Relaxation variation of the nature of the phase transition in a ferroelectric semiconductor

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(Submitted 18 April 1994; resubmitted 25 August 1994)
Zh. Eksp. Teor. Fiz. **106**, 1747–1755 (December 1994)

The second-order ferroelectric phase transition, which is close to the Lifshitz point and the tricritical point on the phase diagram, is shown to evolve in time into a sequence of second- and first-order transitions. As the temporal variations of the temperature dependence of the dielectric constant of the ferroelectric semiconductor $Sn_2P_2S_6$ suggest, the exposure of the crystal at a fixed temperature in the para phase near the second-order phase transition point gives rise to an intermediate state (presumably incommensurate). Illuminating the sample promotes the formation of such a state, while a constant electric field directed parallel to the spontaneous polarization axis narrows the temperature range within which such a state exists. Qualitatively the experimental data are described by the mean-field approximation within a model that assumes the coefficients of the thermodynamic potential of a uniaxial intrinsic ferroelectric with a single direction of modulation in the incommensurate phase to be linear functions of the charge carrier concentration on the trapping level, which varies with time exponentially as the system relaxes to the equilibrium state at a fixed temperature. © *1994 American Institute of Physics.*

1. INTRODUCTION

When the phase diagrams of crystals with structural phase transitions (PT) contain higher-order critical points (the tricritical point, or TCP, and the Lifshitz point, or LP), new dynamic and structural effects determined by the compound influence of order-parameter fluctuations and defects may manifest themselves.[1–3]

Mobile charged defects also play a special role in the critical behavior of crystals. For instance, in ferroelectric semiconductors the instability of the crystalline structure is related to the kinetics of the electronic subsystem. In Mamin's simple model,[5] the variation of the electron concentration on the attachment levels can change the LP and TCP positions on the phase diagram and considerably modify the critical anomalies of the crystals' thermodynamic characteristics. One can expect effects of prolonged relaxation of crystal properties to manifest themselves in both the incommensurate (IC) phase (anomalous temperature hysteresis, the memory effect) and the vicinity of the transition directly from the initial high-symmetry phase to the commensurate low-symmetry phase.

The nonequilibrium nature of the electronic subsystem is only one possible factor determining the kinetics of phase transitions. In a broader perspective the study of nonequilibrium phase transitions is interesting in view of the theoretically predicted[2,6] possibility of observing the formation of spatially coherent structures over fairly long periods in the critical region with strongly developed fluctuations of the order parameter.

These possibilities of qualitative variations in the critical behavior of crystals in a PT close to TCP and/or LP determine the feasibility of studying the temperature dependence of the thermodynamic functions experimentally for different nonequilibrium states of the system under investigation. The possibility of such experiments becomes real in the case of $Sn_2P_2S_6$ The Lifshitz point ($x_{LP}\approx 0.28$) and the tricritical point ($x_{TCP}\approx 0.6$) ferroelectric semiconductors lie side by side on the temperature vs concentration diagram for mixed crystals $Sn_2P_2(Se_xS_{1-x})_6$ (see Ref. 7). The latter is "virtual" because, as selenium content increases, the line of transitions $T_0(x)$, directly in the paraelectric phase to the ferroelectric, which already became "virtual" for $x>0.28$, changes its order from second to first at $x_{TCP}\approx 0.6$. When $x>x_{LP}$ holds, this second-order transition line $T_0(x)$ ($P2_1/c \Rightarrow Pc$) splits into PT lines of the second $[T_i(x)]$ and first $[T_c(x)]$ orders, which limit the IC phase.

Earlier the ferroelectric semiconductors examined were found to exhibit highly nonequilibrium properties in the nature of the phase transitions: the IC phase can be induced by laser light in $Sn_2P_2(Se_xS_{1-x})_6$ crystals with a selenium content below x_{LP} (see Ref. 8). In addition, Greznev, Mamin, and Motrya[9] established that for $Sn_2P_2S_6$ the temperature of the phase transition between the IC phase and the ferroelectric phase depends sensitively on the heating or cooling rate.

