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Polarization switching in layered ferroelectric structures

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Abstract. The dielectric properties of thin-film ferroelectric structures are studied. The effects of compensation charges at the interfaces between layers (e.g. between a ferroelectric and a non-ferroelectric layer) are considered; on the assumption that these charges are mobile within the interface region, we show that they control the domain boundaries between regions of opposite ferroelectric polarization and are thus responsible for the way in which polarization switching takes place. Using a Landau–Devonshire model for the ferroelectric, we demonstrate hysteresis curves (stored charge against applied voltage) in ferroelectric capacitor structures that explain the long-standing problem of why the switching of polarization occurs over a finite voltage range. In particular, the model shows how non-switching ferroelectric layers can be stabilized in thin-film capacitor structures, and why this produces hysteresis curves of the form that is observed experimentally.

1. Introduction

Structures comprising layers of ferroelectrics and paraelectrics continue to attract increasing interest because of their potential device applications. The commonly observed property of such structures is the hysteresis loop (variation of stored charge Q with applied voltage V) obtained in a capacitor geometry with metal electrodes on the surfaces. Curiously, although ferroelectrics have been studied for many years, the basic shape of the hysteresis loop has never to our knowledge been explained in principle. In the region where polarization reversal takes place, experimental measurements always show a continuous variation of Q with V, whereas it is always assumed that theoretical models predict a discontinuous variation when the polarization reverses. The absence experimentally of a discontinuous change is therefore normally attributed to imperfections (e.g. domain structures) within the sample.

It is the purpose of this paper to show that one can straightforwardly model the effect of domains in a ferroelectric (FE) capacitor. The hysteresis loop for FE structures will always be of the continuous form described above so long as the structure contains non-switching layers, which may either be FE layers formed during cycling through the hysteresis loop or paraelectric (PE—materials of high linear dielectric susceptibility) layers grown into the structure. The key feature of the polarization reversal process is the behaviour of the space charge—compensation charge—that exists at the surfaces between the different FE and PE layers. The compensation charge is formed in response to what is usually called the depolarization field, i.e. the electric field produced by the normal component of polarization at an interface. We assume that the compensation charges are mobile within the interface region, but do not migrate between interfaces (except perhaps on a long time scale). This enables domains of opposite polarization to co-exist in the FE regions, with continuity of the

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electrostatic fields. When polarization reversal occurs in response to change in the external voltage V applied to the structure, the domain boundaries change so as to favour one or other polarization orientation; the motion of the domain boundaries must be associated with motion of the compensation charges within the interfaces. On this basis, and using the Landau–Devonshire theory for a ferroelectric, we obtain calculated hysteresis behaviour which is entirely characteristic of that observed experimentally.

The outline of this paper is as follows. In section 2, we discuss the fields and compensation charges in a simple FE/PE capacitor structure so as to clarify the role of compensation charge in determining the macroscopic electrostatic properties. Throughout, we assume that the spontaneous dipole moments are polarized normal to the plane of the film. The FE layer is described using the Landau–Devonshire model for a ferroelectric (section 3), and section 4 describes the polarization reversal process and the form of the hysteresis loop when the FE layer consists of both positively and negatively polarized domains. The most striking features of the analysis, in comparison with a bulk FE structure, are (i) that the hysteresis loops show polarization reversal over a finite range of V, (ii) the loop can be asymmetric with respect to Q and V and (iii) the susceptibility does not diverge at the transition temperature. Although there is not a lot of experimental measurement as yet on actual layered ferroelectrics, there is evidence that all these features are usually observed in measurements on layered ferroelectric structure. However, there is ample evidence that most if not all structures which are grown as a single FE layer actually form a so-called non-switching layer close to the electrodes. In section 5 we replace the PE layer by non-switching FE layers at each electrode (the non-switching characteristics can be achieved by suitable space charges at the interfaces). The resulting hysteresis curves closely resemble those measured experimentally, which are thus explained here for the first time using a first-principles model.

The work in this paper resembles to some extent the approach of Miller *et al* (1990, 1991), who have measured the behaviour of thin-film ferroelectric capacitors, and modelled this behaviour, including the effects of space charge at the interfaces. Zurcher *et al* (1995) have also performed model calculations appropriate for SBT capacitors; they model a multi-layer structure including interface charges by adjusting the charges and polarizations self-consistently using a Gauss-loop technique. Tagantsev *et al* (1995) discuss the identification of the non-switching layer. In order to model the hysteresis behaviour, these authors all use an assumed empirical hysteresis loop for the ferroelectric material. We are able to derive this type of hysteresis loop directly from first principles by a simple application of Landau theory and the boundary conditions for the fields and charge in layered FE and FE/PE structures.

2. Basic model of FE/PE structure

The basic structure that we will consider is shown in figure 1. Two planar layers 1 and 2, thicknesses L_1 and L_2, are placed between the metallic plates of a parallel plate capacitor structure, with applied voltage V_0. Surface charge densities Q_1 and $-Q_2$ exist at the top and bottom plates, and $\sigma_c = Q_2 - Q_1$ at the interface. The fields D_i, E_i and P_i ($i = 1, 2$) in the two media are assumed to be uniform, and directed along the z-axis normal to the layers (with the downward direction in figure 1 taken as the positive z-direction). The assumption of uniformity implies that the interface regions, in which the space charges exist and in which the fields will not be uniform, are small in dimension compared to the dimensions L_1 and L_2, and so we can for the present ignore the finite extent of the surface charge distribution. The application of Landau theory to the description of surface polarization

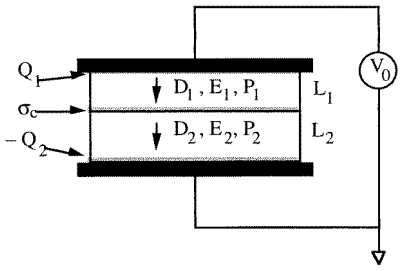

Figure 1. Basic two-layer structure: media 1 and 2 placed between the plates of a capacitor, with charge densities Q_1, σ_c and $-Q_2$ at the three interfaces.

non-uniformity has been discussed, for example, by Tilley (1993), and size effects in this context discussed by Wang and Smith (1995, 1996).

