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Thermal activation of ferroelectric switching

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By applying the theory of thermally activated nucleation to the switching of ferroelectric domains, a method is developed to experimentally obtain the value of both the activation enthalpy, $\Delta H$, and activation volume, $V^*$, for the thermally activated process involved in ferroelectric switching. The method was applied to the switching of a soft lead zirconate titanate and values of $\Delta H = (0.16 \pm 0.02)$ eV and $V^* = (1.62 \pm 0.16) \times 10^{-25}$ m$^3$ were obtained at the coercive field. These values imply that the energy, $\Delta U$, required for the formation of switching nuclei is mainly supplied by the work done by the electric field. A comparison of these values with those obtained from theoretical considerations suggests that the switching is achieved by the sideways expansion of nuclei formed at the domain boundaries in the form of low amplitude and long wavelength fluctuations of the domain walls. © 2008 American Institute of Physics. [DOI: 10.1063/1.2822179]

I. INTRODUCTION

The switching of domains in ferroelectric materials by an applied electric field and/or mechanical stress is believed to occur by the formation of new domain nuclei with favored orientation of polarization, which subsequently expand and grow at the expense of the existing domains. The sites where the nucleation of the new domains occurs has been a matter of some speculation, but there is a general consensus that imperfections of some kind, probably domain walls, are the preferred sites.1–10

Earlier calculations indicated that the formation of spike shaped nuclei with reverse polarization would require an implausibly large activation energy (of the order of $10^8$ K T).6 so that even if these nuclei were able to expand with the help of thermal fluctuations, the critical field or stress needed to produce switching would be extremely high; much higher than is experimentally observed in many ferroelectric materials. In order to overcome this difficulty and help to explain how nuclei of reversed polarization can come into existence, some effects that could decrease the nucleation energy have been invoked by other researchers, among these: crystal inhomogeneities, weak spots, lattice defects, surface layer, and small residual nuclei.6,7 Other authors8–10 have considered the effects of multielectron fluctuations, which can be regarded as depolarization nuclei, but concluded that not even these can explain the Landauer paradox unless the contribution of the depolarizing field in the nucleation process is suppressed. It is, however, possible, to obtain much lower, and reasonable, values of for the nucleation energy of nuclei of suitable shape formed as steps on existing domain walls if the elastic misfit energy is ignored.9–11

Other studies12,13 based on a modification of the Avrami equation,14 have attempted to calculate the volume fraction of domains switched by a constant electric field of short duration as a function of time. The classical Avrami approach deals with the calculation of the volume fraction transformed as a function of time in phase transformations driven by the difference in the free energies of the original and new phases. In the ferroelectric switching studies the dependence of the switching rate, $j$, on the applied field, $E$, is introduced through the empirical Merz equation, $j \propto \exp(-\alpha/E)^{12,13}$ where $\alpha$ is a temperature dependent material parameter.

Micromechanical modeling has also been used to calculate, by numerical methods, both the polarization and strain changes produced by electric fields and mechanical stresses and to reproduce the shape of both the polarization-electric field, $(P-E)$, and longitudinal strain-electric field butterfly, $(\varepsilon-E)$, hysteresis loops.15,16 In these models the switching is opposed by finite energy barriers capable of being overcome by the applied fields when the reduction in the potential energy of the body equals the size of the energy barrier, i.e., in thermodynamic terms, when the change in the internal energy, $\Delta U$, of the body is equal to the work done, $W$, on the body by the external constraints; that is, when the change in enthalpy, $\Delta H = \Delta U - W$, is zero. These constitutive models have also been modified by some authors to account for the effects of temperature on the coercive field of lead zirconate titanate (PZT) ferroelectrics.17

There is evidence for the existence of rate and temperature dependent processes, often referred to as relaxation processes, in the switching of some ferroelectrics, and it seems justified to consider the polarization switching in these materials as a thermally activated process. The switching of domains that produces a change in shape as well as a change in polarization can be driven by a mechanical stress as well as by an electric field, so that the rate of change of strain and the rate of change of polarization must be manifestations of the same atomic and structural processes producing the switching. It is therefore appropriate to apply the theory of reaction rates to the ferroelectric switching, following the method developed for the thermally activated plastic deformation of crystalline materials by the movement of dislocations.18,19 It is shown that with this approach it is possible to gain an insight into the atomic and structural mecha-
nisms involved in ferroelectric switching. This is illustrated by the analysis of experimental \( P-E \) and \( e-E \) data for a ferroelectric ceramic (PZT-5H).