This paper presents the results of a study of the temporal dependence of the dielectric constant of the $Sn_2P_2S_6$ crystal within a broad temperature range, including the vicinity of the second-order PT temperature. It also examines the effects of a constant electric field and sample illumination on the relaxation processes.

2. EXPERIMENTAL RESULTS

Our investigations were carried out with a $6\times6\times3\,mm^3$ sample fabricated from a $Sn_2P_2S_6$ single crystal grown by the Bridgman method. The electric contacts were formed by thermal deposition of gold on the (100) polar cuts. The system of thermostating and measuring the dielectric response of the sample was computer-controlled. The measuring field was 0.05 V/cm. The relative error in measuring ε' was 0.1% and that in measuring ε'' was 0.5%. The

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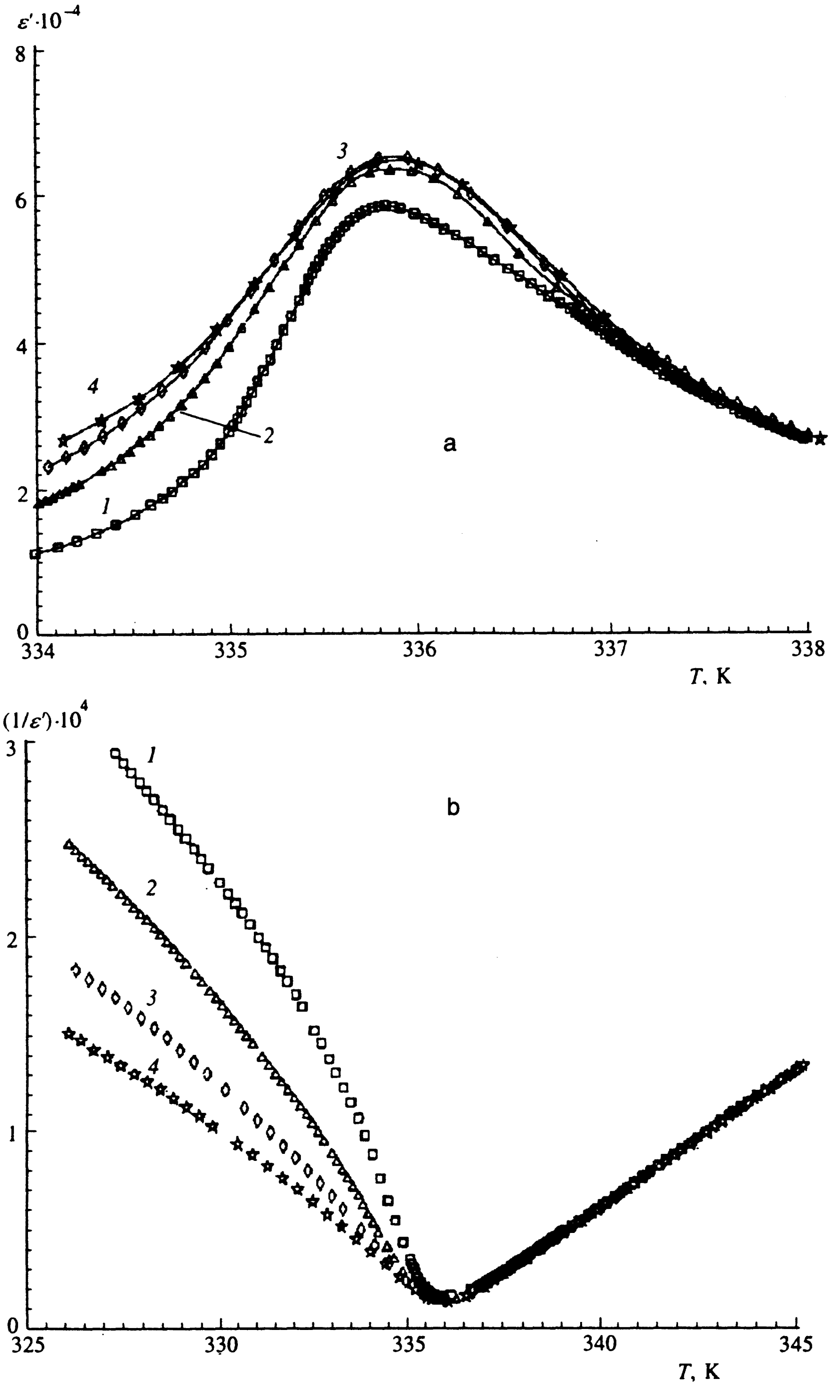

