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# CRITICAL PHENOMENA IN FERROELECTRIC-SEMICONDUCTOR CRYSTALS $Sn_2P_2S_6$: DIELECTRIC INVESTIGATION

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The influence of the external electric field on the phase transition of the uniaxial ferroelectric $Sn_2P_2S_6$ is investigated. It is shown that direct longitudinal electric field suppresses the temperature anomaly of dielectric susceptibility at the second order phase transition (PT), satisfying regularity expected for tricritical point (TCP). The long term crystal exposure in paraphase near the PT temperature ($T_0$) results in the appearence of an intermediate state, that has dielectric properties, typical for an incommensurate phase. This effect is the consequence of proximity of the ferroelectric PT to the Lifshitz point (LP) on the phase diagram and is explained on the base of the assumption that the coordinates of LP depend on the nonequilibrity degree of electronic subsystem in investigated ferroelectric-semiconductors. At $T - T_0 < 10$ K on the temperature dependence of $Sn_2P_2S_6$ dielectric susceptibility measured in slow cooling mode deviation from the Curie-Weiss law was observed which can be described by logarithmic multiplicative correction of the type $|\ln\tau|^{1/3}$, where $\tau = (T - T_0)/T_0$. It is assumed, that the observed critical behaviour of uniaxial ferroelectric is caused by evidence of order parameter fluctuations correlation in the vicinity of tricritical Lifshitz point in which the line of TCP and the line of LP merge on the phase diagram.

*Keywords: Uniaxial ferroelectric, ferroelectric-semiconductor, tricritical point, Lifshitz point, tricritical Lifshitz point, correlation of fluctuations.*

## INTRODUCTION

Uniaxial proper ferroelectric $Sn_2P_2S_6$ undergoes the second order phase transition ($T_0 = 337$ K, symmetry change $P2_1/c \leftrightarrow Pc$). Pecularity of this PT is determined by following circumstances. Firstly it is near the Lifshitz point and tricritical point. On the temperature-composition diagram for mixed crystals of $Sn_2P_2(Se_xS_{1-x})_6$ the mentioned points lie at $x_{LP} \sim 0.28$ and $x_{TCP} \sim 0.6$ respectively.[1] Secondly, $Sn_2P_2S_6$ crystals possess along with ferroelectric properties the semiconductive one too. For this it is possible the influence of the nonequilibrity of electronic subsystem on the PT character.[2] According to earlier investigations of specific heat and order parameter critical anomalies in ferroelectric phase of $Sn_2P_2S_6$ at increasing temperature the crossover from tricritical behaviour to critical one was observed.[3] It is interest to study the temperature behaviour of dielectric susceptibility of the proper uniaxial ferroelectric at continuous PT, which is close to LP and TCP on phase diagram. In this paper we consider three aspects of the $Sn_2P_2S_6$ crystals dielectric properties investigation: the influence of external bias electric field on the temperature anomaly of dielectric susceptibility; long term relaxation of dielectric characteristics in critical region; on the base of dielectric data analysis of the manifestation of the strongly developed order parameter fluctuations correlations.

## EXPERIMENTAL PROCEDURE

The investigation of temperature dependences was carried out at frequency range 0.1 Hz ÷ 10 kHz in sinusoidal measuring field with amplitude 0.05 V/cm. The separate definition of real ($\varepsilon'$) and imaginaly ($\varepsilon''$) part of complex permittivity by computer controlled system was no worse than 0.1% for $\varepsilon'$ and 0.5% for $\varepsilon''$. Temperature dependences were measured in cooling mode after 3 hours annealing of the sample in the paraphase at 373 K. The cooling rate is constant and varies from 0.02 K/min to 0.2 K/min. At the investigation of long term relaxations the temperature was stabilized with accuracy of $\pm 0.002$ K. The measuring and regulation of temperature was also carried out by computer controlled devices using platinum thermoresistor Pt-100. The single crystals obtained from melt by a Bridgeman technique or from the vapour phase by the gas transport method was tested. The samples were $x$-cut plates of approximately $6 \times 5 \times 3$ mm$^3$ size with thermaly evaporated gold electrodes. The direction of spontaneous polarization vector of $Sn_2P_2S_6$ crystals is close to [100] crystallographic direction.