II. THEORETICAL FORMULATION

It is proposed that the critical step in domain switching is the formation, with the help of thermal fluctuations, of nuclei of critical size with a favored orientation of polarization, which can subsequently expand with little or no resistance under an electric field, \( E \), or shear stress, \( \tau \). In this process the switching rate is, therefore, controlled by the rate of formation of the critical nuclei, and not by the rate of expansion of the nuclei, even if this is opposed by a viscous drag resistance. Although for the formulation of the problem there is no need to specify \textit{a priori} the nature and configuration of the nuclei nor their nucleation sites, we shall justify the view, shared by other researchers, that domain walls are the preferred sites for their nucleation.1–13 To support this view, we note that domain boundaries in ferroelectrics, which have noncentrosymmetric crystal structure, cannot be coherent planes. Instead they have to be a region of finite thickness, where the atomic displacements, adding up to a crystallographic twin stacking fault, are spread over several parallel atomic planes. (A reflection stacking fault for head to head, or tail to tail, non-180° domains and a rotation stacking fault for head to tail and 180° domains.) The width of domain walls has been reported as being in the range of 1–10 nm.1–6,9,10 The atomic offsets and misalignments that generate the diffuse and distorted structure of these domain boundaries have been confirmed both by transmission electron microscopy investigations20–22 and \textit{ab initio} calculations.23 It has been suggested that this structure makes the domain walls highly mobile and, by implication, favorable sites for the formation of steps and domain nucleation.20

The switching of non-180° domains produces a change in shape at constant volume that can be induced by both an electric field and/or mechanical stress. If diffusion and phase changes are excluded, the only atomic mechanism available to produce such a deformation in a crystal is the movement of dislocations. Accordingly, we can model the formation of a “critical nucleus” as the nucleation of a group or stack of \( n \) dislocations loops of Burgers vector \( \mathbf{b} \), which can expand on parallel glide planes along the domain wall. If, after nucleation, each loop sweeps an area \( A_{\mathbf{b}} \) in a body of volume \( V \), the resulting shear strain, in the glide plane, in the direction of \( \mathbf{b} \) is \( \gamma = n|\mathbf{b}|(A_{\mathbf{b}}/V) \). If the number of nucleation sites per unit volume is \( \rho \), the macroscopic plastic shear strain experienced by the body in the direction of \( \mathbf{b} \), on the glide plane, is \( \gamma = \rho A_{\mathbf{b}} n|\mathbf{b}| \).

The associated change in polarization, \( dP_{\pi} \), produced by the same switching along an arbitrary direction, defined by the unit vector \( \vec{\pi} \), is related to the magnitude of the volume switched, \( V_{\pi} \), spontaneous polarization, \( P_0 \), and the angle between \( P_0 \) and \( \vec{\pi} \) before and after the switching, and is given by

\[
dP_{\pi} = \rho V_{\pi} \delta[\vec{\pi} \cdot P_0] .
\]

If all of the domains in the material have the same orientation, as in an ideally poled sample, the earlier expressions give the macroscopic changes in strain and polarization of the body. However, if there is a random distribution of orientations of the switching domains, the macroscopic strain and polarization of the body can only be obtained by an averaging of the strain and polarization over all of the orientations.

If \( \Gamma \) is the rate of formation of nuclei, the strain rate produced by the switching (nucleation and expansion of the nuclei) can be written as

\[
\dot{\gamma} = \frac{d\gamma}{dt} = \rho A_{\mathbf{b}} n|\mathbf{b}| \Gamma .
\]

And the corresponding rate of change in polarization is

\[
\dot{\pi} = \frac{dP_{\pi}}{dt} = \rho V_{\pi} \delta[\vec{\pi} \cdot P_0] \Gamma .
\]

The same expressions (1) and (2) would be obtained if the changes in polarization and strain were induced by the action of an applied electric field or mechanical stress.

