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Microscopic characterization of low-field switching in ferroelectric triglycine sulfate

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Low-field (<1 kV/cm) switching has been investigated for thin plates ($0.06 < d < 0.15$ cm) of triglycine sulfate by means of field pulses with a linear rise time. The dependence of the maximum current density, j_m , with the field value E_m at which this maximum occurs is $j_m \cong B_1(E_m - E_{cw1})^{3/2}$, for $0.3 < E_m < 0.5$ kV/cm, and $j_m \cong B_2(E_m - E_{cw2})$, for $0.5 < E_m < 1.0$ kV/cm. This is satisfactorily explained taking into account the dominant role played by sidewise and forward domain wall motion, respectively. © 1998 American Institute of Physics.
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INTRODUCTION

Ferroelectric switching in triglycine sulfate (TGS) using external field pulses has been investigated extensively by various authors¹⁻⁴ since the late 40's. While the high-field behavior was satisfactorily explained⁵ by random bulk switching of the individual dipoles, the low-field behavior was only tentatively explored in terms of forward and side-wise domain wall motion driven by the action of the switching fields with rectangular pulses. More recently the switching kinetics, especially in ferroelectric ceramics with prospective applications for computer memories, have been investigated in great detail.⁶⁻⁸ The range of fields investigated in PZT thin films is high (200–1000 kV/cm) and the switching time dependence of systems such as the two-dimensional Ising model⁷ and the finite size Kolmogorov–Avrami⁸ model were also investigated.

EXPERIMENTAL

In this work we are just concerned with low fields, below 1 kV/cm. A Hewlett Packard generator, model 33120A, has been used to apply alternatively negative and positive rectangular field pulses, $E(t)$, which are amplified with a Kepco bipolar amplifier, model BOP 1000M, capable of producing pulses of ± 1000 V and ± 40 mA. As rectangular pulses are gradually amplified they get an almost linear initial variable rise time, as it is shown in Fig. 1, and we may consider the applied field as $E(t) = (E_0/t_0)t$, for the initial relevant part of the pulse. The switching current density, $j(t)$, is shown as well in Fig. 1. As this curve can be approximated to an isosceles triangle,⁹ a simple relation between the maximum current density, $j_m = j(t_m)$, and the switching time, t_s , can be obtained at a fixed temperature as

$$\int_0^{t_s} j(t) dt \cong \frac{1}{2} j_m t_s = 2P_s \Rightarrow t_s = \frac{4P_s}{j_m},$$

where P_s is the spontaneous polarization. Both $j_m = j(t_m)$ and $E_m = E(t_m)$ have been observed and measured from a Hewlett Packard oscilloscope, model 54603B.

Three samples were cut from single TGS crystals, grown from water solution. Samples dimensions were $d_1 = 0.15$ cm, $A_1 = 1.1$ cm²; $d_2 = 0.08$ cm, $A_2 = 0.36$ cm²; and $d_3 = 0.06$ cm, $A_3 = 0.64$ cm². The ferroelectric axis was parallel to the direction of the applied field. All the experiments were performed at RT ($T \cong 20^\circ\text{C}$).

RESULTS AND DISCUSSION

Figure 2 shows the resulting curve j_m vs E_m for the three samples. The observed data display the expected low-field behavior, which is very similar qualitatively to that observed with squared and shorter pulses by Fatuzzo and Merz³ in another range of field values.

In the initial regime (I) the maximum current density, $j_m(E_m)$, grows faster than linearly with E_m from a threshold domain wall switching coercive field, E_{cw} , to E_m^* , being E_m^* the field corresponding to the transition from the regime I to regime II.

In the subsequent region (II), $j_m(E_m)$ grows linearly with E_m , i.e., for $E_m > E_m^*$ up to a much higher fields, at which a change to bulk random switching eventually would take place.

To describe microscopically the behavior depicted in Fig. 2, we assume that domain wall switching proceeds from small remnant counter polarized domains at one surface and that both, forward and sidewise motion are involved. We assume as well that the sidewise domain wall velocity, $v(\text{swm}) = v_1(E)$ has a field dependence different from that of the forward domain wall velocity, $v(\text{fwm}) = v_2(E)$. At low fields above the threshold E_{cw} (known to be much smaller than E_{cb} , the random bulk coercive field) the tips of preexisting microdomains are expected to arrive first at the opposite surface. The lateral growth of the counter polarized domains is then expected to proceed more slowly ($v_1 < v_2$).