## INFLUENCE OF THE EXTERNAL BIAS ELECTRIC FIELD ON DIELECTRIC SUSCEPTIBILITY TEMPERATURE DEPENDENCES

In Figure 1 for $Sn_2P_2S_6$ crystals growed from the melt dielectric permittivity in slowly cooling mode (0.1 K/min) at various bias field strength are presented. It is necessary to mention, that even in weak bias field (~10 V/cm) the obtained data do not depend on the polarity of external field. This evidences about the absence of internal bias field in investigated sample in paraelectric phase. The increase of the external field strength $E_b$ results in the shift of dielectric permittivity $\varepsilon'(T)$ temperature dependence maxima to high temperatures, the value of $\varepsilon'$ in maxima decreasing. Experimental data are in good agreement with the well known correlation[4]

$$T_m = T_0 + \frac{3}{4}\frac{2\beta}{\alpha_T} E^{2/3} \tag{1}$$

Here are present the coefficients of thermodynamical potential density function

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

which for $Sn_2P_2S_6$ have the following values[5]: $\alpha_T = 1.6\cdot 10^6 \mathrm{J\cdot M\cdot Cl^{-2}\cdot K^{-1}}$; $\beta = 7.4\cdot 10^8 \mathrm{J\cdot M^5\cdot Cl^{-4}}$; $\delta = 1.4\cdot 10^{-10}\cdot \mathrm{J\cdot M^3\cdot Cl^{-2}}$; $g = 2.2\cdot 10^{-27} \mathrm{J\cdot M^5\cdot Cl^{-2}}$.

It is convenient to analyse the pecularity of influence of the external bias electric field on the dielectric permittivity temperature anomalies in proper ferroelectric by using "invariant" $Q$ that was firstly introduced by Wetwanskii and Fugiel[6] which equals the ratio $\varepsilon_{T_m}(0)/\varepsilon_{T_m}(E)$ at $T_m$. Here $\varepsilon'_{T_m}(E)$ is the maximal value of dielectric permittivity in external field $E_b$, $T_m$—temperature of $\varepsilon(E)$ maxima; $\varepsilon'_{T_m}(0)$—the value of permittivity in zero field at $T_m$. The scheme of the $Q$ value determination is demonstrated on the insertion to Figure 1. As shown in Reference 6 "invariant" $Q$ doesn't depend on external bias field $E_b$ and $Q = 2$ for the second order PT, $Q =$

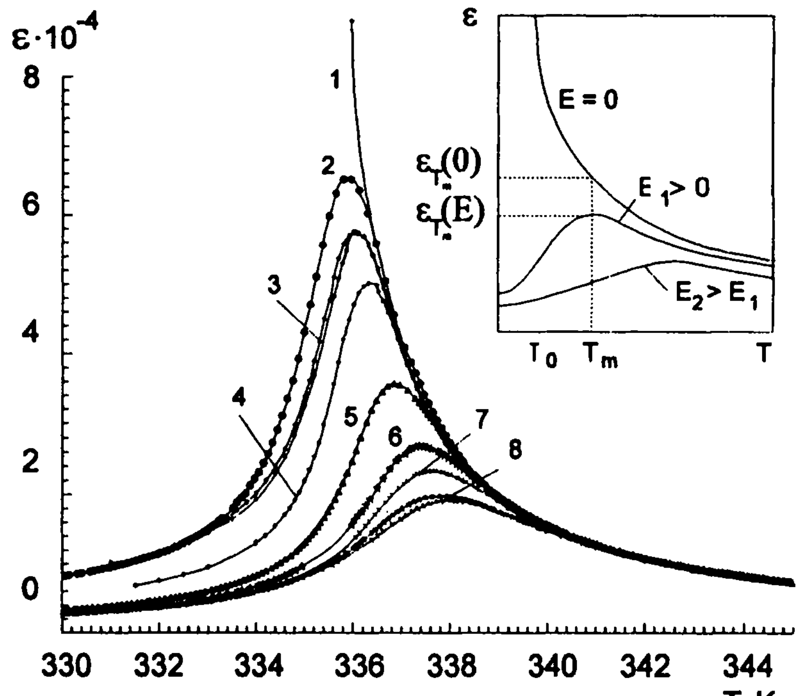


FIGURE 1 Influence of the bias electric field on the dielectric permittivity anomaly in $Sn_2P_2S_6$ (1—extrapolated ε value for zero internal field, 2—0 V/CM, 3—±10 V/CM, 4—50 V/CM, 5—150 V/CM, 6—300 V/CM, 7—450 V/CM, 8—±750 V/CM). On the insertion the scheme of the "invariant" $Q = \varepsilon_{T_m}(0)/\varepsilon_{T_m}(E)$ determination.