Following the classical theory of nucleation by random fluctuations, the nucleation rate \( \Gamma \) is given by the Arrhenius type expression

\[
\Gamma = v \exp(-\Delta G/kT) = v \exp(\Delta S/k) \exp(-\Delta H/kT) = n_0 \exp(-\Delta U - W^*). \quad (3)
\]

The usual symbols have been used for the thermodynamic potentials that satisfy the relations

\[
\Delta G = \Delta F - W^* = \Delta H - T\Delta S = \Delta U - T\Delta S - W^* , \quad (4)
\]

where \( F, H, U \), and \( W^* \) are Gibbs and Helmholtz free energies, enthalpy, and internal free energy of activation respectively. \( W^* \) is the work done by both the electric field, \( E \), and/or the shear stress, \( \tau \), acting at the nucleation site, usually referred to as the effective field and effective stress. The frequency, \( v \), is related to the correlated fluctuations of the group of atoms involved in the formation of the nucleus. For simplicity, the entropy, \( S \), is included in the pre-exponential term, \( n_0 \). Its value is difficult to calculate even for the case of a single dislocation and high impossible for a dislocation group.24,25 For a small electric field or mechanical stress at high temperatures, the rate of activation of nuclei in the reverse direction (against \( E \) and \( \tau \)) would not be negligible but here we shall deal with conditions where only the activation in the forward direction needs to be considered. Hence, only one exponential term appears in the rate Eq. (3).

The work term for the nucleation of the critical nuclei, \( W^* \), is the sum of an electrical, \( W_e^* \), and a mechanical, \( W_m^* \), term

\[
W^*(T) = W_{e^*} + W_m^* = \delta|E \cdot P_0|V^* + \pi|b|A^* ,
\]

where \( V^* \) is the volume of the activated nucleus, which can be properly called an activation volume. \( \pi \) is the effective shear stress resolved on the glide plane of the dislocations and in the direction of their Burgers vector, and \( A^* \) is the activation area swept by each one of the \( n \) dislocations involved in the formation of the nucleus. A more rigorous ex-
pression for the mechanical work term would be the summation $\Sigma_i \tau_i |b_i| A_i$ if the nucleus were composed of a group of dislocations with different Burgers vectors, but this can always be averaged to the simplified expression used in the earlier equations.

If there are $n$ dislocations participating in the formation of the nucleus and the separation between their glide planes is $d$, the relation between $V^*$ and $A^*$ is given by $ndA^*=V^*$.

The polarization rate, in the direction of $E$, can be finally written as

$$j_E = \frac{dPE}{dt} = \rho V_s \delta [E \cdot P_0] \nu \exp \left( -\frac{\Delta G}{kT} \right) = j_0 \exp \left( -\frac{\Delta H}{kT} \right).$$

(6)

And the shear strain rate is given by

$$\dot{\gamma} = \frac{d\gamma}{dt} = \rho A_m |b| \nu \exp \left( -\frac{\Delta G}{kT} \right) = \dot{\gamma}_0 \exp \left( -\frac{\Delta H}{kT} \right).$$

(7)

Both the electric field, $E$, and the stress, $\tau$, in the earlier equations are the effective electric field and stress acting at the nucleation site. If there are structure dependent internal electric and stress fields in the material, the effective field is the difference between the applied and the internal fields.

The pre-exponential terms in the rate Eqs. (6) and (7) are complex structural factors. They depend on the orientation of the switching domains, on the volume density of nucleation sites, and entropy factor, and it is practically impossible to estimate them. Fortunately, without knowing them, it is still possible to use the rate equations to obtain experimentally the activation parameters, $\Delta H$ and $V^*$.

