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CRITICAL BEHAVIOUR IN A FIELD FOR UNIAXIAL FERROELECTRICS NEAR THE LIFSHITZ POINT

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Abstract The results of the studies of the influence of a constant electric field, directed along the spontaneous polarization axis, on the temperature behaviour of the dielectric constant of the proper uniaxial ferroelectric $Sn_2P_2S_6$, bears witness to the proximity of the second-order ferroelectric phase transition (PT) to the tricritical point. They also confirm the dependence of the Lifshitz point coordinates in the mixed $S_2P_2(Se_xS_{1-x})_6$ crystal phase diagram on the degree of non-equilibrium of the electron subsystem in these semiconductors.

INTRODUCTION

$Sn_2P_2(Se_xS_{1-x})_6$ crystals provide an instance of a Lifshitz point (LP), i.e. a triple point which separates a direct second-order PT from a paraelectric phase to a commensurate ferroelectric phase, from a transition between these phases via on intermediate incommensurate (IC) phase[1]. For these solid solutions $x_{LP}\approx0.28$[2], and the IC phase in the temperature-composition diagram occurs for $x>x_{LP}$. As would be expected, the PT lines, i.e. the $T_i(x)$ and $T_c(x)$ lines which border the IC phase, merge smoothly at $x\rightarrow x_{LP}$. In this case the value of the modulation vector in the $T_i(x)$ line decreases continuously.

The $Sn_2P_2S_6$ - like crystals are the proper uniaxial ferroelectrics. The long-range dipole interaction gives rise to a considerable spatial anisotropy in the order parameter fluctuations. Therefore, the Lifshitz point in these ferroelectrics belongs to a new class of universatility which was defined in [3] as a "dipole Lifshitz point".

The character of the critical behaviour of these crystals can be explained by the proximity of the LP and a tricritical point (TCP) in the phase diagram. In this case the

LP line and the TCP line may merge at a higher-order critical point, i.e. at a tricritical Lifshitz point (TCLP) [4]. An analysis of the anomalies of the thermodynamical properties of the $Sn_2P_2(Se_xS_{1-x})_6$ crystals performed earlier [5] within the framework of the mean-field approximation indicates the occurrence of a TCP for $x_{TCP}\approx 0.6$ in the temperature-concentration phase diagram at atmospheric pressure. According to estimate in [5], the TCLP can be reached by hydrostatic compression of the crystal for $x\approx 0.14$.

The values of the critical indices for the temperature dependence of the heat capacity and order parameter indicate the presence of a crossover to Lifshitz tricritical behaviour. For instance, for the $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystal the critical index for the order parameter β has an extremely low value, i.e. $\beta=0.2$ [2]. For $Sn_2P_2S_6$, the Curie-Weiss law appears to be violated in the paraelectric phase [6], and the discrepancy is described satisfactorily by a logarithmic multiplicative correction. Just this behaviour was predicted on the basis of renormalization-group calculations [3] for the TCLP in uniaxial ferroelectrics with a single direction of modulation in the IC phase.

$Sn_2P_2(Se_xS_{1-x})_6$ crystals are ferroelectric semiconductors, allowing the possibility of a dissequilibrium of the electron subsystem affects their critical behaviour. Indeed, a long-period relaxation of dielectric properties in the paraelectric phase in the vicinity of the PT (at $T-T_0\leq 3K$) has been observed in $Sn_2P_2S_6$ [7]. Evidence of intermediate state formation was found (after protracted crystal exposition, for example at $T=T_0+1K$), with dielectric properties similar to those of on IC phase [7].

Thus, the LP coordinates depend on the degree of electron subsystem non-equilibrium in the crystals under study. This conclusion is confirmed by a LP coordinate shift due to laser irradiation observed earlier [8].

In the present paper, the dielectric properties of the $Sn_2P_2S_6$ crystals under the influence of an external constant electric field have been studied. . The proximity of the ferroelectric second-order PT to the TCP [9] can be estimated from the field dependence of the dielectric temperature anomalies. Furthermore, for proper ferroelectrics the IC phase can be elucidated from the data on the influence of the bias electric field on the dielectric constant anomalies at the PT's bordering the IC phase. The earlier data on the dielectric non-linearity of the $Sn_2P_2(Se_xS_{1-x})_6$ crystals with $x>x_{LP}$, for which

diffraction experiments [10] showed directly the occurrence of the IC phase, are fairly well described in the mean-field approximation [11].

EXPERIMENTAL RESULTS

Figure 1 presents the temperature dependence ε(T) of the dielectric constant of the $Sn_2P_2S_6$ crystal, measured at 10 kHz frequency in a cooling mode at 0.1 K/min temperature reduction rate after "annealing" in the paraphase for 3 hours at T_0+1K. The method of measurement has been described elsewhere [7].

