remanent strain and polarization of the crystal during the switch. Note in Fig. 2 that for a 180° switch the remanent strain components do not change and hence stress cannot drive 180° switching. However, a 90° switch causes changes in both the remanent strain and remanent polarization and therefore both applied stress and electric field can contribute to 90° switching.

The assumption that a single crystal is comprised of only one domain variant is not a physical reality. In general, single crystals, including the grains in a polycrystal, are comprised of multiple domains, and these domains are arranged in complex configurations. From a continuum physics perspective, the behavior of the crystal can be determined from the domain configuration and the evolution of the positions of the domain walls. The tracking of domain wall locations is akin to dislocation dynamics analyses of the deformation of metal crystals and represents a significant computational effort. As an alternative, it is useful to devise a continuum theory that is dependent on a smaller set of parameters or internal variables. The most natural choices for the internal variables describing the state of a single crystal are the volume fractions of the domain

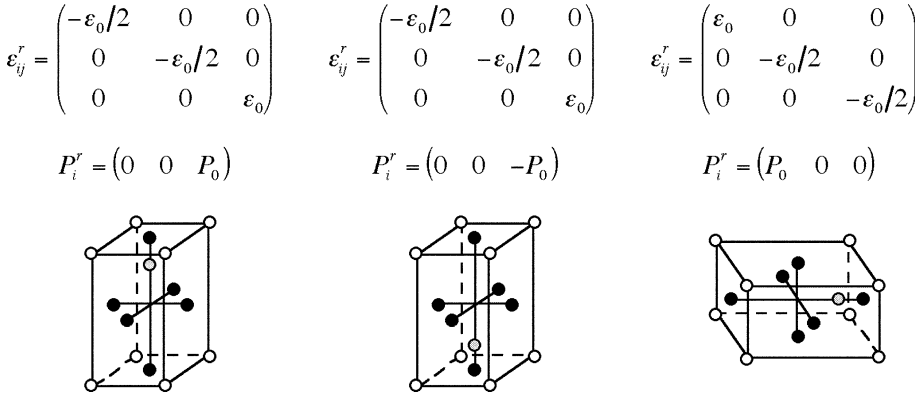

Fig. 2. Three of the possible six domain variant types for a tetragonal single crystal material. The components of the spontaneous strain and polarization are listed above each of the domain variant types. Transformation between the left and middle variants represents 180° switching, and transformation between the left (or middle) and the right variant represents 90° switching.

variants [11–17]. In order to further simplify the task of determining the average behavior of multiple domains researchers have either assumed a simple but specific domain geometry [16,17], or have applied the Ruess approximation which assumes that the states of stress and electric field are homogeneous throughout the crystal [11–15]. The Reuss approximation allows for a very simple analysis of the kinematics and effective linear properties of a single crystal comprised of multiple domain variants without the knowledge of the specific domain configurations. Specifically, the averaged remanent strain, remanent polarization and piezoelectric properties of the crystal are simply the volume averages of the respective variant quantities. Therefore, given the volume fractions of each domain variant type and the evolution of these volume fractions, Eqs. (1.1) and (1.2) serve as the constitutive model for the single crystal. The challenge resides in determining how the domain volume concentrations evolve. This task is best accomplished within the framework and machinery of irreversible thermodynamics. Specifically, the volume concentrations of the domain variants c^I, represent internal thermodynamic state variables. However, these volume concentrations are not independent internal variables. For example, consider the 90° switch from the domain variant on the left ($+z$) of Fig. 2 to that on the right ($+x$). If this *transformation system* is active, then the volume concentration of the $+z$ domains decreases at exactly the same rate that the volume concentration of the $+x$ domains increase. Since the volume concentrations are not independent it is useful to identify transformation increments $\dot{f}^\alpha$ for each of the possible transformation systems. For a tetragonal crystal there are six possible domain types and each of these domains can switch to the other five, hence there are thirty transformation systems in a tetragonal crystal and $\alpha = 1, \ldots, 30$. Each of the transformation systems can be active independently of one another, and to determine what systems will be active there is a diving force G^α associated with each transformation system. The driving force is defined such that the dissipation increment, $\dot{w}_D$ associated with the transformation increment $\dot{f}^\alpha$ is given as $\dot{w}_D = G^\alpha \dot{f}^\alpha$. This driving force is given as