The D-fields are related to the free charge density ρ by Gauss' law:

$$\boldsymbol{\nabla} \cdot \boldsymbol{D} = \rho. \tag{2.1}$$

Since the D-fields are assumed to be uniform, $\rho = 0$. At an interface normal to $\boldsymbol{D}$, D has a discontinuity given by

$$\Delta D = \sigma \tag{2.2}$$

where σ is the free charge surface density at the interface. Throughout this paper we use the word 'charge' to refer only to real charges; we avoid the explicit use of bulk and surface pseudo-charges $\rho_p = -\boldsymbol{\nabla} \cdot \boldsymbol{P}$ and $\sigma_p = -P_n$ associated with the polarization $\boldsymbol{P}$. We use the term 'compensation charge' for the free space charge at an interface (sometimes this is called 'screening charge' or 'depolarization charge').

In the structure in figure 1, the surface charge densities and the fields are related by

$$D_i = Q_i = \varepsilon_0 E_i + P_i \ (i = 1, 2). \tag{2.3}$$

When the external voltage V_0 is zero, equilibrium is attained only if there are no macroscopic electric fields in the structure, and so the equilibrium conditions are

$$E_i = 0 \qquad D_i = Q_i = P_i. \tag{2.4}$$

Note that if at least one of the media has a non-zero spontaneous ferroelectric polarization P_i, equilibrium cannot be reached without the presence of compensation charges, which presumably appear during the growth of the structure or during its cooling when the ferroelectric moment develops. Most ferroelectrics are essentially insulators, so the appearance of compensation charges (perhaps associated with deep traps) will normally occur on a slow time scale (perhaps seconds or longer). The question then arises of how these charges change when V_0 is charged. Clearly, so long as the time scale of changes in V_0 is short compared to the vertical movement of the free charges, the compensation charge σ_c within the interface layer will remain constant. This condition implies that if, for example, the effective capacitance of the parallel plate structure is measured by varying V_0 and observing the changes in the charge Q supplied by the voltage source, then the capacitance effects should dominate over conductance effects. Thus, we assume that the compensation charge is unable to move vertically (i.e. across the layers) in the structure; on the other hand, we shall assume that the charges are mobile laterally within the charged layer when we come to consider domains in the ferroelectric (section 4).

Consider now the response of the system to changes δV_0 in the applied potential, measured as the change δQ in charge density Q supplied by the voltage source. For convenience, V_0 is converted to an effective average field $E_0 = V_0/L$, where $L = L_1 + L_2$. The basic assumption is that the compensation charges are not mobile normal to the layers, so σ_c remains constant over the time-scale of the measurement. Therefore the change δD in the D-field is the same throughout the structure, i.e.

$$\delta D = \delta D_1 = \delta D_2 = \delta Q = \delta Q_1 = \delta Q_2. \tag{2.5}$$

The dielectric susceptibilities of the two media are defined as

$$\varepsilon_i(E_i) = \frac{\partial D_i}{\varepsilon_0 \partial E_i} \tag{2.6}$$

where the susceptibility $\varepsilon_i(E_i)$ is assumed to be expressible as a function of the field E_i. With δD uniform, it is clearly more appropriate to deal with the reciprocal susceptibilities. The changes in the E-fields are given by

$$\varepsilon_0 \delta E_i = \varepsilon_i(E_i)^{-1} \delta D \tag{2.7}$$

and the overall voltage change is

$$\delta V_0 = L \delta E_0 = L_1 \delta E_1 + L_2 \delta E_2. \tag{2.8}$$

We can thus immediately obtain the effective medium result for the susceptibility of the structure along the field axis (the z-axis):

$$\varepsilon_{zz}^{-1} = \frac{\varepsilon_0 \delta E_0}{\delta D} = \frac{f_1}{\varepsilon_1(E_1)} + \frac{f_2}{\varepsilon_2(E_2)} \tag{2.9}$$

where $f_i = L_i/L$ are the volume fractions of the two media, with $f_1 + f_2 = 1$. This type of result is well known from the effective medium theory of superlattices. Note the initially surprising feature of ε_{zz} that, if one of the materials, 1 say, undergoes a second order phase transition so that $\varepsilon_1 \to \infty$, then ε_{zz} does not diverge at the transition. Physically, this is because the layers act as capacitors in parallel, whose total capacitance is limited by the smaller capacitance.

This approach can be extended to cover the application of finite fields E_0. The susceptibilities ε_i should be viewed as non-linear functions of the field E_i, and all fields can be viewed as functions of the independent variable Q. The defining equations are

$$\begin{aligned} \frac{\mathrm{d}E_i}{\mathrm{d}Q} &= \frac{1}{\varepsilon_i(E_i)} \\ \frac{\mathrm{d}E_0}{\mathrm{d}Q} &= f_1 \frac{\mathrm{d}E_1}{\mathrm{d}Q} + f_2 \frac{\mathrm{d}E_2}{\mathrm{d}Q}. \end{aligned} \tag{2.10}$$

Hence, one can find E_0 as a function of Q, so long as the functions $\varepsilon_1(E_1)$ and $\varepsilon_2(E_2)$ are known. In order emphasize the physics of this approach, we make the essentially trivial point that the expressions above are those that would be obtained by considering the equivalent circuit of figure 2, comprising two capacitors in parallel containing the media 1 and 2. The compensation charge σ_c is simply the total charge $Q_2 - Q_1$ trapped between the capacitors, which will not change whatever the applied voltage, so long as conduction through the media can be ignored.