FIG. 1. The temperature curves of (a) ε' and (b) $1/\varepsilon'$ at different temperature variation rates: curves *1*, 0.02Kmin^{-1}; curves *2*, 0.05 K min^{-1}; and curves *3*, 0.2 K min^{-1}.

temperature was stabilized to within ± 0.002K, and the rate of temperature change was varied within 0.3–0.01 K min^{-1}.

The temperature dependence of ε' for the $Sn_2P_2S_6$ was measured during cooling after annealing for three hours in the para phase at 373 K. At a cooling rate of 0.1 K min^{-1} the ε' vs T dependence obeys the Curie-Weiss law within a broad temperature range, but the ε^{-1} vs T dependence is extrapolated to a zero value at $T_0=335.2$ K, while the temperature corresponding to the maximum in the ε' vs T dependence is 335.95 K. When the cooling rate of the sample was reduced, a departure from the above-mentioned law was observed: The value of ε' decreased in the temperature interval from T_0 to T_0+2 K. The temperature of the maximum in the ε' vs T dependence lowers in the process (Fig. 1).

Prolonged temperature stabilization in the para phase at $T>T_0+2$ K does not (to within 1%) cause a change in ε'. However, the temporal relaxation of ε' was noticeable in the T_0-to-T_0+2 K range and also in the ferroelectric phase. The temporal variation of the dielectric constant is described by the exponential law

$$\varepsilon'_t=\varepsilon'_0+\Delta\varepsilon' e^{-t/\tau}. \qquad (1)$$

The data on the temperature variation of the relaxation curves $\varepsilon'(T)$ was used to find the temperature dependence of

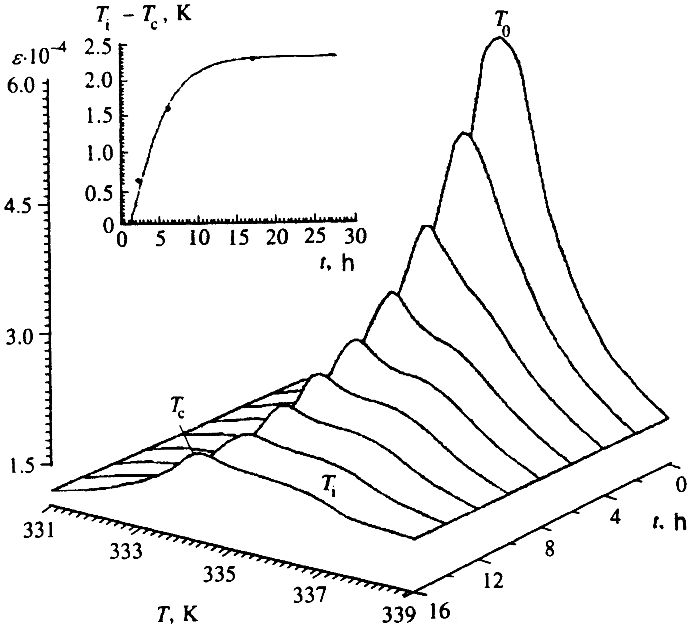

FIG. 2. The temperature curves of the dielectric constant of $Sn_2P_2S_6$ crystals after exposure at $T = 336.2$ K. The inset depicts the temporal dependence of the temperature interval $T_i - T_c$ at the same exposure temperature (the ○ symbols stand for the experimental data, and the curve represents the theoretical results).

the relaxation time τ (see Ref. 10). We established that there is a difference between the relaxation mechanisms of the dielectric constant in the para phase and the ferroelectric phase. For $T < T_0$ the value of τ is practically temperature-independent, with the relaxation of ε' caused by the transformation (coarsening) of the domain structure. It is characteristic of the mechanism for temporal relaxation of ε' in the para phase in the vicinity of T_0 that the temperature dependence of τ is close to linear. What is important is that according to the temporal variations of the Cole-Cole plot[11] for $Sn_2P_2S_6$ the temperature dependence of the equilibrium value of the static dielectric constant $\varepsilon'_\infty(0)$ in the vicinity of T_0 departs considerably from the Curie–Weiss law: $\varepsilon'(0)$ reaches its maximum below T_0, and the temperature dependence of $\varepsilon'_\infty(0)$ clearly exhibits a bend near $T_0 + 2$K.