At a somewhat higher field, E_m^* , the tips of the growing microdomains arrive quickly at the opposite surface at about the same time as the lateral walls of neighboring microdomains (which are considered to be spaced at roughly regular intervals¹⁰) meet each other. From E_m^* upwards the side-wise domain wall motion is expected to become so fast that the lateral growth keeps pace with the forward motion of the

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FIG. 1. Plot of a positive field pulse, $E(t)$, after amplification, and the corresponding $j(t)$, indicating the meaning of $E_m = E(t_m)$, and $j_m = j(t_m)$.

broad tip, causing the switching process to be controlled by the forward domain wall motion which proceeds at a lower rate ($v_1 > v_2$). In the following we make this argument quantitative, starting from the general rate equations which give (dP_d/dt) in response to a field $E = (E_0/t_0)t$, and we show that good consistency with the observed low-field switching behavior is obtained.

Being dN the number of dipoles per unit of volume that contributes to the switching in a time interval dt , the general rate equation is given by⁵

$$\frac{dN}{dt} = \frac{1}{\tau} \left[(N_b + N_a) \sinh \left(\frac{T_C}{T} \frac{E + \beta P_d}{E_{S0}} \right) - (N_b - N_a) \cosh \left(\frac{T_C}{T} \frac{E + \beta P_d}{E_{S0}} \right) \right]. \quad (1)$$

Here $(N_b + N_a) = N$ is the total number of dipoles per unit of volume in the whole crystal, $1/\tau$ is the transition probability for $E \rightarrow 0$ at $T > T_C$ (Curie temperature), E is the external field, βP_d the polarization field, and $E_{S0} = \beta N \mu$ the saturation field, with $\beta = 4\pi T_C / C$, the mean field coefficient, C the Curie constant, and μ the elementary dipole moment. Since at low fields all switching process takes place at domain walls no screening effects need to be considered.

It must be noted that, for domain wall switching, only the two monolayers of unit cells in contact at the wall will

FIG. 2. Maximum switching current, j_m vs field, E_m , for three TGS sample plates, showing the different behavior at the regimes I and II.

participate in the switching process. So, we call N_{bw} the number of dipoles per unit volume susceptible of being aligned with the field, and N_{aw} the number of dipoles per unit volume already aligned. Therefore $N_{bw} + N_{aw} = N_w$ will be much smaller than $N = 1/v_c$ being $v_c = abc \sin \hat{\beta}$ the volume of the unit cell. Here $a = 9.15 \text{ \AA}$, $b = 12.69 \text{ \AA}$, $c = 5.73 \text{ \AA}$ are the dimensions of unit cell¹⁰ and $\hat{\beta} = 105^\circ$, the monoclinic angle.

Particularizing the general rate equation for domain wall switching is all we need to get the switching current time evolution. Then, considering quasi-cylindrical domain walls surrounding the initially grown up microdomains (from the bottom to the top of the crystal plate),

$$N_{bw} \cong \frac{n}{V} \left[\frac{2\pi[\bar{r}(t) + s]d}{sb} \right],$$

the density of dipoles of the outer monolayer to be aligned by the field, is only slightly larger than

$$N_{aw} \cong \frac{n}{V} \left[\frac{2\pi\bar{r}(t)d}{sb} \right],$$

the density of dipoles of the inner already switched monolayer. We have used in these expressions $n \cong A/2\pi(\bar{r}_m)^2$ as the number of prepolarized nuclei in the surface area A of the plate, being $\bar{r}_m$ the maximum radius of the growing domains. V is the total volume of the sample ($V = Ad$), d is the thickness of the sample, and $s \cong (ac \sin \hat{\beta})^{1/2}$, a kind of average dimension of the unit cell perpendicular to the ferroelectric axis.