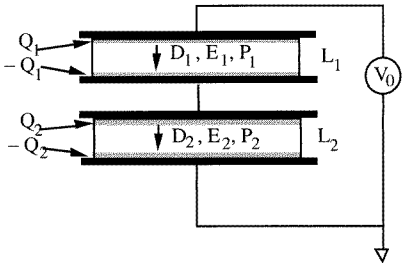

Figure 2. Equivalent circuit for figure 1.

3. Polarization in Landau-model FE/PE structure

We consider the polarization and susceptibility for a ferroelectric (FE)–paraelectric (PE) layered structure consisting of a ferroelectric medium (FE, layer 1) and a paraelectric medium (PE, layer 2). We use the Landau–Devonshire model description for the FE layer (see, for example, the classic text of Lines and Glass, 1977), in which the Landau free energy for a bulk FE of polarization P_F in an electric field E_F is written

$$F_F = \tfrac{1}{2}AP_F^2 + \tfrac{1}{4}BP_F^4 - E_F P_F \tag{3.1}$$

where the equilibrium conditions are

$$\frac{\partial F_F}{\partial P_F} = 0 \qquad \text{i.e. } E_F = AP_F + BP_F^3 \tag{3.2}$$

and

$$\frac{\partial F_F}{\partial E_F} = -P_F. \tag{3.3}$$

The parameter A varies with temperature as $A = A_0(T - T_0)$, with T_0 the bulk transition temperature, and $B > 0$.

It is convenient to use normalized fields e_F and p_F:

$$p_F = P_F/P_0 \qquad e_F = \varepsilon_0 E_F/P_0 \qquad \text{with } P_0 = \sqrt{A_0T_0/B}. \tag{3.4}$$

The equilibrium condition (3.2) becomes

$$p_F(t + p_F^2) = e_F\chi_0 \tag{3.5}$$

where $\chi_0 = (A_0T_0\varepsilon_0)^{-1}$ and $t = (T - T_0)/T_0$ is the reduced temperature. The normalized D-field is

$$d_F = D_F/P_0 = e_F + p_F \tag{3.6}$$

and the dielectric susceptibilities are

$$\chi_F = \frac{\partial P_F}{\varepsilon_0 \partial E_F} = \frac{\partial p_F}{\partial e_F} = \frac{\chi_o}{t + 3p_F^2} \qquad \varepsilon_F = \frac{\partial D_F}{\varepsilon_0 \partial E_F} = \frac{\partial d_F}{\partial e_F} = 1 + \chi_F. \tag{3.7}$$

For the PE layer, characterized by a linear polarization susceptibility

$$\chi_P = \frac{\partial P_P}{\varepsilon_0 \partial E_P} \tag{3.8}$$

the corresponding expressions are

$$e_P = \varepsilon_0 E_P/P_0 \qquad p_P = P_P/P_0 = e_p\chi_P \qquad \varepsilon_P = 1 + \chi_P. \tag{3.9}$$

In the FE/PE structure of figure 1, the charges on the top and bottom plates, Q_1 and $-Q_2$, can be written as

$$Q_1 = \sigma_F + Q \qquad Q_2 = \sigma_P + Q. \tag{3.10}$$

Here, Q is the charge provided by the external voltage source V_0, and σ_F and σ_P are defined so that Q can be taken as 0 when $V_0 = 0$. The fixed compensation charge between the layers is $\sigma_c = \sigma_P - \sigma_F$. The internal electric fields are given by

$$E_i = (D_i - P_i)/\varepsilon_0 = (\sigma_i + Q - P_i)/\varepsilon_0 \qquad (i = \text{F or P}) \tag{3.11}$$

where the contribution $-P_i/\varepsilon_0$ is the so-called depolarization field. In reduced units, with $q = Q/P_0$ and $s_i = \sigma_i/P_0$,

$$e_i = q + s_i - p_i. \tag{3.12}$$

The overall effective macroscopic field in the structure is

$$e_0 = \varepsilon_0 E_0/P_0 = f_F e_F + f_P e_P \tag{3.13}$$

where f_F and f_P are the fractions of the FE and PE layers ($f_F + f_P = 1$). In order that $q = 0$ in the overall equilibrium situation in which there is no applied voltage and the fields e_0, e_F and e_P are all zero, the offset charge densities s_F and s_P must be taken to be

$$s_F = p_0 \qquad s_P = 0 \tag{3.14}$$

where $p_0 = \sqrt{-t}$ is the solution of equation (3.5) for the equilibrium reduced polarization in zero applied field.

The fields may be found by integration of equations (2.10), but it is easier in this model simply to use e_F as the independent variable and find q and e_0 etc as functions of e_F.