These facts point to the complex kinetics of the ferroelectric PT in the $Sn_2P_2S_6$: the PT changes its nature as the system approaches equilibrium. A graphic proof of this is provided by the experimental data obtained in the following circumstances. After annealing in the para phase the sample was cooled at a rate of 0.1 K min^{-1} to $T_0 + 1$ K. As noted earlier, at this rate of temperature decrease in the para phase no departure from the Curie–Weiss law can be observed. At that temperature the sample was maintained for a certain time t (e.g., for two hours). After that the sample temperature was raised somewhat (to $T_0 + 4$K), and at a rate of 0.1 K min^{-1} the sample underwent a "cooling–heating" cycle in the $T_0 - 2$K to $T_0 + 4$K range. As the stabilization time t increases, two peaks on the ε' vs T curve clearly manifest themselves (Fig. 2). In the cooling regime the temperature distance between the peaks, $T_i - T_c$, increases with time but becomes practically constant for $t > 17$ hours (inset in Fig. 2). The position of the low-temperature peak typically exhibits temperature hysteresis. The shape of the temperature anomalies in ε' remain practically unchanged when frequency varies from 10 Hz to 100 kHz. In equilibrium two peaks are also observed in the ε'' vs T dependence (Fig. 3), with the low-temperature peak on the ε'' vs T curve lying below the respective peak on the ε' vs T curve.

The intermediate state in $Sn_2P_2S_6$ disappears after the sample is heated to a state in which it is in the para phase and also after prolonged exposure of the crystal in the ferroelectric phase. It is noteworthy that illuminating the sample with the temperature stabilized in the para phase near T_0 facilitates the formation of an intermediate state. For instance, while keeping the sample in the dark at $T_0 + 1$K for six hours causes two peaks to appear on the ε' vs T curve, with the temperature interval $T_i - T_c$ between the peaks of 1.5 K, illuminating the sample with 2-mW white light for the same time increases the interval to $T_i - T_c = 2.3$ K.

A constant electric field applied parallel to the [100] polar axis narrows the interval $T_i - T_c$ in which the intermediate state exists (Fig. 4). Here T_c grows linearly $(T_c(E) = T_c(0) + kE)$ and T_i decreases quadratically $(T_i(E) = T_i(0) - fE^2)$ as the electric field gets stronger (the inset in Fig. 4). The intermediate state obtained by keeping the sample in the dark at $T_0 + 1$K for six hours vanishes in fields $E > 450$ V cm^{-1}.

3. DISCUSSION

The data prompt the conclusion that the ferroelectric second-order PT with $T_0 = 335.2$ K observed when the temperature varies at the rate $dT/dt > 0.1$ K min^{-1} commonly used in experiments, is transformed into a sequence of two transitions when the cooling rate is changed or the temperature in the critical region is stabilized: a second-order transition (T_i) and a first-order transition (T_c). The general shape of the $\varepsilon'(T)$ dependence and the presence of temperature hysteresis in the vicinity of T_c resemble the observed behavior of the dielectric constant in the consecutive phase transitions, from the paraelectric phase to the IC phase (T_i) and