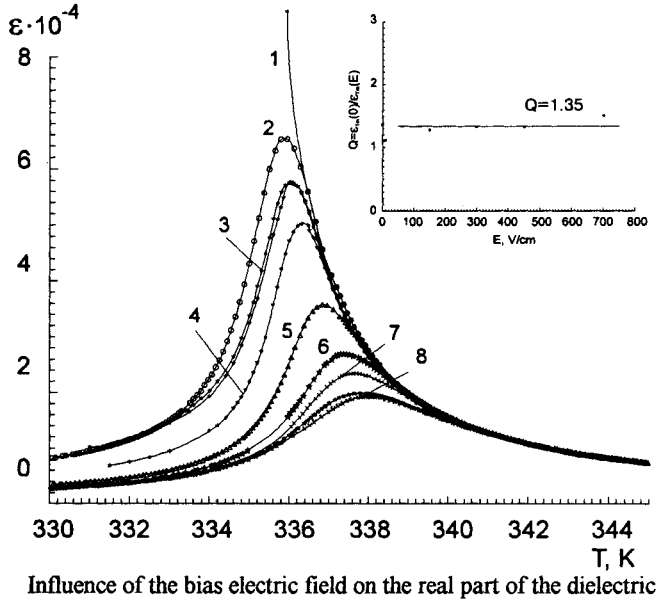

FIGURE 1. Influence of the bias electric field on the real part of the dielectric permittivity anomaly in $Sn_2P_2S_6$ (1-extrapolated ε value for zero internal field, 2 - 0 V/cm, 3 - ±10 V/cm, 4 - 50 V/cm, 5 - 150 V/cm, 6 - 300 V/cm, 7 - 450 V/cm, 8 -±750 V/cm) and (insert) the critical invariant Q value determined from ε '(T) for the $Sn_2P_2S_6$ crystal at various external bias electric fields.

Under increasing strength of the constant electric field imposed along the [100] direction (the spontaneous polarization axis lies in the (010) symmetry plane of the monoclinic unit cell and is close to the [100] direction, and the symmetry change at the PT is $P2_1/c \Leftrightarrow Pc$), the dielectric constant anomaly is dampened. This satisfies qualitatively the regularity criterion for continuous PT. The relationship between the maximum in ε(T) and the temperature at which it if occurs is a quantitative measure of

the field dependence of the proper ferroelectric dielectric constant in the critical region. For $Sn_2P_2S_6$, the ratio $Q=\varepsilon(0,T_{max})/\varepsilon(E,T_{max})$ at the temperature of maximum $\varepsilon(T)$ for a given bias electric field strength is nearly constant (insert in Figure 1).

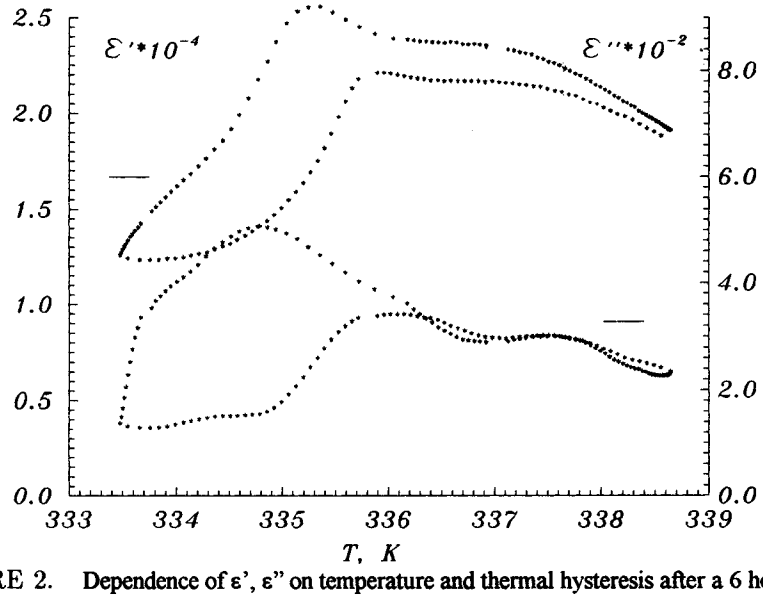

FIGURE 2. Dependence of ε', ε" on temperature and thermal hysteresis after a 6 hour $Sn_2P_2S_6$ sample exposure at T=336.2K.