$$G^\alpha = \sigma_{ij}\Delta\varepsilon_{ij}^{r,\alpha} + E_i\Delta P_i^{r,\alpha} + \frac{1}{2}\sigma_{ij}\Delta s_{ijkl}^{E,\alpha}\sigma_{kl} + E_k\Delta d_{kij}^{\alpha}\sigma_{ij} + \frac{1}{2}E_i\Delta\kappa_{ij}^{\varepsilon,\alpha}E_j. \tag{2.2}$$

Here again the Δ represents the difference (to minus from) in the property for the specific transformation system α. Then the switching criteria $G^\alpha = G_c^\alpha$ are applied to determine if a given transformation system is active.

It is worth mentioning that the transformation systems defined here are analogous to slip systems in single crystal metal plasticity. Furthermore, the driving forces G^α and critical levels of driving forces G_c^α are analogous to the resolved shear stress and critical resolved shear stress on a slip system. Hence, the derivation of the incremental constitutive law described here is identical to derivations for continuum slip plasticity models. Details of this derivation can be found in Huber et al. [*12]. One significant difference between domain switching theories and continuum slip plasticity is that the transformation increments $\dot{f}^\alpha$ are tied directly to the volume concentrations of the domain variants. Since no volume concentration of any variant type can be less than zero and the sum of all volume concentrations must be one, there are additional constraints on which transformation systems are allowed to be active. In addition to the driving force on a system achieving its critical level, the system can only be active if it does not decrease the volume concentration of any variant type to below zero. This additional constraint enforces the "lock-up" or saturation conditions for domain switching. Consider the schematic on Fig. 3. The rectangles represent a two-domain system separated by a single 180° domain wall. Initially there are equal volume concentrations of each domain variant type. As electric field is applied to the sample in the upward direction, the domain wall remains stationary until the field causes the driving force on the domain wall to reach a critical level. Then the domain wall starts to move to the left, incrementally switching downward oriented domains to the upward direction and creating non-linearity in the electric displacement versus electric field behavior. Note that for each domain state, A, B or C, the position of the domain wall would remain unchanged if the electric field were removed and the resultant electric displacement behavior due to such and unloading is denoted by the dashed line. Hence, within incremental domain switching models the remanent state of the crystal can reside in intermediate states and need not be equal to the spon-

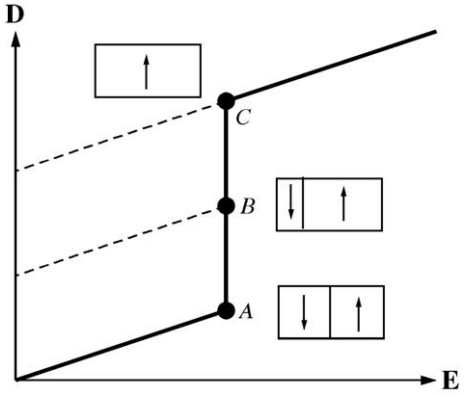

Fig. 3. The electric displacement, **D,** versus electric field, **E**, response of a non-hardening, two domain, 180° switching system with incremental domain wall motion. The domain wall positions corresponding to points on the curve are illustrated in the boxes. Possible unloading paths are illustrated as dashed lines.

taneous strain and polarization state of the underlying unit cells. Finally, saturation is illustrated at state *C*. At state *C* the domain wall has switched all of the available domains to the upward direction and therefore the material can only respond to further electrical loading in a linear fashion.