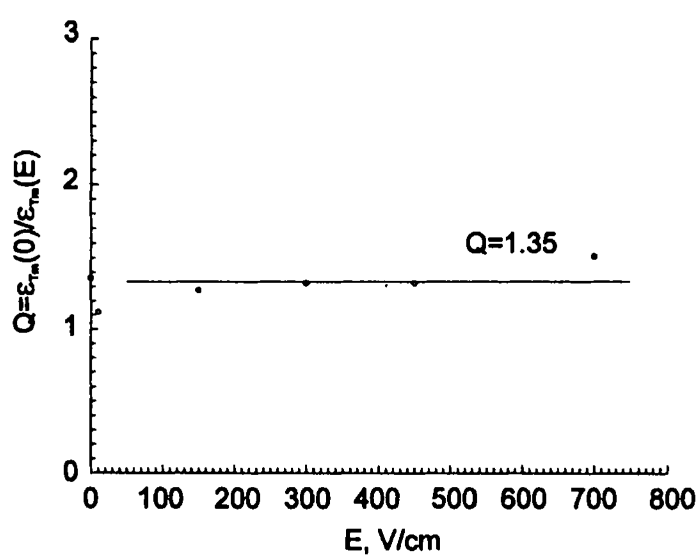


FIGURE 2 Critical invariant $Q$ value determined from $\varepsilon'(T)$ for $Sn_2P_2S_6$ crystal at various external bias electric fields.

4/3 for TCP. For $Sn_2P_2S_6$ crystals as it is seen from Figure 2 the value of $Q$ weakly on the $E_b$ variation. The mean value of $Q$ is equal to 1.35, that is very close to the preduced value 1.33 for TCP. Earlier it was obtained that for triglycine sulfate $Q$ = 1.8–1.9, and for triglycine selenate $Q$ = 1.4–1.6.[6] Thus, the obtained value of $Q$ for $Sn_2P_2S_6$ show on second order PT proximity to TCP on the phase diagram.

## LONG TIME RELAXATION OF THE DIELECTRIC CONSTANT ANOMALIES

For the ferroelectrics-semiconductors considered, considerable manifestations of non-equilibrium in the character of the PT have been observed, i.e., the IC-phase can be induced by laser radiation field in the $Sn_2P_2(Se_xS_{1-x})_6$ crystals with Se content less than $x_{LP}$.[7] Moreover, as it was found,[8] the temperature of the PT between the IC-phase and the ferrophase in $Sn_2P_2Se_6$ depends considerably on the cooling or heating rate.

Here we report on the result of the studies on the time dependence of dielectric permittivity of $Sn_2P_2S_6$ crystal in the wide temperature range which involves the vicinity of the second-order PT temperature. The influence of lighting and constant electric field on the relaxation processes has also been studied.

Investigations were carried out for the sample made from $Sn_2P_2S_6$ single crystal grown by Bridgeman method.

Temperature dependences $\varepsilon'(T)$ for $Sn_2P_2S_6$ crystal were measured in cooling mode after 3 hours annealing in the paraphase at 373 K. At 0.1 K/min cooling rate, $\varepsilon'(T)$ obeys the Curie-Weiss law within a wide temperature range, however, $\varepsilon^{-1}(T)$ is extrapolated to zero value at $T_0 = 335.2$ K. The deviation from that law is observed with the sample cooling rate reduction, i.e., $\varepsilon'$ values decrease within the range of $T_0$, $T_0 + 2$ K. In this case, the temperature of the maxima in $\varepsilon'(T)$ decreases too.

Long-term temperature stabilization in the paraphase at $T > T_0 + 2$ K does not result (with 1% accuracy) in $\varepsilon'$ variation. However, time relaxation of $\varepsilon'$ is distinctly revealed in $T_0$, $T_0 + 2$ K interval as well as in the ferrophase. Time variation of dielectric constant is described by exponential law

$$\varepsilon'_t = \varepsilon'_0 + \Delta\varepsilon' \exp(-t/\tau). \tag{3}$$

The temperature dependence of relaxation time $\tau$ was derived from the data on temperature variation of relaxation curves $\varepsilon'(T)$.[9]