III. RELATIONSHIPS BETWEEN THE ACTIVATION PARAMETERS

If the energy barrier for nucleation is independent of both $E$ and $\tau$, the following relations are obtained by partial differentiation of Eqs. (4) and (5):

$$\frac{\partial G}{\partial E}_{\tau,\tau} = -\delta [E \cdot P_0] V^*,$$

(8)

$$\frac{\partial G}{\partial \tau}_{\tau,E} = -n|b| A^*. $$

Partial differentiation of Eq. (6) when the shear stress $\tau$ is constant gives

$$\left[ \frac{\partial E}{\partial \ln(j/j_0)} \right]_{E,\tau} = kT \delta [E \cdot P_0] V^*, $$

(9)

and

$$\Delta H = \left[ \frac{\partial \ln(j/j_0)}{\partial(-1/kT)} \right]_{E,\tau}. $$

(10)

Using the relation

$$\left[ \frac{\partial \ln(j/j_0)}{\partial T} \right]_{E,\tau} \left[ \frac{\partial T}{\partial \ln(j/j_0)} \right]_{T,\tau} = -1, $$

(11)

$$\Delta H = V^* \delta [E \cdot P_0] T \left[ \frac{\partial E}{\partial T} \right]_{\tau,j_0}. $$

(12)

Similar relationships are obtained from partial differentiation with respect to the shear strain $\gamma$, when $E$ is constant

$$\left[ \frac{\partial \tau}{\partial \ln(\gamma/\gamma_0)} \right]_{E,T} = kT \frac{\partial E}{\partial \ln(\gamma/\gamma_0)} T \left[ \frac{\partial \gamma}{\partial T} \right]_{\gamma,j_0}. $$

(13)

These relations will be used to obtain, experimentally, values for the activation parameters that characterize the energy barrier and the nucleation mechanism controlling the rate of polarization and strain switching. It is important to note that the partial derivatives assume a constant value of the pre-exponential structural factor.

The activation volume, $V^*$, was obtained experimentally by measuring the change in the electric field when the rate of polarization was changed and using Eq. (9). The activation enthalpy was obtained from the measurement of changes in the rate of polarization at constant electric field when the temperature was changed, Eq. (10), or from the changes in electric field needed to keep the polarization rate constant when the temperature was changed, Eq. (11).

IV. EXPERIMENTAL DETAILS AND MATERIALS

The material chosen for the study was a “soft” PZT-5H provided by Morgan Matroc Transducer Division, Southampton, UK. It has a morphotropic phase boundary composition (Zr/Ti=52/48) and x-ray diffraction (XRD) analysis revealed the predominance of tetragonal phase with the coexistence of some rhombohedral phase. Due to commercial confidentiality, the dopants used to soften the material are not known. This material was chosen because it exhibits a very consistent and reproducible poling behavior, producing very stable hysteresis loops that are recoverable after repeated poling and depoling so that any set of experiments could be carried out using the same specimens. All of the specimens used came from the same batch of material. They were disk shaped with a diameter of 10 mm and thickness of 1 mm. Platinum electrodes were fired on at 900 °C.

The lattice parameters of the tetragonal unit cell in PZT-5H where obtained from XRD and they are $a_0=b_0=0.4051$ nm and $c_0=0.4086$ nm. The relative dielectric permittivity for unpoled material is 1827, the Young’s modulus is 200 GPa, provided by Morgan Matroc Transducer Division, and the saturated polarization, $P_s$, from the saturated $P-E$ loops and multiplying it by the geometric factor, 1/0.83 (we used
that relevant for tetragonal structure), required to account for the fact that $P_s$ in a polycrystalline ceramic is not equal to $P_0$ in a single crystal.\textsuperscript{27}

The $P$-$E$ and $e$-$E$ (longitudinal strain-electric field) hysteresis loops were obtained using a combined polarization-displacement-electric field system. The electric field was applied at a constant rate using a triangular wave function at frequencies between 0.1 and 2.0 Hz. The sample was placed in a silicon oil bath container in which the temperature could be varied between $-10$ and $220$ °C, but the investigation was limited to the temperature range $-10$ to $30$ °C. Above $30$ °C the structure of the material changed, as evidenced by a change in the shape of the $P$-$E$ loops and a decrease in both the saturation polarization and the coercive field (Fig. 1). In order to make sure that the internal structure remained stable during the experiments and did not change during testing at different frequencies and temperatures, the following procedure was carried out: after testing the specimen at a given frequency and temperature, a $P$-$E$ loop was repeated at a reference frequency of 1 Hz and temperature of 300 K to verify that exactly the same loop was recovered after each test.