The domain switching theories for single crystals reviewed here can be grouped into two categories, models that assume a complete switch [*1,2–6,*7,8,9,*10] and incremental switching theories [11–17]. Both types of theories rely on the mechanism of domain switching in their derivation and are useful for gaining insight into the electromechanical behavior of ferroelectrics. A significant application of these theories is within micro-electromechanical models of the behavior of ferroelectric polycrystals. Most of the works already cited make an attempt to model polycrystalline behavior by some type of averaging of single crystal behavior. These models assume that the polycrystal is comprised of a collection of randomly oriented single crystal grains. The determination of the polycrystal behavior then relies on averaging schemes of differing levels of approximation. The simplest models use the Ruess approximation where the stress and electric field are assumed to be homogeneous throughout the polycrystal [*1,3,5,*7,9]. The next level of approximation uses some type of self-consistent averaging scheme where the single crystal grains are usually treated as spherical inclusions embedded in an infinite effective medium matrix [2,9,*12,13–17]. Lastly, computations have also been performed which assume that the polycrystal is an aggregate of randomly oriented cubic grains. Each grain is then treated as a single finite element and the polycrystal behavior is computed with the finite element method [6,8]. Ultimately, all of these micro-electromechanical models are able to capture the fundamental behaviors of ferroelectric polycrystals. The primary drawback of these models is that they contain an enormous number of internal variables, i.e. the domain states of each grain, that must be tracked throughout the deformation history of the material. This feature of these models makes them difficult to implement within finite element computations that solve for the inhomogeneous electromechanical fields near features like electrode and crack tips. In order to address this problem phenomenological models based on a reduced number of internal variables have been proposed and implemented over the past few years.

3. Phenomenological constitutive theories

The role that is envisioned for the phenomenological constitutive models reviewed in this section is for the analysis of the inhomogeneous electromechanical fields occurring in devices and structures fabricated from ferroelectric ceramics. To further extend the analogies between non-linear ferroelectric response and metal plasticity, the phenomenological models described here are akin to J_2 flow plasticity theory. As with J_2 flow theory, the models cannot be expected to perfectly predict the response of the material to arbitrarily complex loading histories, however they must reproduce all of the qualitative multi-axial behaviors of ferroelectric polycrystals. Furthermore, it is important that these models be as simple as possible, in the sense that the number of internal variables describing the thermodynamic state of the material is small.

Prior to a discussion of the phenomenological theories, it is informative to consider the types of polycrystalline ferroelectric behavior that have been experimentally observed and that the models must be required to reproduce. Fig. 4 is a schematic of the types of constitutive behavior that have been measured under uniaxial electromechanical loading [*18,19,20] and multi-axial electrical loading [*21]. Figs. 4a and b are the electric displacement versus electric field hysteresis loop and the strain versus electric field butterfly loop. The hysteresis and butterfly loops indicate that there is a significant coupling between the remanent strain and remanent polarization. Figs. 4c and d illustrate the electric displacement and strain behavior of a poled polycrystalline material under the application of a compressive stress. Of note on Fig. 4c is that the compressive stress cannot completely depolarize a poled polycrystalline specimen, i.e. there does exist a finite level of remanent polarization after the stress is removed. Lastly, Fig. 4e illustrates the results of polarization rotation experiments [20]. In this experiment an electric field is applied to a previously poled sample at an angle θ to the original polarization direction. Then, the change in electric displacement in the electric field direction is recorded as a function of the applied electric field. This experiment is currently the only multi-axial and non-proportional loading configuration investigated to date and it provides an excellent test of the qualitative accuracy of phenomenological constitutive theories. Finally, in addition to the behaviors depicted in Fig. 4, Refs. [*18,19,20] also report hysteresis and butterfly loops for coupled electromechanical loading, specifically the strain and electric displacement versus electric field response is measured under the application of a constant compressive stress. The experiments reported in [*18,19,20,*21] provide a minimal set of behaviors that every multi-axial phenomenological theory must be tested against.