The data obtained allow one to conclude that under the variation of cooling rate or at temperature stabilization in the critical region the ferroelectric second order PT with $T_0 = 335.2$ K observed in $Sn_2P_2S_6$ at conventional for experiments temperature variation rate $dT/dt > 0.1$ K/min is transformed in the sequence of two second-order ($T_i$) and first-order ($T_c$) transitions. General form of the dependence $\varepsilon'(T)$ and the presence of a temperature hysteresis in the vicinity of $T_c$ are similar to the behavior of dielectric permittivity observed at the sequential PT from the paraelectric phase to the incommensurate (IC) phase ($T_i$) and from the IC-phase to the ferrophase ($T_c$) in $Sn_2P_2(Se_xS_{1-x})_6$ crystals with Se content $x > x_{LP} = 0.28$.[5] The shape of field E-T diagrams for the intermediate state also coincides with that for the IC-phases of proper ferroelectrics.[10] These facts allow one to assume that the intermediate state

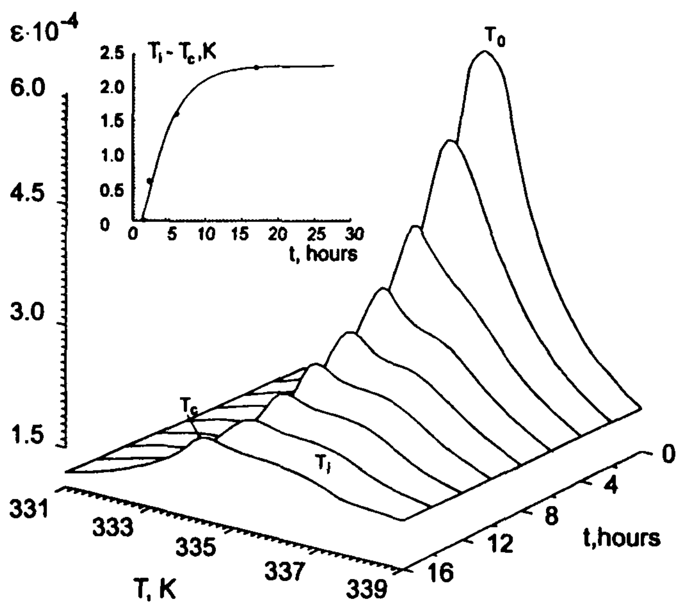


FIGURE 3 Time evolution of the dielectric permittivity anomalies in $Sn_2P_2S_6$ single crystals, and the time dependence of the intermediate state interval $T_i - T_c$.

which arises at the temperature stabilization of $Sn_2P_2S_6$ crystal in the vicinity of $T_0$ is the IC-phase

Crystals of $Sn_2P_2S_6$ family are the ferroelectrics-semiconductors. The relationship between the PT order parameter (spontaneous polarization) and the charge carriers plays an essential role in these crystals. An effective influence of lighting on the thermo-optical memory effect in the IC-phase of $Sn_2P_2S_6$ crystal with characteristic record time of about 5 hours[11] testifies that fact. Electron subsystem relaxation with exponential time variation of charge carriers density $m$ on the trapping level in the energy gap at the temperature fixation[12] seems to be a probable cause of long-time kinetics of $Sn_2P_2S_6$ ferroelectrics in the critical region

$$m = m_0 + \Gamma[1 - \exp(-t/\tau)]. \tag{4}$$

For $Sn_2P_2(Se_xS_{1-x})_6$, coefficients in (2) $\delta \sim (x_{LP} - x)$, $\beta \sim (x_{TCP} - x)$ and $g > 0$.[5] At $\delta < 0$, the IC-phase occurs with temperature width[4]

$$T_i - T_c \approx \frac{\delta^2}{4g\alpha_T}. \tag{5}$$

According to Reference 12, coefficients $\alpha_T$ and $\delta$ depend linearly on $m$:

$$\alpha_T(m) = \alpha_T + am, \quad \delta(m) = \delta + bm. \tag{6}$$

Thus, at $b < 0$, the IC-phase may appear in $Sn_2P_2S_6$ crystal and increase with time. Temperature interval between two anomalies in the dependence of $\varepsilon'(T)$ for $Sn_2P_2S_6$ really processes a time rise (Figure 3). In according with the estimation[2] for $Sn_2P_2S_6$ $\tau \approx 5 \div 300$ min and $T_i - T_c$ grows to 2.5 K.

The data on the time variation of the temperature dependence of dielectric permittivity in $Sn_2P_2S_6$ ferroelectric-semiconductor crystal as well as those on the influence of biasing electric field on the temperature interval of the existence of the intermediate state are described in terms of the model which assumes the relaxational splitting of the second-order PT (close to the LP) immediately from the paraelectric phase to the ferroelectric phase into the second-order and first-order PT which restrict the IC-phase. In this case, the main role in the transition kinetics is played by the relaxational process of carriers concentration variation changes on the trapping level. To obtain more complete notion of the nature of this effect, the diffractional studies of arising relaxational intermediate state are required. It is also important to take account the approach of the system to the TCP in the process of relaxation into the equilibrium state.