After a long-term temperature stabilisation of the $Sn_2P_2S_6$ crystal in the paraphase close to T_0, two anomalies arise in the $\varepsilon(T)$ dependence (see Figure 2). The low-temperature anomaly possesses a temperature hysteresis, whereas no hysteresis is seen for the high-temperature one. It has been assumed [7] that the state bounded by the first-order (T_c) and the second-order (T_i) PT corresponding to these anomalies is the IC phase.

An external electric field applied along the spontaneous polarization axis reduces the temperature interval et the intermediate state (Figure 3). In this case, T_c increases and T_i decreases, both satisfying the linear and square dependence on the electric field strength E, respectively (Figure 4). It is significant that the dielectric constant increases due to the field-induced fusion of both $\varepsilon(T)$ anomaliès at T_i and T_c. In the region of the single fused anomaly, a further increase of the electric field strength results in the reduction of the dielectric constant at the maximum (Figure 3).

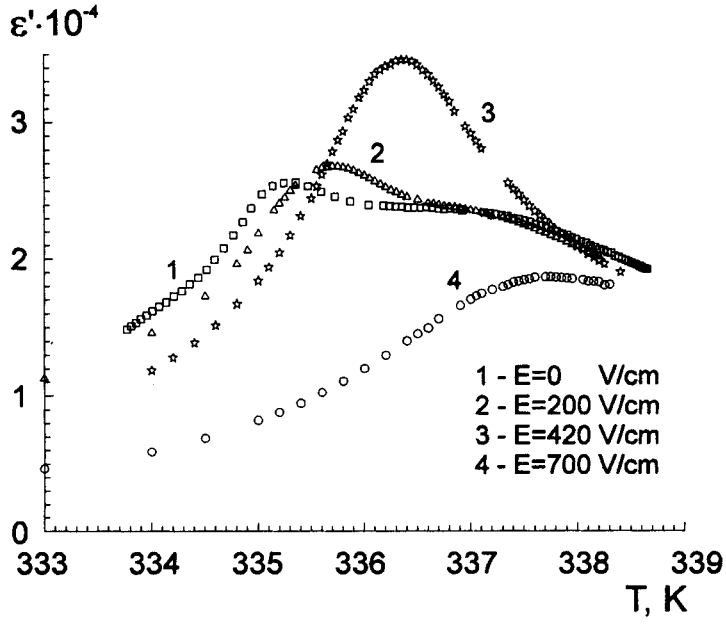

FIGURE 3. Influence of external bias electric field on the temperature interval of existence of the intermediate state, showing dielectric permittivity anomaly in $Sn_2P_2S_6$.

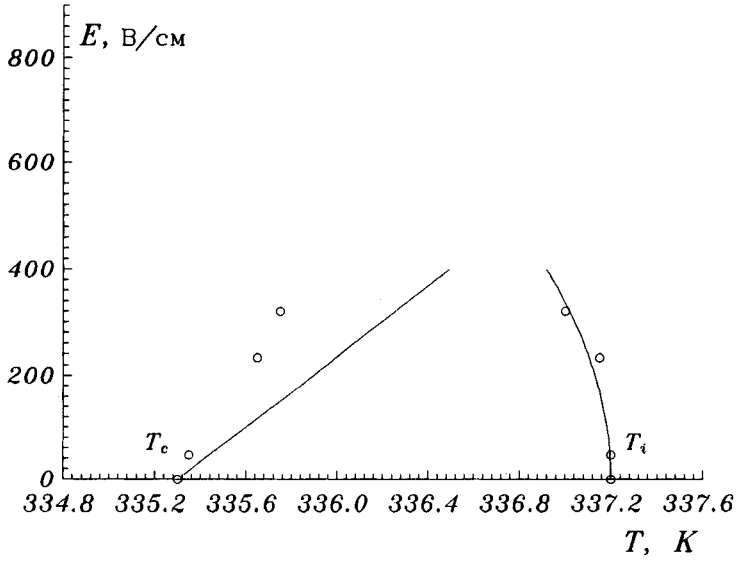

FIGURE 4. Reduction of temperature interval of intermediate state with external DC bias field after thermal exposure at T=336.2K (o-experimental, solid line - theoretical estimates from equations (4)(5)).

DISCUSSION OF RESULTS

Earlier [9] the "critical invariant" Q (i.e. a parameter having a certain value for PT belonging to the given class of universality) was introduced. The parameter Q is defined as a ratio independent of the temperature and field strength:

$$Q = \frac{\varepsilon(0, T_m)}{\varepsilon_m(E, T_m)},$$

where $\varepsilon_m(E,T_m)$ is the maximum value of the dielectric constant in a bias electric field E parallel to the spontaneous polarization axis and T_m is the temperature of the maximum; $\varepsilon(0,T_m)$ is the dielectric constant at the same temperature in the absence of the bias field (E=0).