Two uniaxial phenomenological constitutive models for ferroelectric constitutive behavior [*22,*23] have appeared recently and have revived interest in this area of research. Cocks and McMeeking [*22] assumed that the remanent strain and remanent polarization could be used as internal variables describing the thermodynamic

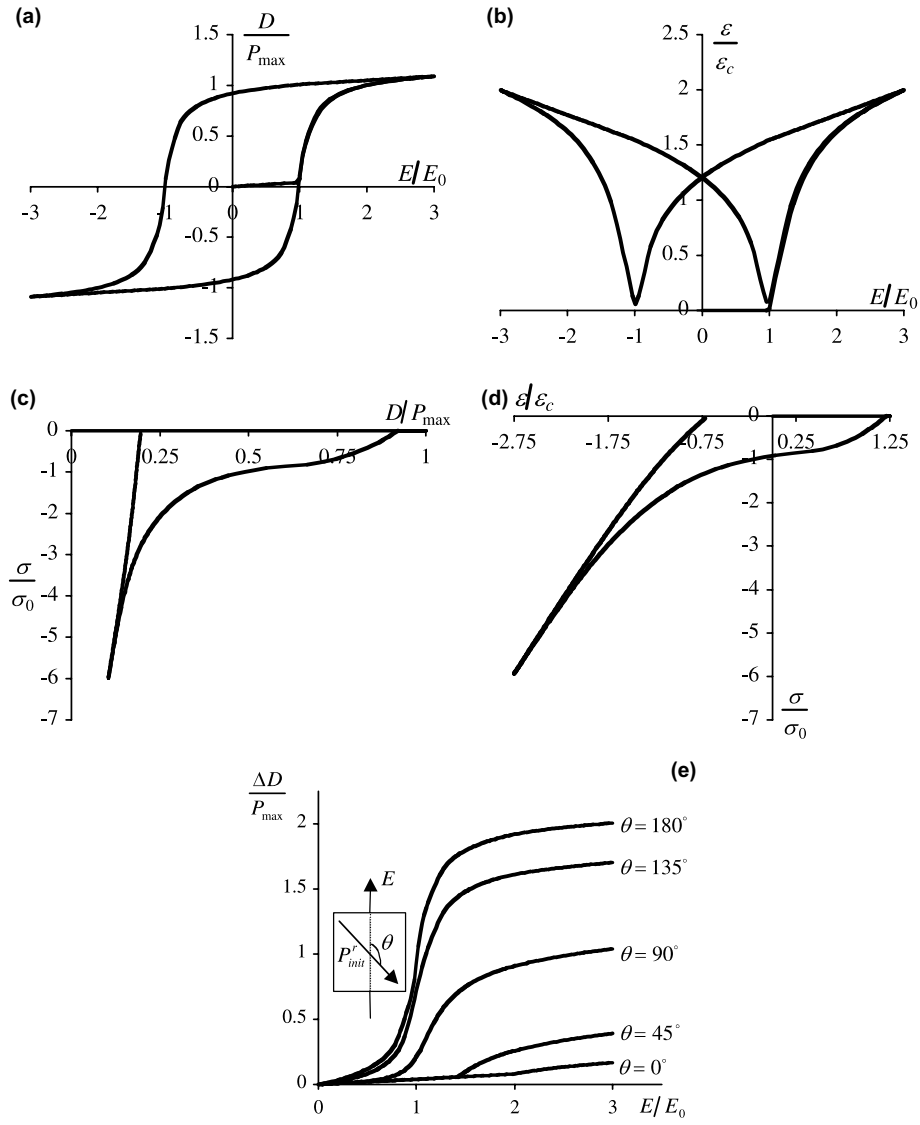

Fig. 4. (a) Uniaxial electric displacement, D, versus electric field, E, hysteresis loop. (b) Uniaxial strain, ε, versus E butterfly loop. (c) Depolarization due to compressive stress, σ. (d) Stress versus strain during depolarization. (e) Polarization rotation. All of these behaviors were generated with the phenomenological theory presented in Refs. [*26,31] and agree very favorably with the experimental observations reported in Refs. [*18,*21].

state of the material. They then postulated a free energy of the material decomposed into reversible and irreversible or remanent parts. As in metal plasticity, reversible behavior was assumed to occur within a switching (i.e., yield) surface and irreversible remanent strain and polarization were allowed to develop for loading states on the switching surface. Back stresses, back electric fields and hardening laws arise naturally within the proposed thermodynamic setting. The independent work of Kamlah and Jiang [*23] outlines a more general formulation with unspecified internal variables. They point out that given a set of internal variables $q_1, \ldots, q_n$, then the remanent strain, remanent polarization, and linear elastic, piezoelectric and dielectric properties will all depend on these internal variables. Then, thermodynamically consistent driving forces associated with each of the internal variables are identified and a switching surface is postulated in this driving force space.