The analysis and reliability of the results would have been simplified and improved if the $P$-$E$ hysteresis curves were obtained by controlling the current density instead of the field and using this as the independent variable. However, we did not have the necessary equipment to do this. The procedure followed is acceptable since it has been shown that changing the controlling variable has no great effect on the shape of the hysteresis loops.\textsuperscript{28}

\section*{V. EXPERIMENTAL RESULTS}

Typical $j$-$E$, $P$-$E$, and $e$-$E$ hysteresis loops at different frequencies at a temperature of 300 K are shown in Fig. 2. It can be seen in Fig. 2(c) that the strain rate is a maximum and changes its sign at the coercive field, $E_c$. Furthermore, the ratio, $e/e',$ between the measured longitudinal strain rate and the rate of change of polarization, is $3/4$ of the ratio, $[(c_0-a_0)/a_0]/P_0$ between the unit cell shear strain and spontaneous polarization for the tetragonal structure. From this it can be inferred that at the coercive field most of the switching is provided by the rotation of non-180° domains from an orientation orthogonal to parallel to the applied field and that the measured longitudinal strain, $e$, is nearly equal to the shear strain, $\gamma$. This conclusion is valid regardless of the
possible presence of some rhombohedral structure because all the twinning shears possible in these structure average to nearly 90°.

The activation volume and activation enthalpy were calculated at zero polarization (coercive field). This is the point in the $P$-$E$ loop corresponding to the fastest switching rate at all the testing temperatures and frequencies. This choice ensures that all the measurements were made with the same internal structure. From $P$-$E$ loops of the types shown in Figs. 1 and 2, the plots of Figs. 3–5 were obtained. From these the activation volume and activation enthalpy were calculated using Eqs. (9)–(11), with the assumption that both the internal energy, $\Delta U$, and the entropy, $\Delta S$, were temperature independent. The current density in Figs. 3 and 4 was corrected for the temperature dependence of $P_0$ in the pre-exponential term. Additionally, values of the activation volume obtained at various points along the $P$-$E$ loop for different values of $P$ are shown in Fig. 6. $V^\ast$ has a nearly constant value of $(1.62\pm0.16) \times 10^{-23}$ m$^3$ at and around $P = 0$ and it increases rapidly on approaching saturation. This could be due to both rapid structural changes and the development of internal fields and internal stresses on approaching saturation.

The activation enthalpy, $\Delta H$, measured at around $P = 0$ is obtained from the linear plots in Figs. 4 and 5, using Eqs. (10) and (11), respectively. Both procedures yield practically the same value, $\Delta H = 2.61 \pm 0.39 \times 10^{-20}$ J = $(0.16 \pm 0.02)$ eV and $\Delta H = 2.48 \pm 0.37 \times 10^{-20}$ J = $(0.16 \pm 0.02)$ eV, respectively; having been obtained by two different procedures, this agreement gives confidence to the assumed constancy of the pre-exponential factor during the imposed changes. The sum

$$\Delta U = \Delta H + \delta_0 E \cdot P_0 V^\ast = (0.16 + 0.32) \text{ eV} = 0.48 \text{ eV}$$

is the experimental value for the internal energy of activation measured at 300 K at an applied field of 1.0 MV/m.

VI. INTERPRETATION OF THE EXPERIMENTAL RESULTS

The activation volume obtained from the experiments is very large as it corresponds to a volume of 2416 tetragonal unit cells. Its value is similar to that obtained by other researchers from mechanical stress relaxation experiments performed on poled PZT of the same or similar composition.26,29 This, together with the low value of the activation enthalpy at 300 K implies that the thermal contribution to the nucleation process is relatively small and that most of the activation energy is supplied by the work done by the electric field.