At $T < T_0$, $\tau$ does not depend, in fact, on the temperature and relaxation of $\varepsilon'$ is due to the domain structure rearrangement. Near-linear temperature variation of $\tau$ is peculiar to the mechanism of $\varepsilon'$ time relaxation in the paraphase close to $T_0$. It is important to note, that, according to the time variations of Cole/Cole diagrams in $Sn_2P_2S_6$,[9] the temperature dependence of equilibrium value of static dielectric permittivity, $\varepsilon'_{t\to\infty}(0)$ in the vicinity of $T_0$ deviates essentially from the Courie-Weiss law. Maximum in $\varepsilon'_{t\to\infty}(0)$ is reached below $T_0$ and the temperature dependence of $\varepsilon'_{t\to\infty}(0)$ reveals a clear band near $T_0 + 2$ K.

The data given above testify the complex kinetics of the ferroelectric PT in $Sn_2P_2S_6$ crystal, i.e. the change in its character when the system approaches the equilibrium state. The evolution of the temperature dependence of $\varepsilon'$ and $\varepsilon''$ during temperature stabilization at $T_0 + 1$ K is a prominent verification of this fact. With increasing stabilization time t, two maxima are distinctly revealed in the dependences $\varepsilon'(T)$ (Figure 3). In the cooling mode, the temperature separation of these maxima $(T_i - T_c)$ increases with time nearly reaching the saturation at $t > 17$ hours near 2.3 K. Temperature hysteresis is specific to the low temperature maximum location. The shape of $\varepsilon'(T)$ anomalies is almost constant with frequency variation within 1 Hz–100 KHz limits. In the equilibrium state, two maxima are also observed in the dependence $\varepsilon''(T)$ with low-temperature maximum of $\varepsilon''(T)$ being on the temperature axis below the corresponding maximum of $\varepsilon'(T)$.

Intermediate state in $Sn_2P_2S_6$ vanishes after sample heating to the paraphase as well as after the prolonged crystal exposure in the ferrophase.

It is important to note that sample lighting during temperature stabilization in the paraphase in the vicinity of $T_0$ promotes the intermediate state formation. So once the sample exposure at $T_0 + 1$ K in darkness for 6 hours results in the formation of two maxima in the dependence $\varepsilon'(T)$ with temperature separation of $T_i - T_c = 1.5$ K, then during the sample lighting by 2 mW power white light the value of $T_i - T_c = 2.3$ K is reached for the same exposure time.

Constant electric field applied along the polar [100] direction reduces the interval of the existence of the intermediate state (i.e., $T_i - T_c$, see Figure 4). In this case, $T_c$ increases linearly ($T_c(E) = T_c(0) + kE$) and $T_i$ decreases quadratically ($T_i(E) = T_i(0) - fE^2$) with electric field strength. Intermediate state produced by sample exposure at $T_0 + 1$ K in the darkness for 6 hours, vanishes at $E > 450$ V/cm.

It is important, that in intermediate state dielectric permittivity at $T_i$ and $T_c$ grows when $E_b$ increase. At the vanishing of intermediate state (if $E_b > 450$ V/cm) the maxima on the temperature dependences $\varepsilon'(T)$ is suppressed by bias electric field (Figure 4).