Constitutive theories derived within the framework of irreversible thermodynamics, like [*22,*23], are very attractive. However, there are other approaches proposed recently that are worthy of note. Kamlah and Tsakmakis [24] and Landis and McMeeking [25] developed phenomenological constitutive theories with a form similar to that of metal plasticity with switching surfaces and flow rules. Instead of using a thermodynamic framework, these models rely on carefully devised rules and conditional statements to model ferroelectric or ferroelastic behavior, respectively. Another approach used to model polycrystal behavior was proposed by Huber and Fleck [*21]. Huber and Fleck devised a

pseudo-isotropic single crystal by orienting the spontaneous polarization directions of the domain variants towards the 20 vertices of a regular dodecahedron. Then transformation systems between these domain variants with driving forces defined in the same way as Eq. (2.2) allow for switching and changes in the remanent state of the material. Huber and Fleck then assume that this devised single crystal can be used to model polycrystalline behavior, and they show that this model is able to reproduce the behavior observed in the polarization rotation experiments.

Returning to theories that are formulated within the framework of irreversible thermodynamics, Landis [*26] developed the multi-axial generalization of the uniaxial model of Cocks and McMeeking [*22] by assuming that the internal variables characterizing the thermodynamic state of the material are the components of the remanent strain tensor and the remanent polarization vector. The components of these types of theories include a description of the free energy with a hardening or "remanent potential", a switching surface and a flow rule. First, the Helmholtz free energy of the material is assumed to be separable into the form

$$\Psi = \Psi^{\text{rev}}(\varepsilon_{ij}, D_i, \varepsilon^r_{ij}, P^r_i) + \Psi^{\text{rem}}(\varepsilon^r_{ij}, P^r_i). \tag{3.1}$$

Here Ψ^{rev} represents the reversible part of the Helmholtz free energy and is equal to the stored elastic, piezoelectric and dielectric energy per unit volume. Then, the remanent potential Ψ^{rem} represents an additional part of the free energy associated with only the remanent state of the material. The physical interpretation of this quantity is that remanent straining and polarizing of a material results in the generation of internal stresses and electric fields. While these internal fields must average out to zero, the energy associated with them does not and this excess energy is captured in a conceptual way by Ψ^{rem}. Next, the Clausius–Duhem inequality can be applied to Eq. (3.1) requiring that the dissipation increment for the material must be non-negative, i.e.

$$\begin{aligned}
&\sigma_{ij}\dot{\varepsilon}_{ij} + E_i\dot{D}_i - \dot{\Psi} \geqslant 0 \\
&\quad \rightarrow \underbrace{\left(\sigma_{ij} - \frac{\partial \Psi^r}{\partial \varepsilon^r_{ij}} + \frac{1}{2}\frac{\partial s^E_{pqrs}}{\partial \varepsilon^r_{ij}}\sigma_{pq}\sigma_{rs} + \frac{\partial d_{rpq}}{\partial \varepsilon^r_{ij}}E_r\sigma_{pq} + \frac{1}{2}\frac{\partial \kappa^\sigma_{pq}}{\partial \varepsilon^r_{ij}}E_pE_q\right)}_{\hat{\sigma}_{ij}} \dot{\varepsilon}^r_{ij} \\
&\quad + \underbrace{\left(E_i - \frac{\partial \Psi^r}{\partial P^r_i} + \frac{1}{2}\frac{\partial s^E_{pqrs}}{\partial P^r_i}\sigma_{pq}\sigma_{rs} + \frac{\partial d_{rpq}}{\partial P^r_i}E_r\sigma_{pq} + \frac{1}{2}\frac{\partial \kappa^\sigma_{pq}}{\partial P^r_i}E_pE_q\right)}_{\hat{E}_i} \dot{P}^r_i \geqslant 0.
\end{aligned} \tag{3.2}$$