Therefore, considering that $r(t) \gg s$,

$$N_w = N_{bw} + N_{aw} \cong \frac{2n}{V} \left[\frac{2\pi\bar{r}(t)d}{sb} \right] \gg N_{bw} - N_{aw} \cong \frac{n}{V} \left(\frac{2\pi d}{b} \right),$$

and taking into account that $E_m + \beta_w P_{dm} \ll E_{S0}$, which implies $\tanh x \cong x$, we can write

$$\frac{N_{bw} + N_{aw}}{N_{bw} - N_{aw}} \tanh \left(\frac{T_C}{T} \frac{E_m + \beta_w P_{dm}}{E_{S0}} \right) \cong 2 \left(\frac{\bar{r}}{s} \right) \left(\frac{T_C}{T} \frac{E_m + \beta_w P_{dm}}{E_{S0}} \right)$$

which is sufficiently larger than one for domain wall switching ($\beta_w \ll 1$, as it is shown later), and allows us to neglect the second term in Eq. (1). Substituting N_w and multiplying this equation by μ , we get

$$j(t) = \frac{dP_d(t)}{dt} \cong \frac{1}{\tau} \left[N_w(t) \mu \sinh \left(\frac{T_C}{T} \frac{E(t) + \beta_w P_d(t)}{E_{S0}} \right) \right]. \quad (2)$$

To get Eq. (2) in final form we need to put $N_w(t)$ in terms of $P_d(t)$. In an interval dt the net increase in the number of dipoles switched by the field is

$$\delta N_w = \frac{n}{V} \frac{2\pi d \bar{r} \delta \bar{r}}{\nu_c},$$

and consequently,

$$\delta P_d = \frac{n}{V} \left(\frac{2\pi \mu d}{s^2 b} \right) \bar{r} \delta \bar{r}. \quad (3)$$

Integrating Eq. (3) from $t=0$ to $t=t(t \leq t_m)$ and taking $P_d(0) \equiv -P_s$, at $\bar{r}(0) \equiv 0$,

$$2\pi \frac{n}{A} N \mu \frac{\bar{r}^2(t)}{2} = -P_d(t) - (-P_s) = P_s \left(1 - \frac{P_d(t)}{P_s} \right)$$

which connects $\bar{r}(t)$ with $P_d(t)$ and allows us to put down the factor $N_w(t)\mu$ as

$$\begin{aligned} \frac{2n}{V} \frac{2\pi d}{sb} \mu \bar{r}(t) &= \left[4\mu \left(\frac{\pi n N}{Ab} \right)^{1/2} \left(\frac{P_s}{N\mu} \right)^{1/2} \right] \left(1 - \frac{P_d}{P_s} \right)^{1/2} \\ &= M \left(1 - \frac{P_d}{P_s} \right)^{1/2}, \end{aligned} \quad (4)$$

where M is a time-independent factor.

The switching current, dP_d/dt , is obtained in final form substituting Eq. (4) into Eq. (2) as

$$\begin{aligned} j(t) &= \frac{dP_d(t)}{dt} \\ &= \frac{M}{\tau} \left(1 - \frac{P_d(t)}{P_s} \right)^{1/2} \sinh \left(\frac{T_C}{T} \frac{E(t) + \beta_w P_d(t)}{E_{s0}} \right). \end{aligned} \quad (5)$$

Making use of the fact that $j_m[E_m(t_m)]$ correspond to the maximum switching current for $t=t_m$, $E_m=E(t_m)=(E_0/t_0)t_m$, which implies

$$\left(\frac{d^2 P_d}{dt^2} \right)_m = 0 \quad \text{at } t=t_m,$$

the time derivative of Eq. (5) leads directly to

$$\begin{aligned} \left(1 - \frac{P_{dm}}{P_s} \right)^{1/2} &= \left[\frac{(1/2)(dP_d/dt)_m(1/P_s)}{\left(\frac{T_C}{T} \right) \left[\left(\frac{E_0}{t_0} \right) + \beta_w \left(\frac{dP_d}{dt} \right)_m \right]} \right] \frac{1}{E_{s0}} \\ &\quad \times \tanh \left(\frac{T_C}{T} \frac{E_m + \beta_w P_{dm}}{E_{s0}} \right) \end{aligned} \quad (6)$$

which substituted into Eq. (5) for $P_d(t)=P_d(t_m)=P_{dm}$, $E=E_m$, and taking into account that $\sinh x \sim x$, for $x \ll 1$, results in

$$\begin{aligned} j_m(E_m) &= \frac{M}{\tau} \left(\frac{T_C}{T} \right)^{-1/2} \left[\frac{(1/2)(j_m t_m)/P_s}{(E_m + \beta_w j_m t_m)/E_{s0}} \right]^{1/2} \\ &\quad \times \left(\frac{T_C}{T} \frac{E_m + \beta_w P_{dm}}{E_{s0}} \right)^{3/2}. \end{aligned} \quad (7)$$