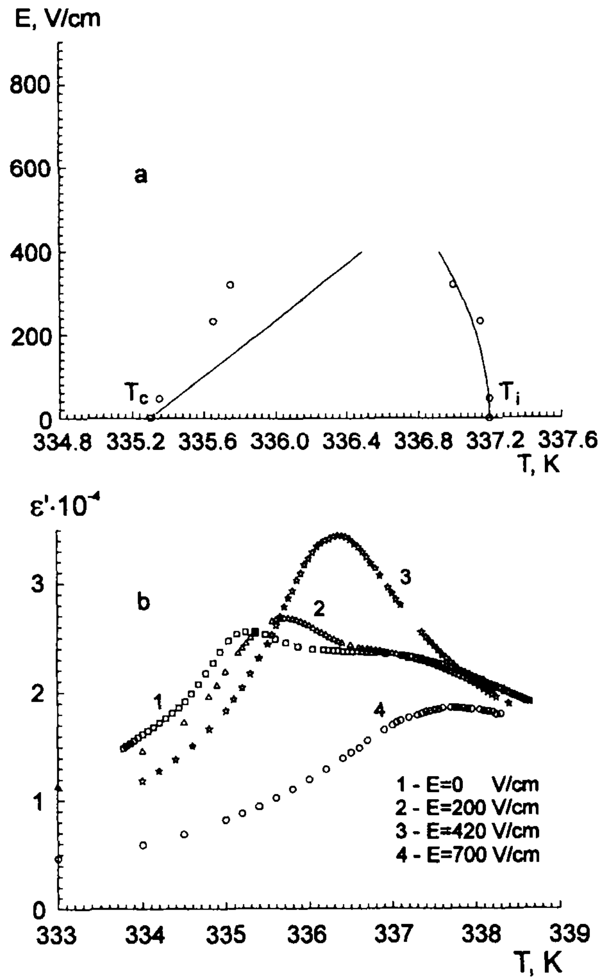


FIGURE 4 Influence of the external bias electric field on temperature interval of the existence of intermediate state (a) and on the view of dielectric permittivity anomaly in $Sn_2P_2S_6$ (b).

## MANIFESTATION OF THE CORRELATION FOR ORDER PARAMETER FLUCTUATION ON THE DIELECTRIC SUSCEPTIBILITY DATA

In the vicinity of phase transitions the anomalies of thermodynamic functions may differ appreciably from the predicted one in a mean field approximation. It is due to the presence in the critical region of clearly marked order parameter fluctuations, and the determinative role plays the force of an interaction between the fluctuations. The anomalies are described by the power functions, e.g., for temperature behaviour susceptibility[4] $\chi \sim \tau^{-\gamma}$, where $\gamma$ is critical index. In a mean field approximation $\gamma = 1$ for the second order phase transition and also for the tricritical point. Critical behaviour of the system is modified by the presence of a long-range dipole-dipole interaction, depressing the long-range fluctuation of the order parameter. This kind of situation is realized in proper ferroelectrics. Thus, uniaxial ferroelectrics are typ-

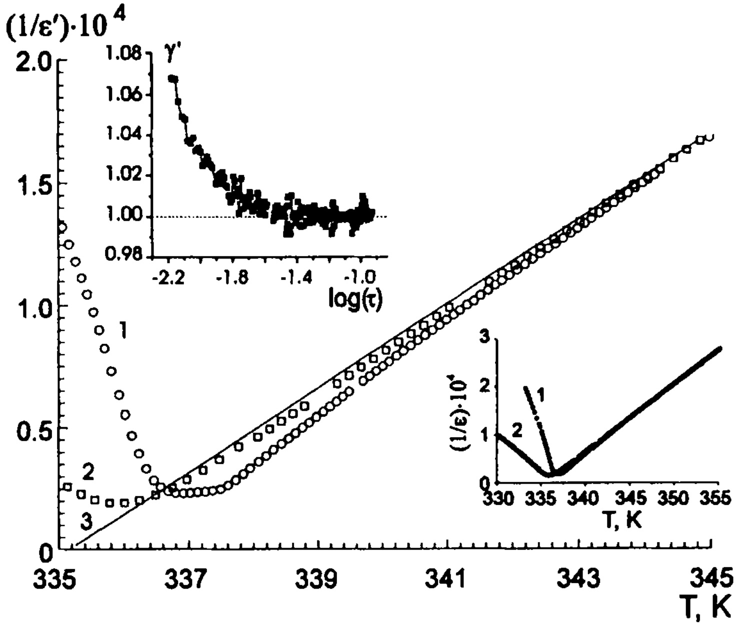


FIGURE 5 Temperature dependence of $1/\varepsilon'$ value in $Sn_2P_2S_6$ crystals obtained by gas transport method (1) and Bridgeman method (2). On the insertion the temperature variation of critical index effective value is shown.

ical of only weak logarithmic corrections to power functions, describing the anomalies of properties at the second order PT[13]: $\chi \sim \tau^{-1}(\ln \tau)^{1/3}$.

The situation is more complicated in the presence of multicritical points on the state diagram. As it was mentioned earlier for uniaxial ferroelectrics the close vicinity of the LP and TCP was observed in $Sn_2P_2(Se_xS_{1-x})_6$, where $x_{LP} \approx 0.28$, $x_{TCP} \approx 0.6$.[5] The concentrational and baric (for $Sn_2P_2S_6$) thermodynamic paths according to the estimations[5] lie near the tricritical Lifshitz point (TCLP). By means of renormgroup calculations in Reference 14 was determined the asymptotic behaviour for the LP and the TCLP with a single direction of modulation for uniaxial ferroelectrics. Thus, for the realized LP of a new type (dipole LP) it is expected $\gamma \approx 1.17$ and for the TCLP only logarithmic corrections to power functions with $\gamma = 1$ are possible.