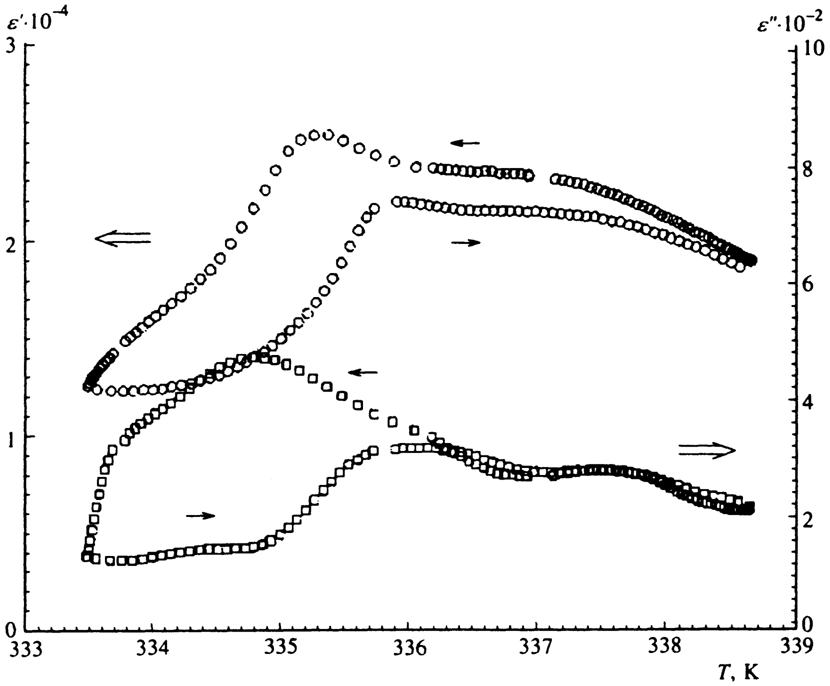

FIG. 3. The temperature hysteresis of $\varepsilon'(T)$ and $\varepsilon''(T)$ after exposing the sample to a temperature of $T=336.2$ K for six hours.

from the IC phase to the ferroelectric phase (T_c), in $Sn_2P_2(Se_xS_{1-x})_6$ crystals with selenium content $x>x_{LP}=0.28$ (see Ref. 12). The shape of the field E vs T diagrams for the intermediate state also coincides with the shape of such diagrams for IC phases in intrinsic ferroelectrics.[13] These facts suggest that the intermediate state that appears when the temperature of the $Sn_2P_2S_6$ crystal is stabilized near T_0 is an IC phase.

Crystals of the $Sn_2P_2S_6$ family are ferroelectric semiconductors. The relation between the PT order parameter (spontaneous polarization) and the charge carriers plays an important role in such crystals. This is confirmed by the strong influence of light on thermo-optical memory in the IC phase of the $Sn_2P_2Se_6$ crystal, with a characteristic writing time of about five hours.[12] A possible reason for the prolonged kinetics of the $Sn_2P_2S_6$ ferroelectrics in the critical region may be the relaxation of the electronic subsystem with an exponential temporal variation of the charge carrier concentration m on the trapping level in the forbidden band at a fixed temperature:[5]

$$m=m_0+\Gamma(1-\exp(-t/\tau)). \tag{2}$$

For uniaxial ferroelectrics the thermodynamic potential density is given by the following series:

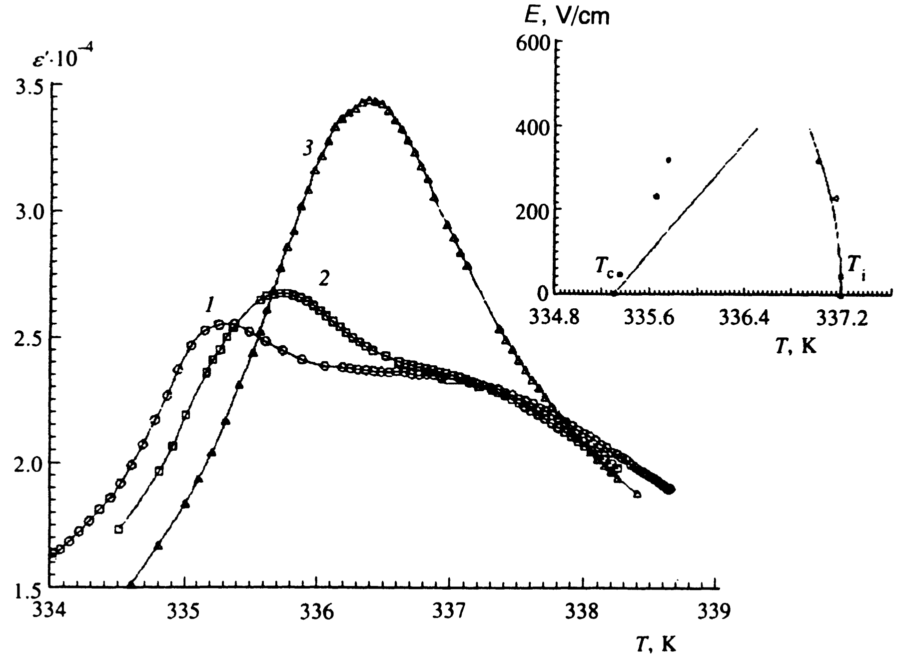

FIG. 4. The effect of a biasing external electric field on the shape of the anomaly in $\varepsilon'(T)$ after exposing the sample to a temperature of $T=336.2$ K for six hours (curve 1, $E=0$; curve 2, $E=200$ V cm^{-1}; and curve 3, $E=420$Vcm^{-1}). The inset depicts the narrowing of the temperature interval in which the intermediate state brought on by the biasing external electric field exists (the ○ symbols stand for the experimental data, and the curves represent the theoretical results).

$$\Phi=\Phi_0+\frac{\alpha}{2}\,\eta^2+\frac{\beta}{2}\,\eta^4+\frac{\delta}{2}\left(\frac{\partial\eta}{\partial Z}\right)^2+\frac{g}{2}\left(\frac{\partial^2\eta}{\partial Z^2}\right)^2+\cdots, \tag{3}$$

where $\alpha=\alpha_T(T-T_0)$. The second-order PT in $Sn_2P_2S_6$ is described by the potential specified by Eq. (3) with the following coefficients: $\alpha_T=1.6\times10^6$ $J\cdot m\cdot C^{-2}$ K^{-1}, $\beta=7.4\times10^8$ $J\cdot m^5\cdot C^{-4}$, $\delta=1.4\times10^{-10}$ $J\cdot m^3\cdot C^{-2}$, and $g=2.2\times10^{-27}$ $J\cdot m^5\cdot C^{-2}$ (see Ref. 12).

For $Sn_2P_2(Se_xS_{1-x})_6$ we have $\delta\sim(x_{LP}-x)$, $\beta\sim(x_{TCP}-x)$, and $g>0$. For $\delta<0$ the IC phase with a temperature width

$$T_i-T_c\approx\frac{\delta^2}{4g\alpha} \tag{4}$$

is realized.

If, following Ref. 5, we assume that α_T and δ are linear functions of m, i.e.,

$$\alpha_T(m)=\alpha_T+am,\qquad \delta(m)=\delta+bm, \tag{5}$$

Eqs. (2) and (4) yield

$$T_i-T_c=\approx\frac{[\delta+bm_0+b\Gamma(1-\exp(-t/\tau))]^2}{4g[\alpha_T+am_0+a\Gamma(1-\exp(-t/\tau))]}\cdot \tag{6}$$

Thus, for $b<0$ the $Sn_2P_2S_6$ crystal acquires an IC phase, and the phase grows with time. In the experiment the sample was cooled from the annealing temperature T_0+40 K to T_0+1 K at a rate of 0.1 min^{-1}. Under such temperature variations the electronic subsystem of the crystal remains "overheated" and at T_0+1K tends to equilibrium as the stabilization time grows. Figure 2 shows that the temperature interval between the two anomalies in the temperature dependence of ε' for $Sn_2P_2S_6$ does increase with time.

We estimate how a nonequilibrium electronic subsystem affects the kinetics of the phase transition into the ferroelectric semiconductor $Sn_2P_2S_6$. The relaxation time τ_m of the electron concentration in the attachment levels is given by the following relation:

$$\tau_m=\{\gamma[n_0+N_c\exp(-U_0/kT)]\}^{-1}, \tag{7}$$

and the equilibrium concentration of such electrons is

$$m_0=\frac{n_0M}{n_0+N_c\exp(-U_0/kT)}\cdot \tag{8}$$

According to Refs. 5 and 14, we can assume that $Sn_2P_2S_6$ is characterized by the following parameters: $n_0\approx10^8-10^{10}$ cm^{-3}, the conduction electron concentration; $N_c\approx10^{19}$ cm^{-3}, the density of states in the conduction band; $M\approx10^{18}$ cm^{-3}, the attachment level concentration; $U_0\approx0.7$eV, the distance on the energy scale from the bottom of the conduction band to the attachment levels; and $\gamma_n\approx10^{-13}$ $cm^3\cdot s^{-1}$, a rate coefficient. For $T=335$ K we have $\tau_m=5-300$ min and $m_0=5\times10^{14}cm^{-3}$.