Further insight into the switching mechanism and the shape of the nuclei can be gained by comparing the value of $\Delta U$ obtained experimentally with that calculated for the energy of formation of a nucleus of size $V^\ast$. The energy increase arising from the formation of the nucleus at 0 K is the sum of the depolarizing energy, $\Delta U_{\text{dep}}$, the misfit strain energy, $\Delta U_{\text{str}}$, due to the shape change of the nucleus and the domain wall energy, $\Delta U_{\text{wall}}$ due to the incoherent boundary formed at the edge of the nucleus, i.e.,
\[ \Delta U = \Delta U_{\text{dep}} + \Delta U_{\text{el}} + \Delta U_{\text{dw}}. \]

Both the depolarizing energy and elastic strain energies are strongly dependent on the shape of the nucleus. In the calculation we use the available solutions for an ellipsoidal inclusion that undergoes both a uniform change in polarization and strain while embedded in a nontransforming matrix.\(^{30,31}\) We assume that the nucleus is formed at a domain wall as a flat protuberance, with a large base, modelled as a flat ellipsoid spread over the wall, with semiaxes, \(a = b > c\). The depolarizing energy is given by\(^{30}\)

\[ \Delta U_{\text{dep}} = \frac{1}{2} \frac{L}{4\pi} P_0^2 \cos \theta V^*, \]

where \(V^*\) is the volume of the nucleus, \(e = \varepsilon_r \varepsilon_0\), is the dielectric permittivity of an isotropic material, \(\theta = 45^\circ\), is the angle between the depolarizing field and the applied field for switching from orthogonal to parallel to the applied field, and \(L/4\pi\) is a factor dependent on the aspect ratio of the spheroid.\(^{32}\) The earlier equation assumes that matrix and inclusion have the same intrinsic polarization, \(P_0\), and the dielectric permittivity.

Similarly, for an ellipsoidal nucleus, with the same elastic constants as the matrix, the misfit strain energy is given by\(^\text{31}\)

\[ \Delta U_{\text{el}} = 2 \eta \mu \gamma^2 V^*, \]

where \(\gamma = 8.64 \times 10^{-3}\) is the twinning shear strain, \(\mu = 50\) GPa is the shear modulus and \(\eta\) is a shape dependent accommodation parameter given by

\[ \eta = \frac{\pi(2 - v) c}{4(1 - v) a}, \]

where \(v = 1/3\) is Poisson’s ratio.

It is apparent that in order to obtain an energy, \(\Delta U\), in agreement with the experimental values, the nucleus has to be a very thin protuberance with a very large base. For example, if \(c/a = 0.1\), then \(L/4\pi = 0.07\) and

\[ \Delta U_{\text{dep}} = 2.53 \times 10^{-20} \text{ J} = 0.16 \text{ eV} \]

and

\[ \Delta U_{\text{el}} = 2.368 \times 10^{-19} \text{ J} = 1.48 \text{ eV}. \]

It should be noted that the elastic misfit energy is considerably greater than the depolarizing energy.

For a ratio \(c/a = 0.05(L/4\pi = 0.038)\) these energies would be reduced to

\[ \Delta U_{\text{dep}} = 1.376 \times 10^{-20} \text{ J} = 0.09 \text{ eV}, \]

\[ \Delta U_{\text{el}} = 1.152 \times 10^{-19} \text{ J} = 0.72 \text{ eV}. \]

The domain wall energy increase, \(\Delta U_{\text{dw}}\), for the nucleus shape considered here is due to the formation of the incoherent boundary at the edges of the nucleus. This is equivalent to the energy of a circular wall of twin dislocations loops, with radius, \(a\), and height, \(2c\). A rough estimate of the surface energy for this configuration can be obtained from the expression\(^{33,34}\)
the view that switching takes place by the expansion of nuclei which form at the domain walls in the form of very flat plates or protrusions with a thickness of the order of the width of the domain walls. Considering the diffuse and distorted configuration of the domain wall, it is possible to regard the switching process as the lateral spreading, by the action of the applied electric field, of low amplitude and long wavelength thermal undulations of the domain walls.

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