The set of the effects of many factors (long-range interaction, multicriticity) stimulates the presence of the crossovers (the change in character) in critical behaviour. Thus, possible crossovers are: from classical (mean field) critical behaviour to fluctuational one at $\tau = G_i$; from critical behaviour to tricritical one at $\tau = \tau_{TCP}$.

Certainly, the defects strongly influence on the critical anomalies of crystal properties at PT. So in approximation of non-interacting defects for a uniaxial ferroelectric in the vicinity of the LP the contribution of the random field-type defects to a heat capacity anomaly has critical index $\alpha = 1.5$[15], and may exceed the fluctuational contribution.

Thus, critical behaviour of uniaxial ferroelectrics in the vicinity of the LP needs further refinement. It concerns first of all the study of a dielectric susceptibility constant which hadn't been reliably analyzed yet. Data of such investigations are presented below.

TABLE I

| Formula | $\varepsilon_0$ | $C$ | $T_0$ | $\gamma$ | Index b |
|---|---|---|---|---|---|
| $\varepsilon = \varepsilon_0 + \dfrac{C}{T - T_0}$ | 41 | 69550 | 335.58 | — | — |
| $\varepsilon = \varepsilon_0 + \varepsilon_1 T + \dfrac{C}{T - T_0}$ | 41 | 70100 | 335.6 | — | — |
| $\varepsilon = \varepsilon_0 + \dfrac{C}{(T - T_0)^\gamma}$ | 41 | 68592 | 336.14 | 1.07 | — |
| $\varepsilon = \varepsilon_0 + \dfrac{C}{T - T_0} \cdot \left\lvert \log \left( \dfrac{t_0}{T - T_0} \right) \right\rvert^b$ | 41 ± 3 | 63424 ± 10168 | 335.58 ± 0.035 | — | 0.33 ± 0.07 |

Figure 5 shows the temperature variation of reciprocal value of a dielectric constant for two $Sn_2P_2S_6$ single crystals (obtained by the Bridgeman and gas-transport techniques), measured at 10 kHz frequency in the field of measurement 0.5 V/cm at a cooling condition with constant rate of 0.1 K/min after annealing in paraphase at 373 K for three hours.

For a "gas-transport" sample at $T < 345$ K the deviation from the linear dependence $\varepsilon^{-1}(T)$ is clearly displayed. For the sample obtained from melt Curie-Weiss law is satisfied in a broad temperature interval (337 ÷ 395 K) with $C = 70500$ K constant. Note, that at $T > 345$ the $\varepsilon^{-1}(T)$ dependences for the two samples coincide in the limits of accuracy of experiment.

The deviation from Curie-Weiss law at $T < 345$ K for a vapour-transport sample is probably due to the presence of the effect of interacting fluctuations of the order parameter. At $T < 337.5$ K the smash of anomaly is clearly present and it is probably due to imperfect crystalline structure. The lack of the observed fluctuational deviation from Curie-Weiss law on the $\varepsilon^{-1}(T)$ dependence in case of the "Bridgeman" sample is probably due to a stronger influence of defects on the anomalies.

Further we shall analyze an undistorted by a long-time relaxation temperature behaviour of a dielectric permittivity for a vapour-transport sample in a paraelectric phase at $T > 337.5$ K. The background value $\varepsilon_0 = 41$ and it equals the dielectric permittivity of $Sn_2P_2S_6$ crystals at $T = 390$ K. Table I presents the data of $\varepsilon_0$, the Curie-Weiss constant $C$, the second-order PT temperature $T_0$, obtained from comparison of the experimental data with the function

$$\varepsilon = \varepsilon_0 + \frac{C}{T - T_0}. \tag{7}$$

The quality of approximation is illustrated by Figure 6. The deviation from Curie-Weiss law is obvious at $\log \tau \approx -1.6$ already.

