

# Discrete nature of the activation fields for the polarization reversal of ferroelectric crystals

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Experiments show that polarization reversal in real ferroelectric crystals is characterized by activation fields which depend on the strength of the external electric field.

A study of the 180° polarization reversal of ferroelectric crystals has revealed that the process can be described by an exponential dependence of the reversal time on the external electric field,  $1/\tau_s = (1/\tau_\infty)\exp(-\alpha/E)$  where  $\alpha$  is the activation energy.<sup>1</sup> Various ferroelectric crystals in external electric fields in the range  $10^2$ – $10^4$  V/cm exhibit two or three regions with different activation fields.<sup>2–5</sup> Attempts have been made to explain the change in the activation field with increasing external electric field on the basis of a change in the relative importance of domain nucleation and the lateral motion of 180° domain walls. The recent development of methods for directly observing the dynamics of domains during polarization reversal (the pyroprobe method, the scanning electron microscope, the method using a nematic liquid crystal, etc.) has now made it possible to resolve this question.

As we have shown previously,<sup>4</sup> in fields up to  $1.5 \times 10^3$  V/cm the TGS crystal exhibits three regions with different activation fields not only on the curves of the polarization-reversal time,  $\ln(1/\tau_s)(1/E)$ , but also on the curves of the density of nucleating domains,  $\ln n(1/E)$ , and of the velocity of the lateral motion of the domain walls,  $\ln v(1/E)$ . The activation fields for domain nucleation ( $\beta$ ), for the lateral motion of domain walls ( $\delta$ ), and that ( $\alpha$ ) which characterizes the overall polarization reversal are related by  $\alpha = (1/3)\delta + (2/3)\beta$  for all three regions.

We should point out that in our experiments the polarization reversal of the ferroelectric in an external electric field occurs under conditions such that there is a thin ( $\sim 5\text{-}\mu\text{m}$ ) layer of a nematic liquid crystal between the polar surface of the sample and the electrode, and this thin layer may be regarded as a dielectric gap. In this case, in contrast with the case of metal electrodes, the polar surfaces of the sample are not equipotentials, so that electrical inhomogeneities may be manifested at the surfaces studied. Furthermore, under these conditions the polarization reversal occurs more slowly because of the degraded conditions for cancellation of the polarization charges. This slower reversal makes it possible to study the reversal over a broad range of fields.

In the present experiments we used the method of nematic liquid crystals<sup>5</sup> to directly observe the dynamics of the domain structure during the polarization reversal of a TGS crystal in fields up to  $6 \times 10^5$  V/cm. We have found several more linear regions on the plots of  $\ln [(1/\tau_s)(1/E)]$ ,  $\ln v(1/E)$  and  $\ln n(1/E)$ . The similar behavior of  $\ln n(1/E)$  and  $\ln v(1/E)$  is evidence for the model of Refs. 1 and 7, which has the lateral motion of domain walls resulting from domain nucleation near a wall. The activation fields  $\alpha$ ,  $\beta$ , and  $\delta$  over the entire field range studied are listed in Table I. For all field ranges we find  $\beta > \alpha > \delta$ , and the relation  $\alpha = (1/3)\delta + (2/3)\beta$  holds.

Direct observations of the domain dynamics revealed that in all ranges of the external field the polarization reversal is qualitatively the same process: A certain number ( $n$ ) of nucleating regions of domains of the opposite polarity arise, and they subsequently grow together by virtue of the lateral motion of domain walls. The relative contributions of domain nucleation and of the lateral motion of domain walls remain essentially the same.

TABLE I. Activation fields for various ranges of the polarization-reversing field for a nominally pure TGS crystal.

	External field, V/cm	Activation field for the polarization reversal, V/cm		
		$\alpha$	$\delta$	$\beta$
I	$3 \times 10^2 - 2 \times 10^2$	35	30	35
II	$2 \times 10^2 - 5 \times 10^2$	$2.5 \times 10^2$	$2.3 \times 10^2$	$2.5 \times 10^2$
III	$5 \times 10^2 - 2 \times 10^3$	$1.6 \times 10^3$	$8.7 \times 10^2$	$1.7 \times 10^3$
IV	$2 \times 10^3 - 1 \times 10^4$	$6.5 \times 10^3$	$5.4 \times 10^3$	$1.0 \times 10^4$
V	$1 \times 10^4 - 1.5 \times 10^5$	$9.0 \times 10^4$	$5.0 \times 10^4$	$1.1 \times 10^5$
VI	$1.5 \times 10^5 - 6.0 \times 10^5$	$4.0 \times 10^5$	$3.5 \times 10^5$	$5.7 \times 10^5$