4. Polarization reversal and hysteresis of the FE/PE structure

When the applied field E_0 is large enough in magnitude, polarization reversal from a negatively polarized to a positively polarized state, or vice versa, can take place. In order to describe this reversal, we must include in the model the possibility of domains in the Fe material. We assume that these domains are 'vertical' within the structure, i.e. that the domain walls are parallel to the fields. We also assume that there is no energy associated with a domain wall. To be sure, this assumption may not be appropriate, but domain wall energy does not play a fundamental part in the behaviour of the system and it is the aim of this paper to examine the basic questions and leave secondary complications aside. Under these conditions, the structure is split into two domains, in which the Fe moments are polarized down and up with polarizations p_+ and p_-, and where the volume fractions are $f_+ = f$ and $f_- = (1 - f)$ respectively. The revised FE/PE capacitor has the structure shown in figure 3, with a fixed volume fraction f_P of PE material (lower section) and fraction $f_F = (1 - f_P)$ of FE material (upper section). The top and bottom metal plates are at potentials V_0 and 0 respectively. In the $p_\pm$ domain, the reduced surface charge densities at the top plate, interface and bottom plates are $(q_\pm + s_\pm)$, $-s_\pm$ and $-q_\pm$ respectively (the overall charge on the structure is 0). Domain wall movement is simulated by allowing the fraction f to change. The crucial assumption is that, whilst the compensation charge at the interface is again incapable of moving vertically within the structure on the time-scale of the measurement, it is capable of lateral transfer between the two domains. Thus, as f changes, the total compensation charge density s_0 at the FE/PE interface, given by

$$s_0 = f s_+ + (1 - f) s_- \tag{4.1}$$

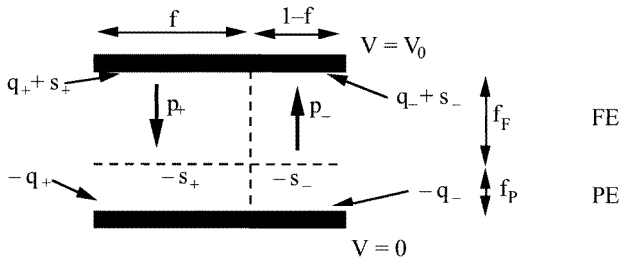

Figure 3. FE/PE capacitor structure containing oppositely polarized domains. The lower section comprises the PE, fraction f_P, and the upper the FE, fraction $f_F = 1 - f_P$. The left side is the positively polarized FE domain, polarization p_+, fraction f, and the right side the negatively polarized domain p_- fraction $1 - f$. The surface charge densities at the interface and on the upper and lower metal plates are as shown.

must remain constant (in the absence of conduction effects), though the individual compensation charges s_+ and s_- in the two domains will change with f, keeping s_0 fixed, in order to satisfy the boundary conditions on the fields.

The reduced fields in the four regions are:

$$\begin{array}{lll} \mathrm{FE}_+ & d_{F+} = q_+ + s_+ & e_F = q_+ + s_+ - p_+ \\ \mathrm{FE}_- & d_{F-} = q_- + s_- & e_F = q_- + s_- - p_- \\ \mathrm{PE}_+ & d_{P+} = q_+ & e_P = q_+/\chi_P \\ \mathrm{PE}_- & d_{P-} = q_- & e_P = q_-/\chi_P. \end{array} \tag{4.2}$$

However, the boundary conditions on the E-fields require that the E-fields are the same in the regions FE_+ and FE_- (e_F), and in the regions PE_+ and PE_- (e_P). Consequently, the charge densities q_+ and q_- in the two domains must be the same:

$$q = q_+ = q_-. \tag{4.3}$$

Furthermore, the difference $\delta s = s_+ - s_-$ is fixed by the polarization difference between the two domains:

$$\delta s = s_+ - s_- = p_+ - p_- \tag{4.4}$$

where p_+ and p_- are the positive and negative solutions of the equation (3.5) determining the polarization in the FE:

$$e_F = p_\pm(t + p_\pm^2)/\chi_0. \tag{4.5}$$

The important feature of equation (4.5) is the existence of a critical field

$$e_c = 2(-t/3)^{3/2} \tag{4.6}$$

such that, if $e_F > e_c$ there is no p_- solution, and if $e_F < -e_c$ there is no p_+ solution. Consequently,

$$f = 1 \text{ if } e_F > e_c \qquad \text{and} \qquad f = 0 \text{ if } e_F < -e_c.$$

We can now consider the behaviour of the system as it is taken around a hysteresis loop by varying the external field e_0 from negative to positive values and back again, with large enough swings to cause complete polarization reversal. It is actually more convenient to think of e_F as the independent variable from which the other quantities, primarily q and e_0, can be determined. The variation in volume fraction f of the FE_+ domain can be obtained by the following argument. Suppose e_F increases towards $+e_c$ for a given value of f;

when e_c is reached, the p_- solution becomes unstable, so e_F must remain at the value $+e_c$ whilst f increases. When f reaches the value $f = 1$ the system takes up a single p_+ domain, and e_F is now able to continue to increase above e_c. Similarly, when e_F decreases towards $-e_c$, at $e_F = -e_c$ f must decrease to 0 before e_F can go below $-e_c$. Thus, in this model, f changes only when the electric field in the FE region reaches its critical values $e_F = \pm e_c$. Whilst f changes, e_F remains constant, but s_+ and s_- change and so do the externally accessible quantities q and e_0. When $|e_F| > e_c$, the quantities p_+ and p_- lose their separate identities since the cubic equation (4.5) has only one solution, and the appropriate interface charge density becomes equal to s_0. In the model developed here, we assume that there is no movement of the domain boundary in the hysteresis loop whilst the field e_F in the switching layer is in the range $-e_c < e_F < +e_c$. This assumption is valid so long as the changes in the external voltage are fast on the time-scale of relaxation of the domain boundaries. Of course, if for example the external voltage is removed, the system may slowly relax to a state with no net polarization by movement of the domain walls, but we do not consider the problem of the dynamics of the slow time-scale response here.