At the second-order PT, the thermodynamical potential density for a proper ferroelectric has a known form of expansion in terms of powers of the order parameter and its space derivatives:

$$\Phi = \Phi_0 + \frac{\alpha}{2}\eta^2 + \frac{\beta}{4}\eta^4 + \frac{\gamma}{6}\eta^6 + \frac{\delta}{2}(\nabla\eta)^2 + \frac{g}{2}(\nabla^2\eta)^2 + \frac{\lambda}{2}\eta^2(\nabla\eta)^2 - \eta E. \quad (1)$$

Here: $\alpha=\alpha_T(T-T_0)$, and the other coefficients do not depend on temperature. In the temperature-composition diagram, $\delta\sim(x_{LP}-x)$ in the vicinity of the LP, while close to the TCP, $\beta\sim(x_{TCP}-x)$. The other coefficients - γ, g, λ - are positive and constant.

For second-order PT in the presence of a bias electric field E, the maximum of the dielectric constant is expected (in a rough approximation) at the temperature

$$T_m = T_0 + \frac{3}{4}\frac{2\beta}{\alpha_T}E^{2/3}, \quad (2)$$

and its value is:

$$\varepsilon_m = \frac{1}{3\varepsilon_0(2\beta)^{1/3}}E^{-2/3}. \quad (3)$$

Hence [9]:

$$Q = \frac{\varepsilon(0, T_m)}{\varepsilon(E, T_m)} = 2.$$

When analysing the effect of the field on the temperature dependence of the dielectric constant of the proper ferroelectric in the vicinity of the TCP, the authors of Ref.[9] obtained Q=4/3. Generally, one can write for the higher-order critical points:

$$Q = \frac{2(n-1)}{(2n-3)}$$

The experimental values of Q obtained at different field strengths E for the $Sn_2P_2S_6$ crystals are shown in Figure 1. As can be seen, the average value of Q is 1.35, which is quite close to that expected for the TCP. These data verify the proximity of the ferroelectric second-order PT to the TCP in $Sn_2P_2S_6$.

As mentioned above, the long-period temperature stabilisation of the $Sn_2P_2S_6$ sample in the paraphase close to T_0 results in the appearance of a state intermediate between the paraelectric phase and the ferroelectric phase. The dielectric properties of this state are similar to those for the IC phase of the proper ferroelectric (Figure 2). Assuming about the presence of the IC phase within the $T_c<T<T_i$ interval, let us consider the influence of the bias field E on this interval.

The field dependence of the temperatures of the PT from the paraelectric phase to the IC phase (T_i) and that from the IC phase to the ferrophase (T_c) have been obtained in [11] within the harmonic approximation to be:

$$T_i(E) \approx T_i(0) - \frac{3B_1E^2}{2\alpha_0^2\alpha_T}, \tag{4}$$

$$T_c(E) \approx T_c(0) + \frac{3B_1E}{[(3B_2 - B_1)\alpha_0\alpha_T^2]^{0.5}}. \tag{5}$$

Here $\alpha_0=\alpha_T(T_i-T_0)$; $B_1=\beta+\Delta$; $B_2=\beta+2\Delta$; Δ is a "gap" arising from the long-range elastic forces [12].

For $Sn_2P_2S_6$, the following coefficients of the thermodynamical potential (1) have been determined [5] $\alpha_T \approx 1.6\cdot 10^6$ J·m· $Cl^{-2}\cdot K^{-1}$, $\beta=7.4\cdot10^8$ J·m^5·Cl^{-4}. We assume that for $Sn_2P_2S_6$ (as well as for $Sn_2P_2Se_6$), the "gap" is $\Delta\approx2.2\cdot10^8$ J·m^5·Cl^{-4}.[5] The field dependence of T_i and T_c calculated by using these values and relations (4),(5) are shown in Figure 4. A satisfactory agreement between calculation and experiment confirms the assumption [7] of the appearance of an IC phase in the $Sn_2P_2S_6$ ferroelectric semiconductor that depends on the degree of non-equilibrium in the electron subsystem.

CONCLUSION

The results of the study of the influence of a constant electric field oriented along the spontaneous polarization axis on the dielectric properties of the proper uniaxial ferroelectric $Sn_2P_2S_6$ allow one to conclude the following:

- the ferroelectric second-order PT in this crystal is close to the TCP;
- the coordinates of the LP in the phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ are a function of the degree of non-equilibrium the electron subsystem in these semiconductor crystals.

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