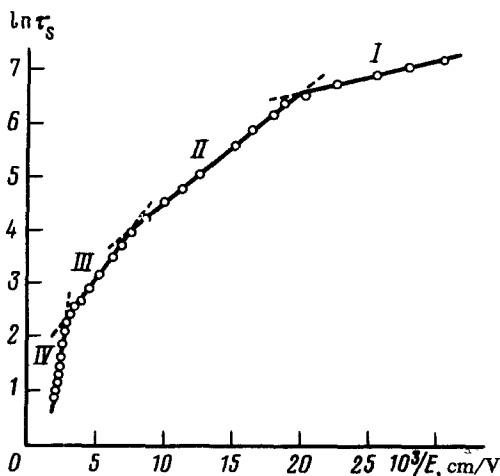


FIG. 1. The polarization-reversal time  $\ln \tau_s$  versus  $1/E$  for a TGS crystal with  $7.5 \times 10^{-3} \% \text{ Cu}$  ( $\alpha_I = 65 \text{ V/cm}$ ,  $\alpha_{II} = 2.1 \times 10^2 \text{ V/cm}$ ,  $\alpha_{III} = 3.4 \times 10^2 \text{ V/cm}$ ,  $\alpha_{IV} = 1.7 \times 10^3 \text{ V/cm}$ ).

Polarization reversal of a real ferroelectric crystal through a mandatory stage of domain nucleation is energetically preferable to a uniform change in the polarization simultaneously throughout the volume of the crystal, even in fields above the theoretical value of the coercive field  $E_c$  ( $\sim 10^5 \text{ V/cm}$ ) for the TGS crystal, predicted by the thermodynamic theory for an ideal crystal.<sup>8</sup>

It was found in this manner that the polarization reversal of a real crystal includes as a mandatory initial stage the appearance of regions of domain nucleation. The discrete nature of the activation fields for the nucleation is evidence of a discrete nature of the distribution of nucleation sites in activation energy. The discrete nature of the activation fields for the lateral motion of domain walls is a consequence of this distribution, and the fact that the values of  $\delta$  are lower than the values of  $\beta$  means that the activation energy for domain nucleation decreases at an existing domain wall. Both processes contribute to the activation field  $\alpha$ .

We believe that the discrete nature of the activation fields stems from the discrete nature of surface states of a real ferroelectric crystal. The existence of such sites in ferroelectric dielectrics was predicted in Refs. 9 and 10, but it has not previously been confirmed experimentally.

On the basis of the model of surface states, the formation of nuclei during polarization reversal from a single-domain state under the influence of an external electric field can be thought of as the excitation of electrons from corresponding levels.<sup>11</sup> This excitation gives rise to a local change in the polarization and thus the appearance of a region of the nucleation of a domain of a new polarization. Assuming<sup>9,10</sup> that the surface states are localized in a layer with the thickness on the order of that of the unit cell ( $\sim 10^{-7} \text{ cm}$ ), and using the values found for the activation fields, we can estimate the energy spectrum of the surface states of the crystal. For a nominally pure TGS crystal, these energies range from  $10^{-3}$  to  $1.5 \text{ eV}$  with a band gap of  $6 \text{ eV}$ . These

energy values evidently correspond to impurity levels in the TGS crystal. The introduction of impurities during the growth process, an annealing, and a bombardment change the density of domain nucleation regions, the number of discrete regions on the field dependence of the switching characteristics, and the values of the activation fields in the corresponding intervals of the external electric field. Figure 1 shows  $\ln\tau_s(1/E)$  for a TGS crystal containing  $7.5 \times 10^{-3} \% \text{ Cu}$ . Comparison of the results for the nominally pure TGS crystal (Table I) with the results for TGS with a Cu impurity clearly reveals that the copper impurity gives rise to additional domain-nucleation centers with low activation fields in the range of fields up to  $2 \times 10^3 \text{ V/cm}$ .

It can be concluded from these experimental results that the initiation of polarization reversal results from electronic transitions in surface states and the discrete nature of the activation fields for the polarization reversal is a fundamental property of a real ferroelectric crystal.

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