Assuming the total interface charge s_0 is fixed, $s_\pm$ are given by

$$s_+ = s_0 + (1 - f)\delta s \qquad s_- = s_0 + f\delta s. \tag{4.7}$$

The charge q is found from

$$q = e_F - (s_\pm - p_\pm) = e_F - s_0 + p_+ f + p_-(1 - f). \tag{4.8}$$

The field in the PE layer is

$$e_P = q/\chi_P \tag{4.9}$$

and the overall applied field e_0 is

$$e_0 = f_F e_F + f_P e_P. \tag{4.10}$$

Numerical calculations (see below) are presented in terms of the renormalized overall field

$$e' = e_0\chi_0. \tag{4.11}$$

Finally, we discuss the initial interface charge s_0. Under conditions of long-term equilibrium with zero applied field e_0, we expect that there are no electric fields in the structure ($e_F = e_P = 0$). This can come about either if the domain fraction f slowly changes to a long-term equilibrium value f_0, but also if s_0 changes by vertical conduction of charge. If $e_F = 0$, the solutions of (4.5) are $p_\pm = \pm p_0$ with $p_0 = \sqrt{-t}$. The origin of q is arbitrary to the extent that the model depends only on the sum $(q + s_0)$, and we define q so that $q = 0$ when the internal fields are zero. Thus, from (4.8), the domain fraction f must have the value

$$f_0 = \frac{s_0 + p_0}{2p_0} \tag{4.12}$$

under the long-term equilibrium conditions. Since f_0 must lie in the range $0 \leqslant f_0 \leqslant 1$, s_0 must lie in the range

$$-p_0 < s_0 < p_0. \tag{4.13}$$

The symmetric situation, in which the sample can initially be found with equal proportions of positively and negatively polarized domains, corresponds to $f_0 = \frac{1}{2}$, for which $s_0 = 0$. If s_0 is non-zero, the hysteresis curves are asymmetric, which is sometimes found to be the case in practice. The calculations below use $s_0 = 0$.

In order to demonstrate typical results using this model, we use numerical values for the FE medium that are loosely appropriate in $BaTiO_3$. The important characteristic

parameter is the quantity χ_0, which we take as 450. In $BaTiO_3$, $P_0 \sim 0.1$ C m^{-2}; the corresponding switching field (at which polarization reversal takes place) is of order $E_c \sim P_0/\chi_0\varepsilon_0 \sim 200$ kV m^{-1}. For the PE medium, χ_P is constant.

Typical hysteresis behaviour is shown in figures 4 and 5. Figure 4 shows the hysteresis curve (plot of q against $e' = \chi_0 e_0$) for $t = -0.3$, $\chi_0 = 450$ and $s_0 = 0$ when there is only an FE layer ($f_P = 0$). The upper and lower solid curves correspond to the solutions p_+ ($f = 1$) and p_- ($f = 0$) respectively, and the vertical dashed lines show the transitions between $f = 1$ and $f = 0$ at $e_0 = e_F = \pm e_c$ (the left-hand dashed line is obtained with e_0 decreasing, and the right hand with e_0 increasing, as shown by the arrows).

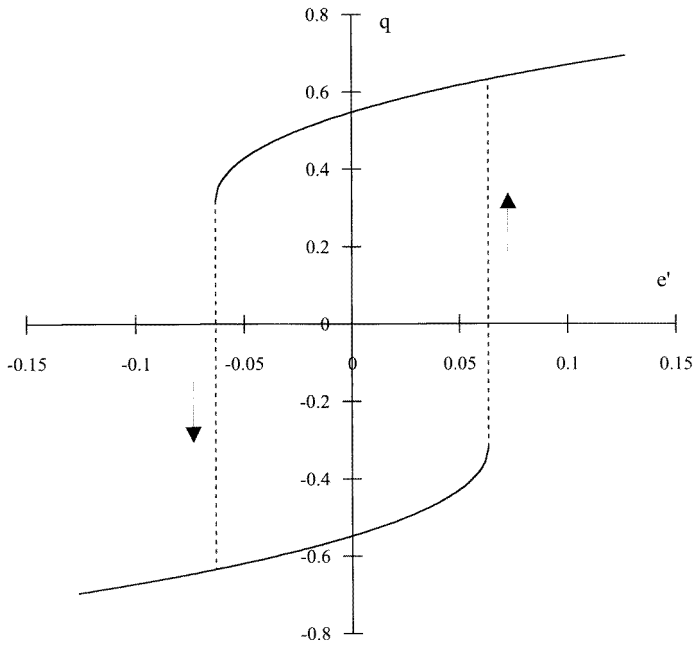

Figure 4. Hysteresis curves (normalized charge q against applied field $e' = e_0\chi_0$) for an FE capacitor, with $t = -0.3$, $\chi_0 = 450$, $s_0 = 0$. The dashed curves indicate the transition regions ($e = \pm e_c$) from $f = 1$ (upper full curve) to $f = 0$ (lower full curve).

Figure 5 shows the hysteresis diagram for a finite fraction $f_P = 10\%$ of PE material (with $\chi_P = 200$). Note here the important feature that the polarization reversal regions in which f changes (dashed lines) do not occur at constant e_0, despite the fact that e_F is constant here ($e_F = \pm e_c$): because q changes during polarization reversal the field e_P in the PE region changes, so e_0 must change. Hence, the polarization reversal does not produce vertical lines on the hysteresis diagram. The type of curve in figure 5 is entirely typical of measured hysteresis curves in nano-structured ferroelectrics (see for example the measurements of Miller *et al* 1990 and Zurcher *et al* 1995), and is indeed also more typical of single layer ferroelectrics without a specifically designed PE layer than is figure 4. This provides support to the accepted notion (reviewed by Tilley 1993) that ferroelectrics often develop a non-switching dielectric layer near one or both of the electrodes, and we consider this case in the following section.