Here the left side of the inequality is the dissipation rate/increment per unit volume. Furthermore, the driving forces $\hat{\sigma}_{ij}$ and $\hat{E}_i$ for changes in the remanent strain and remanent polarization, respectively are identified below their associated quantities. Note that these driving forces contain applied loadings, back fields associated with derivatives of the remanent potential Ψ^{rem}, and terms associated with changes in the linear elastic, piezoelectric and dielectric properties of the polycrystalline material. The next step in these constitutive theories is to identify a switching surface. The switching surface is a region in the generalized driving force space within which the material responds in a linear and reversible fashion. In general this surface is defined as

$$\Phi(\hat{\sigma}_{ij}, \hat{E}_i, \varepsilon^r_{ij}, P^r_i) = 0. \tag{3.3}$$

Then, for states of loading that exist on the switching surface, a flow rule is required to determine the direction of the remanent strain and polarization increments. If it is assumed that the material satisfies the postulate of maximum dissipation then the switching surface must be convex and the remanent increments must be normal to the switching surface such that

$$\dot{\varepsilon}^r_{ij} = \lambda\frac{\partial \Phi}{\partial \hat{\sigma}_{ij}} \quad \text{and} \quad \dot{P}^r_i = \lambda\frac{\partial \Phi}{\partial \hat{E}_i}. \tag{3.4}$$

Here λ is an undetermined multiplier that must be determined within the theory. The derivation of λ and the incremental form of the constitutive law follows the methods for metal plasticity and details can be found in [26*]. Finally, the Eq. (3.2) will now be satisfied if the convex switching surface encloses the origin in $\hat{\sigma}_{ij} - \hat{E}_i$ space.

The thermodynamic structure used to guide the derivation of these phenomenological theories only ensures that the first and second laws of thermodynamics and the postulate of maximum dissipation are satisfied. However, this framework tells us nothing about the specific form of the theory. This is where the significant modeling challenge lies. Specifically, in order to model a given ferroelectric material the hardening potential and the linear elastic, piezoelectric and dielectric properties must be given as functions of the remanent strain and polarization components, and the switching surface must be defined in the driving force space. To maintain simplicity most researchers [*21,*23,*26,27,*28] have assumed that the linear elastic and dielectric properties of the material are isotropic and that the components of the piezoelectric tensor are linearly proportional to the magnitude of the remanent polarization and transversely isotropic about the remanent polarization direction. Also, the most general form of the switching surface has remained relatively simple and is given as

$$\Phi = \frac{3\hat{s}_{ij}\hat{s}_{ij}}{2\sigma_0^2} + \frac{\hat{E}_i\hat{E}_i}{E_0^2} + \frac{\beta\hat{s}_{ij}\hat{E}_iP^r_j}{\sigma_0E_0P_0} - 1. \tag{3.5}$$

Here σ_0 and E_0 are the coercive stress and electric field under either purely mechanical or electrical loading, $\hat{s}_{ij}$ is the deviatoric part of $\hat{\sigma}_{ij}$, P_0 is the maximum possible remanent polarization in a polycrystalline sample, and β is a numerical constant which in some works has been taken to be zero [*22,*23,*28]. Note that Eq. (3.5)

represents a smooth surface and recently Shieh et al. [29] have performed a detailed experimental and theoretical evaluation of polycrystalline switching criteria. They and others [*12,14] have found that self-consistent computations predict that switching surfaces develop corners at loading points. Some evidence of experimentally observed corners appears in [29] as well, although these corners do not appear to be as severe as those predicted by the self-consistent model. It should be noted that the form of the theory discussed here, with remanent strain and polarization components as the only internal variables, does not allow for the development of corners at loading points. However, such features could be introduced to the theory by including additional internal variables to track the development of corners.