The coefficient a in Eq. (5) is determined by the electron–phonon interaction, and its value can be found from the data on the variation, induced by spontaneous polarization, of the bandgap in the ferroelectric phase: $E_g=E_{g0}+a'\eta^2$. According to the data of Ref. 15, $a'=10^{-18}J\cdot m\cdot C^{-1}$ for $Sn_2P_2Se_6$.

The inset in Fig. 2 shows the time dependence, calculated by Eq. (6), of the temperature interval T_i-T_c for the intermediate state, which emerges if the $Sn_2P_2S_6$ crystal is kept in the critical region for a long time.

Below we give an estimate of the effect of a biasing external electric field on the intermediate state in $Sn_2P_2S_6$, assuming that this state is the IC phase. In the one-harmonic approximation and with allowance for long-range elastic forces, the field dependence of the temperature of the phase transitions from the paraelectric phase into the IC phase (T_i) and from the IC phase into the ferroelectric phase (T_c) have the following form:[13]

$$T_i(E)\approx T_i(0)-\frac{3B_1E^2}{2\alpha_0^2\alpha_T},$$

$$T_c(E)=T_c(0)+\frac{3B_1E}{\sqrt{(3B_2-B_1)\alpha_0\alpha_T}}. \tag{9}$$

Here $\alpha_0=\alpha_T(T_i-T_0)$, $B_1=\beta+2\Delta$, and Δ is the "gap" between the values of the coefficient of the invariant η^4 in the potential (3) in the commensurate and IC phases, caused by the nonlinearity of the coupling of the order parameter with the long-range elastic forces.[11]

For $Sn_2P_2Se_6$ the value of Δ is known, $\Delta\approx4\times10^8$ $J\cdot m^5\cdot s^{-4}$, and is assumed[13] not to change significantly if sulfur is substituted for selenium. In the presence of an IC phase the temperature of the paraelectric to the ferroelectric phase transition can be estimated from the known[13] relation $(T_i-T_0)/(T_0-T_c)=1.7$, from which it follows that $T=(T_i+1.7T_c)/2.7$.

Assuming that the coefficient a is a linear function of m, we used Eqs. (9) to calculate the E vs T diagram of the intermediate phase in $Sn_2P_2S_6$ (see the inset in Fig. 4). For a more rigorous estimate one must allow the coefficient β to be temperature-dependent, too. Nevertheless, the approximation used provides a satisfactory description of the effect of an external field on the intermediate state in $Sn_2P_2Se_6$.

4. CONCLUSIONS

The data on the temporal variation of the temperature dependence of the dielectric constants of crystals of the ferroelectric semiconductor $Sn_2P_2S_6$ and on the effect of a biasing electric field on the temperature interval within which an intermediate state exists are described by a model that assumes that the second-order PT directly from the paraelectric phase into the ferroelectric phase, which occurs near the Lifshitz point, undergoes relaxational splitting into second- and first-order transitions limiting the incommensurate phase. Here the relaxational process of variation of the charge carrier concentration in the trapping level plays the main role in the transition kinetics. A detailed understanding of the nature of the new effect requires diffraction studies of the emerging relaxation intermediate state. In analyzing the data one must also take into account the movement of the system towards the tricritical point as it relaxes to equilibrium.

The data obtained also clarify the specific conditions, pertaining to ferroelectric semiconductors, for studying the deviations of the shape of temperature anomalies of thermodynamic functions in the critical region from the conclusions of the theory in the mean-field approximation. The deviations occur because of the well-developed and strongly interacting order-parameter fluctuations and the effect of static and mobile defects. We believe that it is important to apply the conclusions drawn from the theory of nonequilibrium phase transitions to a description of the properties of ferroelectric semiconductors.

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Translated by Eugene Yankovsky