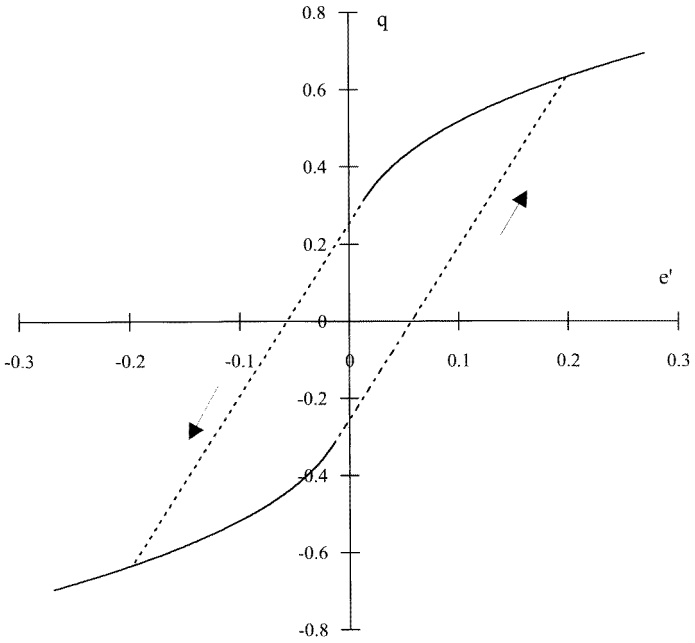

Figure 5. Hysteresis curve for an FE/PE capacitor, with $f_P = 0.1$ and $\chi_P = 200$. Other parameters as in figure 4.

5. Model for FE capacitor with non-switching layers

In practice, most thin-film FE capacitors consist of a single FE layer without a PE layer. Nonetheless, they show hysteresis curves characteristic of structures with a PE layer, like figures 4 and 5. It is therefore concluded that they contain non-switching FE layers. We here develop a model that incorporates such layers. The basic structure is shown in figure 6, in which the layers U and L, adjacent to the upper and lower plates, are assumed to be non-switching, with polarizations respectively positive and negative. The charges on top and bottom plates are $(q + p_0)$ and $(-q + p_0)$ respectively; this ensures that the fields e_U and e_L in the upper and lower layers can be zero when $q = 0$, with polarizations $p_U = p_0$ and $p_L = -p_0$. The total charges on the two intermediate interfaces are $(s_0 - p_0)$ at the U/FE interface, and $(-s_0 - p_0)$ at the FE/L interface (with overall zero charge on the structure). The relative fractions of U, FE and L regions are f_U, $(1 - f_U - f_L)$ and f_L respectively. The central FE layer is again divided into two domains FE_+ and FE_-, with f as the fraction of FE_+ domain. The normalized fields in each region are:

$$\begin{array}{lll} \mathrm{U} & d_U = q + p_0 & e_U = q + p_0 - p_U \\ \mathrm{F}_+ & d_+ = q + s_+ & e_F = q + s_+ - p_+ \\ \mathrm{F}_- & d_- = q + s_- & e_F = q + s_- - p_- \\ \mathrm{L} & d_L = q - p_0 & e_L = q - p_0 - p_L. \end{array} \tag{5.1}$$

The polarizations satisfy the equation

$$p_i(t + p_i^2) = \chi_0 e_i \qquad \text{for } i = \mathrm{U}, \mathrm{F}_\pm \text{ or } \mathrm{L}. \tag{5.2}$$

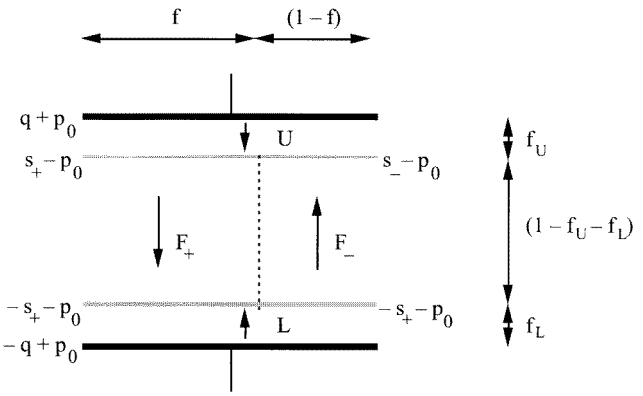

Figure 6. FE capacitor structure with non-switching Fe layers U and L. f_U and f_L are the fractions of the non-switching layers, and f the fraction of the FE_+ domain within the switching FE layer. The charge densities at the interfaces and on the capacitor plates are as shown.