We can distinguish two regimes in the behavior of $j_m(E_m)$:

(I) $E_m \ll \beta_w j_m t_m$ leading to

FIG. 3. Experimental data as in Fig. 2 for the sample with thickness 0.08 cm. The continuous curves represent the fits obtained with the functional dependencies of $j_m = B_1(E_m - E_{cw1})^{3/2}$, for $E_m < E_m^*$, and $j_m = B_2(E_m - E_{cw2})$, for $E_m > E_m^*$.

$$\begin{aligned} j_m(E_m) &\cong \frac{M}{\tau} \left(\frac{T_C}{T} \right) \left(\frac{1}{2} \frac{\beta}{\beta_w} \right)^{1/2} \left(\frac{N\mu}{P_s} \right)^{1/2} \left(\frac{E_m - E_{cw1}}{E_{s0}} \right)^{3/2} \\ &= B_1(E_m - E_{cw1})^{3/2}, \end{aligned} \quad (8)$$

where $-\beta_w P_{dm}$ has been identified with E_{cw1} , the domain wall coercive field for this regime. This is the field dependence, $j_m(E_m)$, found experimentally in Fig. 2 for $E_m < E_m^*$.

(II) $E_m \gg \beta_w j_m t_m$ resulting in

$$j_m(E_m) \cong \frac{M}{\tau} \left(\frac{T_C}{T} \right) \left(\frac{E_m - E_{cw2}}{E_{s0}} \right) = B_2(E_m - E_{cw2}) \quad (9)$$

now with the same field dependence found experimentally in Fig. 2 for $E_m > E_m^*$.

In Fig. 3 the experimental data for one of the samples are shown together with their fits to the Eqs. (8) and (9). From these we get $E_m^* = 0.5$ kV/cm, $B_1 = 199.83$ (mA/cm²)(kV/cm)^{-3/2}, $E_{cw1} = 0.32$ (kV/cm) and $B_2 = 55.79$ (mA/cm²)(kV/cm) and $E_{cw2} = 0.22$ kV/cm, respectively.

This allows an estimation of a domain wall mean field coefficient, as given by $\beta_w = E_m^*/(j_m t_m) = E_m^*/(2P_s) = 0.0001$, which is dimensionless in esu.CGS units. This is much smaller than the bulk effective mean field coefficient for TGS, $\beta = 4\pi T_C/C \cong 1.1$, as might have been expected, because the cooperative effect of the unit dipoles on one side of the wall compensates to a large extent that of the unit dipoles on the other side.

We have used the corresponding basic parameters (see Ref. 9, p. 62, Table 6.1) for TGS crystal in order to determine the frequencies τ_1 and τ_2 for the microscopic jump probabilities at both regimes and we find they are $\approx 10^{13}$ Hz, which is of the order of low lying optical frequencies in TGS. The energy barriers for switching are in both cases small as might be expected.

We may note as well that in the expression of B_1 and B_2 there is a weak dependence on the factor $(n/A)^{1/2}$, through the factor M , that may point out the relevance of the density of preexisting microdomains at the surface of the crystal, related to the growing conditions of a given sample. This would explain the differences in Fig. 2 for the three samples studied. In subsequent measurements we have also observed

that several factors as temperature, humidity, and even the process of measure itself may produce differences in the location of E^* , but the general behavior for the two regimes remains unchanged.

Summarizing, we have seen that a simple microscopic description of low-field switching in TGS, showing a distinct change of regime in the field dependence of the maximum switching current, is satisfactorily carried out starting from the general rate equation, using common sense microscopic considerations. The resulting expressions for $j_m(E_m)$ predict well the observed behavior, and a specific temperature dependence, which will be the object of future works. It may be noted that this approach may be useful to study low field switching in ferroelectric thin films.

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