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Vladimir Fridkin
Institute of Crystallography, Russian Academy of Sciences, Moscow

A. Ievlev
Institute of Crystallography, Russian Academy of Sciences, Moscow

K. Verkhovskaya
Institute of Crystallography, Russian Academy of Sciences, Moscow

G. Vizdrik
University of Nebraska - Lincoln

S. Yudin
Institute of Crystallography, Russian Academy of Sciences, Moscow

See next page for additional authors

Authors
Vladimir Fridkin, A. Ievlev, K. Verkhovskaya, G. Vizdrik, S. Yudin, and Stephen Ducharme

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The paper is devoted to the 75th anniversary of Prof. Lemanov's birthday.

Switching in One Monolayer of the Ferroelectric Polymer

V. Fridkin,[1,2] A. Ievlev,[2] K. Verkhovskaya,[2] G. Vizdrik,[1] S. Yudin,[2] and S. Ducharme[1]

1 Department of Physics and Astronomy and Center for Material Research and Analysis, University of Nebraska–Lincoln, Lincoln, NE 68588-0111, USA

2 Institute of Crystallography, Russian Academy of Sciences, Moscow 119333, Russia

Abstract
The switching in one monolayer of ferroelectric vinylidene fluoride-trifluoroethylene copolymer P[VDF-TrFE] is observed. The kinetics of switching is well described by Landau-Khalatnikov (LK) equation.

Keywords: Ferroelectrics, phase transitions

The investigation of the switching kinetics in the ultrathin Langmuir-Blodgett (LB) ferroelectric films of the copolymer P[VDF-TrFE] with thickness of 2–30 monolayers (ML) was performed in [1, 2]. The switching kinetics of these ultrathin films is well described by the Landau-Khalatnikov equation [3, 4] and shows the critical behavior at $V = V_C$ (V is applied voltage, V_C is coercive voltage). For more thick films (~100 ML) the usual exponential dependence of switching time t_0 on the applied voltage V is observed, governed by the domain-nucleation mechanism of Kolmogorov-Takagi-Ishibashi.

For the first time these results were presented in 2002 on the Russian-Japanese Ferroelectric Symposium in Saint Petersburg, organized by Prof. Lemanov.

The critical behavior of the copolymer film switching may be obtained from the Landau- Khalatnikov (LK) equation for the phase transition of the first order:

$$\xi \frac{dP}{dt} = -\frac{\partial G}{\partial P} = -a(T - T_0)P - \beta P^3 - \gamma P^5 + \frac{V}{d}, \tag{1}$$

where P is the polarization, G is the Gibbs free energy, ξ is the polarization damping constant, which could be temperature dependent, T_0 is Curie temperature, α, β and γ are the Landau-Ginzburg coefficients, V is the applied voltage, and d is the film thickness. The critical behavior of the switching time t_0 on V/V_C is obtained from (1) [2]:

$$\frac{1}{t_0} \cong \frac{1}{\tau}\left(\frac{V}{V_c} - 1\right)^{1/2}, \quad \tau \approx 6,3\frac{\gamma\xi}{\beta^2}, \tag{2}$$

where V_C is coercive voltage. The Landau-Ginzburg coefficients for the copolymer are $\beta \approx -1.9 \times 10^{12}$ J m^5/C^2, $\gamma = 1.9 \times 10^{14}$ J m^9/C^4 [5]. Determination of the critical switching time from kinetics curves for the condition $P(t_0) = P_S/2$ gave $\xi \approx 3.6 \times 10^{10}$ V·m·s/C [2].

The observation of the critical switching and measurement of the $1/t_0 = (1/t_0)\ (V/V_C)$ dependence may be performed by the other method. It can be shown from the LK equation, that the initial derivative dP/dt in the vicinity of $P = P_S$ also reveals the critical behavior:

$$\left.\frac{dP}{dt}\right|_{P=P_S} = \frac{1}{\xi} E_C \left[\frac{V}{V_C} - 1\right] \tag{3}$$

where E_c is the coercive field. The relation (3) is valid both for the first and second order phase transition.

Let us compare the critical switching behavior of the LK mechanism with a domain mechanism of switching, governed by the Kolmogorov-Avrami-Ishibashi (KAI) expression [6]:

$$2t_0 = t_{0m} \exp\left(\frac{V_0}{V}\right) \tag{4}$$

$$\left.\frac{dP}{dt}\right|_{P=P_S} = P_S \frac{1}{t_{0m}} \exp\left(-\frac{V_0}{V}\right) \tag{5}$$

The Equations (4) and (5) show, that in KAI mechanism there is exponential dependence of switching time t_0 on V and there is no peculiarities neither of t_0 nor of $dP/dt|_{P=PS}$ at the coercive voltage V_C. All the experimental data on the switching of ferroelectric crystals and films are in good agreement with KAI mechanism and (4), (5) [6]. To the contrary the experimental data for the ultrathin ferroelectric copolymer films are in good agreement with the LK mechanism and show the critical switching in accordance with (2) and (3) [2, 7].

It means also, that ultrathin (two-dimensional) ferroelectric films show very peculiar switching kinetics, which differs drastically from the KAI mechanism (4, 5).