As yet, the phenomena of strain and polarization saturation in ferroelectric *polycrystals* have not been discussed. As opposed to plastic strains in metals, and as illustrated schematically in Fig. 3, remanent polarization and strain in ferroelectrics are constrained to a finite level. Furthermore, the saturation polarization is dependent on the prevailing level of remanent strain. For example, the maximum level of remanent polarization can only be attained in the material if it is aligned with the maximum level of tensile remanent strain. Under a compressive remanent strain the remanent polarization aligned with the compressive direction can only attain a fraction of its maximum magnitude. This coupling between the polarization and strain saturation states can be employed to explain the depolarization behavior of Fig. 4c. For multi-axial remanent states the saturation conditions can be thought of as a surface in remanent strain and remanent polarization space. Remanent states that are attainable by the material exist within this saturation surface, and those states that are impossible to achieve lie outside of the surface. This feature of ferroelectric constitutive behavior can be incorporated into phenomenological models by requiring the remanent potential, Ψ^{rem}, approaches infinity as the saturation surface is approached. However, the phenomenological framework used to derive these theories cannot predict the saturation conditions a priori and hence the saturation conditions for a polycrystal must be entered into the model. Here again is where an understanding of the underlying crystal structure of the material plays a critical role. Within the original model of Kamlah and Jiang [*23] the definitions of the internal variables are conceptually tied to the micro-electromechanical concept of an approximate domain orientation distribution. This approach is appealing because it offers a direct and intuitive model for predicting the saturation states and uses a small number of internal variables to describe the orientation distribution. In contrast, Landis and co-workers [*30,31] applied the micro-electromechanical model of [*12] to computationally determine the full multi-axial set of strain saturation states for a mechanically loaded polycrystal, and the uniaxial set of polarization and strain saturation conditions. These micro-electromechanically determined remanent strain and polarization saturation conditions were then used as inputs to the hardening potential Ψ^{rem}, and the phenomenological theory was then shown to be able to predict the behaviors illustrated in Fig. 4. While significant progress has been made towards developing a multi-axial constitutive theory for ferroelectrics, future work must continue to focus on verifying and improving the functional descriptions of the model parameters. To this end, new micro-electromechanical simulations and careful multi-axial experimental observations can provide key insights for the development of these models.

4. Applications

Due to the relative infancy of the phenomenological constitutive laws already described, there are currently few modeling tools available to guide the geometric design of ferroelectric devices or for assessing the generation of internal stresses and electric fields that occurs during the poling process. These internal fields can often lead to distortion of the device and cracking at electrode tips and electrode-ceramic interfaces. The ultimate purpose of phenomenological constitutive modeling is to provide fully coupled, multi-axial constitutive laws for ferroelectric ceramics that can be readily implemented within the finite element method. These finite element formulations can then be used to predict the performance of ferroelectric devices and to analyze the fracture processes in these materials and devices. With regard to the analysis of devices, Kamlah and coworkers [32,33] applied the model of [24] to the analysis of a layer of ferroelectric material in a piezoelectric stack actuator. Also, a new finite element formulation [*34] has been applied by Haug [35] with the phenomenological constitutive law of McMeeking and Landis [27] to investigate the fields in actuator layers, near electrode tips, and near crack tips.

A significant liability in structural applications (i.e., actuators) of ferroelectrics is their inherent brittleness. The lack of fracture resistance in ferroelectric ceramics leads to cracking at electrode interfaces, within ceramic layers, and near electrode tips. In the absence of applied electric fields the mode I fracture toughness levels for most PZT ceramics are of the order of $K_{\text{Ic}} \approx 1\ \text{MPa}\sqrt{m}$. Furthermore, electrical coupling in these materials complicates the situation as the application of modest electric fields to the material can reduce or increase measured fracture toughness levels by as much as 30%, and remanent polarization in the material induces fracture toughness anisotropy. A significant body of work has developed on the fracture mechanics of linear piezoelectric materials, see [36] for a review. The pri-

mary shortcoming of linear analyses is that they ignore the effects of switching on the fracture toughness of the material. Hence, the electromechanical fields that are computed from a linear analysis may be significantly different from a non-linear analysis that properly accounts for the switching that must occur near the crack tip. Some efforts at modeling the switch toughening in ferroelectrics with simplified or discrete switching constitutive laws have been able to explain the qualitative toughening effects due to switching [37–39,*40]. However, in order to perform accurate non-linear fracture analyses, it is crucial to have a reliable constitutive law for the ferroelectric material. Along these lines Landis [*41] has recently analyzed the amount of toughening due to ferroelastic switching during steady crack growth with the phenomenological model developed in [*26, *30]. Additional work on electromechanically coupled switching near crack tips is still required to gain a more detailed understanding of the fracture process in ferroelectrics.