As in section 4, we take the field e_F in the FE layer as the independent variable, so $p_\pm$ satisfies

$$p_\pm(t + p_\pm^2) = \chi_0 e_F \tag{5.3}$$

where the subscript $\pm$ indicates whether the upper or lower solution is to be used (the third, intermediate, solution of the cubic equation is unstable). q is found from (4.8) as

$$q = e_F - (s_\pm - p_\pm) = e_F - s_0 + p_+ f + p_-(1 - f) \tag{5.4}$$

with $s_\pm$ given by (4.7). This enables the polarizations in the U and L regions to be found as the solutions of

$$\begin{aligned} p_U(t + \chi_0 + p_U^2) &= \chi_0(q + p_0) \\ p_L(t + \chi_0 + p_L^2) &= \chi_0(q - p_0) \end{aligned} \tag{5.5}$$

with $p_U > 0$ and $p_L < 0$, and $p_0 = \sqrt{-t}$. The overall field is

$$e' = \chi_0 e_0 = \chi_0[f_U e_U + (1 - f_L - f_U)e_F + f_L e_L]. \tag{5.6}$$

Under the long-term equilibrium conditions, when all fields e and the charge q are zero, the polarizations are

$$p_U = p_+ = p_0 \qquad p_L = p_- = -p_0. \tag{5.7}$$

The field e_L in the upper layer need never exceed the critical field e_c, so this layer is never forced into a polarization reversal. As e_0 increases, e_L reaches a limit just below e_c, and the remainder of e_0 is taken up by the other two layers. Similarly, e_F is restricted to $e_F > -e_c$. As with the FE/PE structure, polarization reversal is accomplished by movement of the domain wall in the switching $FE_\pm$ layer.

Figure 7 shows the hysteresis curve for $s_0 = 0$, $\chi_0 = 450$, $t = -0.3$, $f_U = f_L = 5\%$. Note the similarity with figure 4 for the FE/PE capacitor, though the regions in which f changes are less linear than in figure 4. Figure 8 shows the same structure, but with the initial charge $s_0 = 0.2$. This produces an asymmetry in the hysteresis, of the type that is often observed experimentally. Whilst the change is mainly one of shifting the whole loop down the q-axis by 0.2, there are also changes to the shape of the loop near its extremities. Asymmetry can also arise if $f_U \neq f_L$.

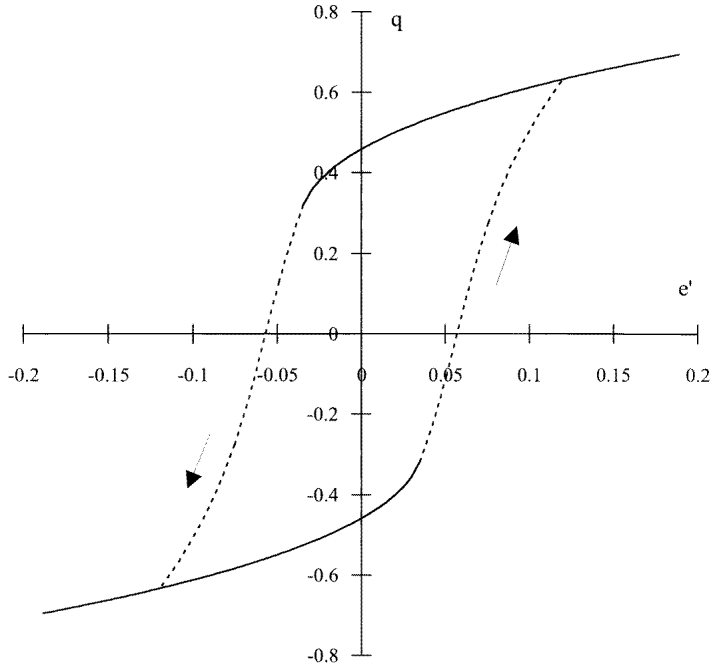

Figure 7. Hysteresis curve for FE capacitor with non-switching layers of fractions $f_U = f_L = 5\%$. $\chi_0 = 450$, $s_0 = 0$, $t = -0.3$. The dashed sections are the regions in which the domain fraction f changes from 0 to 1.

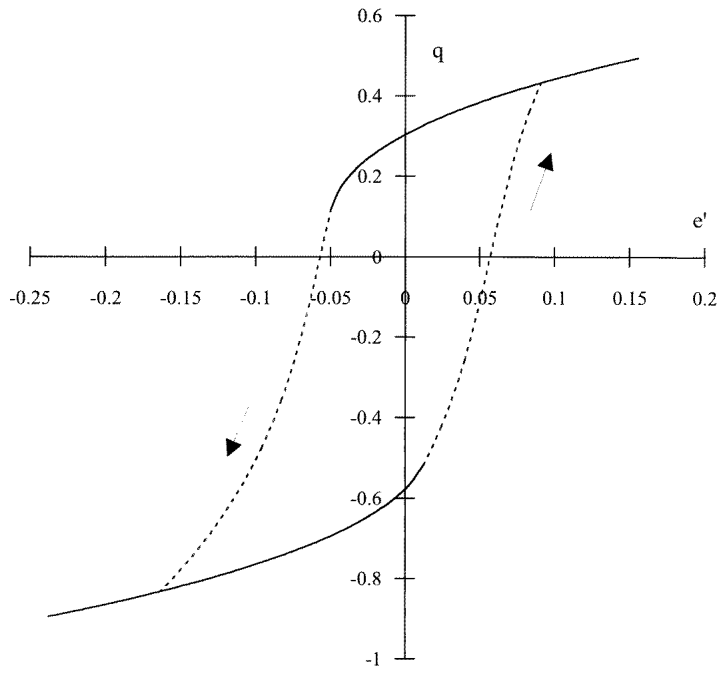

Figure 8. Hysteresis curve for FE capacitor with non-switching layers. Parameters as for figure 7, except that $s_0 = 0.2$.