In the present paper we investigated the switching kinetics in one ML of the ferroelectric copolymer. To do it we have prepared by the LB method [5] the combined film, consisting of two ML of ferroelectric polymer separated by two ML of the nonferroelectric anthraquinone dye (see Fig. 1). Prior measurements of the switching ki-

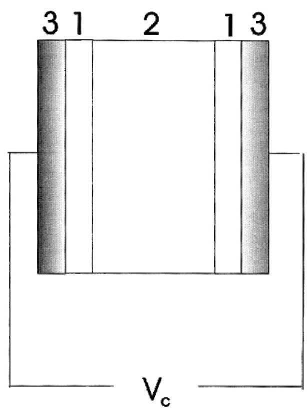

Figure 1. The scheme of the combined film: 1 = monolayer of the ferroelectric copolymer, d_1 – thickness 5–17 Å, $\varepsilon_1 = 7$; 2 = two monolayers of nonferroelectric anthraquinone dye, d_2 – thickness 40 Å, $\varepsilon_2 = 3$; 3 = Al-electrodes.

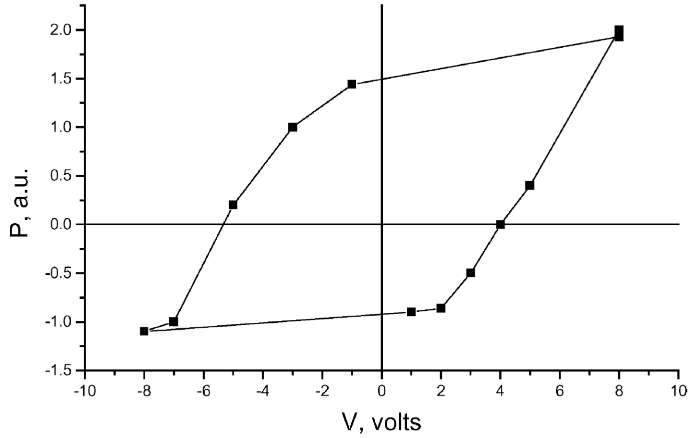

Figure 2. The hysteresis loop of the combined film.

netics the hysteresis loop and coercive voltage (4–5 volts) were obtained (Figure 2). The asymmetry of the hysteresis loop is caused by the difference in the boundary condition for each ferroelectric monolayer. The switching kinetics was measured by the Chynoweth method, described in [2].

In the present paper we have measured the initial slope of the switching kinetics curves for different V (the switching took place in the direction, which corresponds V_C = 4 volts). Figure 3 shows the experimental results. The critical character of the switching is evident: there is no switching at $V < V_C$, and at $V \rightarrow V_C$, $t_0 \rightarrow \infty$. The dependence of $(dP/dt)_{P=PS}$ on V/V_C is linear. To obtain the value of the damping parameter ξ we must determine the coercive field E_C for the combined film from Figure 2:

$$E_C = \frac{V_C}{2d_1 + d_2\frac{\varepsilon_1}{\varepsilon_2}} \qquad (6)$$

where V_C is the coercive voltage, applied to the combined film.

Substituting in (6) the dielectric constant of ferroelectric $\varepsilon_1 \approx 7$ [5], dielectric constant of antrakhinon dye $\varepsilon_2 \approx 3$, d_2 = 40Å and d_1 = 5–17Å (depending on LB technol-

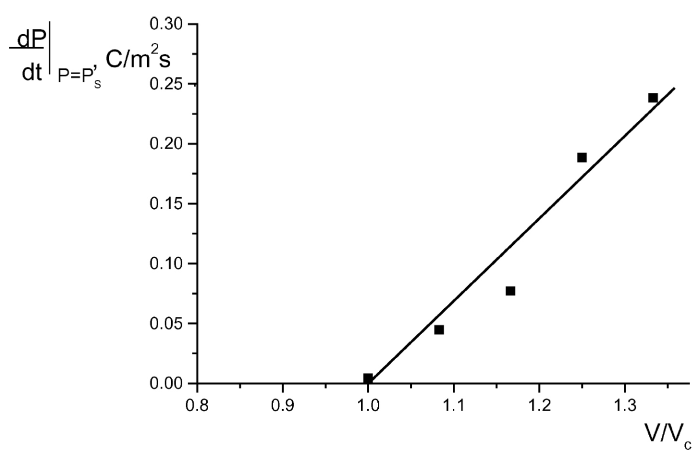

Figure 3. Dependence of $(dP/dT)_{P=PS}$ on V/V_C.

ogy [8]) and neglecting internal and electrode Thomas-Fermi screening, we obtain $E_C \approx (0.3\text{–}0.4) \times 10^9$ V/m. This value coincides very well with intrinsic Landau-Ginzburg value of coercive field in ferroelectric copolymer [1, 2].

The corresponding value of $\xi \approx (0.5\text{–}1.7) \times 10^{10}$ V m · s/C coincides with [2] by the order of value. By the present method estimation of ξ does not depend on β and γ, but supposes the realistic determination of the thickness d_1 and d_2, which depend on the LB technology [6]. Thus, the switching of combined film revealed for the first time the switching kinetics in one monolayer, which is well described by the Landau-Khalatnikov mechanism.

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