5. Summary and future work

The analysis of the performance and reliability of devices fabricated from ferroelectric materials requires a means for the prediction of the inhomogeneous electromechanical fields in such structures. Within a continuum physics setting, these electromechanical fields are governed by standard physical laws including mechanical equilibrium, Gauss' and Maxwell's laws, and the geometrical strain–displacement relationships. The final set of equations that are required to couple these laws and solve a given boundary value problem represent the constitutive behavior of the material. For non-linear ferroelectric materials the constitutive law must provide a history of strain and electric displacement given a history of stress and electric field. Generally the strain and electric displacement in ferroelectric ceramics is additively decomposed into two parts, a reversible part associated with linear elastic, piezoelectric and dielectric behavior and an irreversible or remanent part associated with non-linear domain switching. All physically sound constitutive models for ferroelectrics must in some way be connected to the mechanism of domain switching.

Initial studies on domain switching assumed that an entire single crystal or grain could exist in any one but only one of the possible domain variants allowed by the crystal structure of the material. Hence, the remanent strain and polarization in a region must be equal to the spontaneous strain and polarization of the domain variant type existing in that region. The fundamental component of such models is a switching criterion that determines what stress and electric field states can cause switching from one variant type to another. More recent developments for both single crystal and polycrystalline ferroelectrics are analogous to models for metal plasticity. These models are cast within the framework of irreversible thermodynamics and allow for infinitesimal increments of switching and hence intermediate states of remanent strain and polarization. The single crystal models are analogous to continuum slip plasticity theory and generally identify the volume concentrations of the domain variant types as internal variables. Then driving forces that cause changes in the internal variables are identified and incremental or tangent forms of the constitutive relations can be derived. These single crystal theories have been employed in micro-electromechanical computations to simulate the behavior of ferroelectric polycrystals. Unfortunately, due to their large number of internal variables, these micro-electromechanical polycrystalline models are not efficient for use in finite element methods. To address this difficulty phenomenological constitutive laws for ferroelectric polycrystals have been recently developed. Again, the most promising of these models are formulated within the framework of irreversible thermodynamics. In many respects these models are analogous to J_2 flow theory for metal plasticity.

Future work on the constitutive modeling of ferroelectrics will likely focus on two areas: the refinement and development of constitutive theories, and the implementation of these constitutive theories for the solution of interesting problems. With regards to the refinement of constitutive laws, the micro-electromechanical models represent a unique tool that can and should be implemented to improve the macro-constitutive models. The micro-models are ideal for performing numerical constitutive experiments with complex electromechanical loading histories that would be difficult if not impossible to reproduce in the lab. Such simulations can be tailored to provide useful insights into the functional parameters required in the macro-models. However, such computations should never be taken as a substitute for detailed experimental observations. Future experiments must extract as much information as possible from a given set-up, including both electrical and mechanical measurements. The most useful experiments will either be on coupled electromechanical loading or on spatially multi-axial loading. With regard to the phenomenological theories, measurements of switching surfaces *and* remanent increments *and* property changes will be of great value. In order to measure remanent strain and polarization increments and linear property changes such experiments need to include brief load reversals to measure the instantaneous elastic, piezoelectric and dielectric response and to extrapolate the current levels of remanency. Finally, the second area of future work is the implementation of constitutive laws. Research in this area will include the development of stable and efficient numerical routines for the solution of boundary value problems and the application of these

tools to interesting engineering and materials problems. Such problems will include predictions of the switch toughening of electromechanically loaded cracks and of the performance of ferroelectric devices.

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The papers of particular interest have been highlighted as:
* of special interest;
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