6. Discussion

We have developed a simple model that explains the basic form of the observed hysteresis curves for a ferroelectric/paraelectric (FE/PE) capacitor structure, and for an FE structure that includes non-switching FE layers. The model simply satisfies the electrostatic boundary conditions, assuming that a layer of compensation charge exists at the interfaces between the layers. Polarization reversal takes place through the movement of domain walls separating reversal-phase domains in the switching FE layer. In this model, no energy is associated with the domain walls: we merely assume that the walls move once the field in one or other domain reaches the critical value for polarization reversal, so that overall polarization switching of the structure is effected by domain wall movement. This leads to hysteresis curves (e.g. figures 5, 7 and 8) that are characteristic of experimentally measured curves. Of course, the energy associated with domain wall movement is likely to be non-negligible in real systems, but we would argue that this is a secondary feature of the polarization reversal process. Although in our model we have included only one type of each domain, the arguments and the numerical results are unaltered if the sample is split up into many domains.

The existence of compensation charge at the interfaces is a central feature of the model, as is the assumption that this charge is unable to move across the layers on the time-scale of a typical measurement, though the charge distribution at the interface must be able to move from one domain to another within the interface. Without this compensation charge, the depolarizing fields are so strong that ferroelectric alignment normal to the plane of the FE layer structure would not be possible. We have not associated any energy (other than electrostatic energy) with the compensation charge, nor have we assumed a finite thickness for the charged region; as with the domain wall energy, we expect that such effects will be secondary refinements to the main effects that we have discussed. We also remark that although we have only considered one layer each of the various FE and PE regions, the arguments we have presented are not affected if there are multiple regions: all that matters is the relative fractions of the various constituents. Although the non-switching layers U and L have been shown adjacent to the electrodes, the results are not dependent on the relative placing of the layers.

It is well established that non-switching FE layers exist in thin FE structures, and we have shown that such layers imply hysteresis curves that are of the form measured experimentally. Whilst the details of the mechanism by which these are formed are beyond the scope of this paper, it is worth remarking that the lateral electric fields which cause the motion of the domains walls will be much greater in the absence of non-switching layers than in their presence, as can be seen by the abrupt changes in q in figure 4 (no non-switching layers) as compared to figures 7 and 8. It is likely that such large fields can cause electrical breakdown, which establishes the compensation charge layers at the interfaces and stabilizes the U and L non-switching regions. Once the compensation charges have been formed, probably during initial electrical cycling of the structure, later changes in the charge distributions are much less dramatic. Nonetheless, slow degradation of the hysteresis loop with cycling occurs in many thin-film ferroelectric structures; in our model, this must be associated with the increase in the fractions f_U and f_L of the non-switching regions by vertical motion of the interfaces. Indeed, when $f_U + f_L = 1$ there is no switching region left, and so the structure ceases to be usable as a ferroelectric memory device; note that this does not imply that the material is no longer ferroelectric—the compensation charges merely prevent switching of the polarization.

Finally, it is worth remarking on the analogy between ferromagnets and ferroelectrics. Hysteresis curves have been studied and understood in ferromagnets for many years, and

there is a temptation to assume that hysteresis curves in ferroelectrics can be understood on the same basis. This assumption should be treated with caution for two reasons. First, the molecular field parameter λ which measures the relative influences of the local coupling and the demagnetizing order polarising fields is vastly different in the two cases. In the usual mean field formulation of ferromagnetism, the total field B at a site is written as the sum of an external field B_{ext} and an internal molecular field $B_{int} = \lambda M$, where M is the magnetization in the sample. If $\chi^{(0)} = \partial M/\partial B_{ext}$ is the susceptibility in the absence of the molecular field, then the renormalized total susceptibility is

$$\chi = \frac{\partial M}{\partial B_{ext}} = \frac{\chi^{(0)}}{1 - \lambda\chi^{(0)}}. \tag{6.1}$$

In the high-T phase the uncoupled susceptibility $\chi^{(0)}$ normally has the Curie-law form $\chi^{(0)} \sim C/T$, where C is the Curie constant, and so χ can be written as

$$\chi = \frac{\chi_0}{t} \qquad \text{with } \chi_0 \sim \lambda^{-1}. \tag{6.2}$$

Here t is the reduced temperature $t = (T - T_C)/T_C$ and $T_C = C\lambda$ is the Curie temperature. Demagnetizing effects due to sample shape and configuration give a contribution to the internal field $\Delta B_{int} \approx \alpha M$, with $\alpha \sim 1$. Typically, $\lambda \sim 5000$ or more in ferromagnets, and since $\alpha \ll \lambda$ the internal molecular field dominates over the demagnetizing effects. The situation is completely different in a ferroelectric. In our model ferroelectric we have used a susceptibility in the form $\chi = \partial p/\partial e = \chi_0/t$ (see equation (3.5)) with $\chi_0 = 450$, so the molecular field parameter is $\lambda = \chi_0^{-1} \sim 2 \times 10^{-3}$. Depolarizing effects produce internal fields $\Delta e_{int} \approx \alpha p$ with $\alpha \sim 1$ as for the demagnetizing effects. However, since λ is more than six orders of magnitude less in a ferroelectric than in a ferromagnet, depolarization effects play a much more important part in the former and must be included explicitly in working out the response of a ferroelectric structure, as we have done here. The second crucial distinction between ferroelectrics and ferromagnets is that free charge exists in ferroelectrics, but has no analogue in a ferromagnet. This free charge—what we have called 'compensation charge'—nullifies to a large extent the depolarizing fields and thereby permits the existence of ferroelectricity which would otherwise be inhibited by depolarization effects in layered structures. However, only in the simplest of structures—a single layer FE with metal electrodes whose hysteresis loop is demonstrated in figure 4—are the depolarization effects precisely compensated to the extent that they can be completely ignored. Otherwise, as this paper has shown, the interplay between compensation charges and depolarization effects is crucial in determining the precise form of the hysteresis curves in a layered ferroelectric structure. The detailed effects then observed have no genuine analogues in ferromagnetic structures.

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