An account of a temperature dependence of a background value of a dielectric permittivity using the relation

$$\varepsilon = \varepsilon_0 + \varepsilon_1 T + \frac{C}{T - T_0} \tag{8}$$

does not refine the quality of approximation. It is more adequate to observed $\varepsilon(T)$ dependence representation in a form of a power function

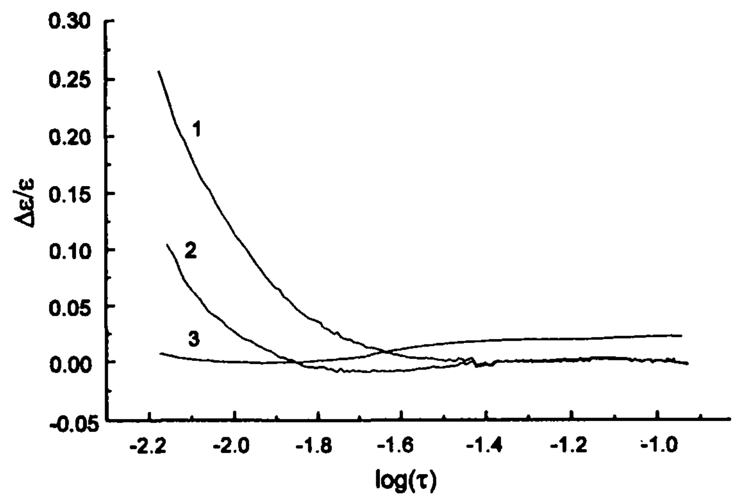


FIGURE 6 The deviation of $Sn_2P_2S_6$ paraelectric phase dielectric constant temperature dependence from used for approximation laws: 1—Curie-Weiss law; 2–power function; 3—Curie-Weiss law with multiplicative logarithmic correction.

$$\varepsilon = \varepsilon_0 + \frac{C}{(T - T_0)^\gamma}. \tag{9}$$

The best approximation is reached at an exponent $\gamma = 1.07$. However in this case the comparison is not satisfactory for $\log \tau < -1.8$. Thus, the observed behaviour of the dielectric permittivity of $Sn_2P_2S_6$ crystal is not described at a constant value of the critical index.

The effective index is determined as

$$\gamma_{eff} = -\frac{\partial \ln(\varepsilon - \varepsilon_0)}{\partial \ln(T - T_0)}.$$

It was determined that $\gamma_{eff}$ value is equal to a unit in a deep paraphase but is increases to 1.07 near $\log \tau = -2.2$.

The power function with a temperature dependent exponent can be substituted by Curie-Weiss law with a multiplicative logarithmic correction

$$\varepsilon = \varepsilon_0 + \frac{C}{T - T_0} \cdot \left| \log\left(\frac{t_0}{(T - T_0)}\right) \right|^b. \tag{10}$$

The best comparison with the experimental data (in the whole temperature interval the deviation is not higher than 3 percent, (see Figure 6) is reached with the parameters given in Table I. The increment of the amplitude of logarithmic correction at cooling to the PT shows that clear deviation from the Curie-Weiss law is observed at $T - T_0 < 10$ K.

To discuss the character of critical behaviour of a dielectric permittivity of $Sn_2P_2S_6$ crystal in the vicinity of the second-order PT it is convenient to present data in coordinates $\{(\varepsilon - \varepsilon_0)/[C/(T - T_0)]\}^{1/b} = f[\log(\tau)]$ (Figure 7). In the region of fulfilled Curie-Weiss law, i.e. at $\log \tau > -1.5$ a horizontal section is observed. However at $\log \tau < -1.5$ the linear interval on the discussed dependence is absent. Thus,

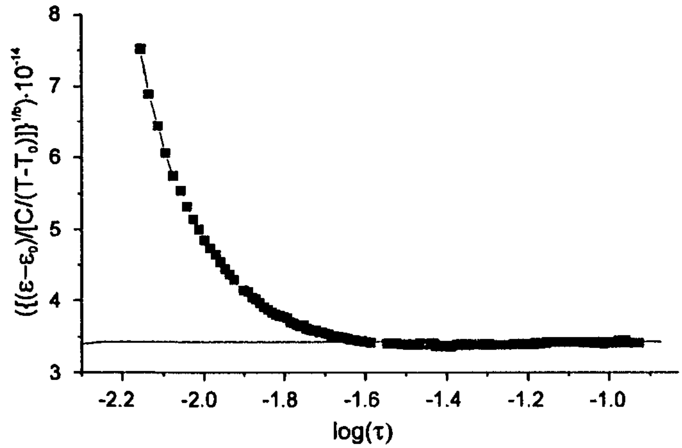


FIGURE 7 Dependence dielectric permittivity $Sn_2P_2S_6$ from logarithm of temperature plotted in special coordinates for detection of logarithmical change of $\varepsilon'$

though the logarithmic miltiplicative correction to Curie-Weiss law refines the quality of comparison with the experimental $\varepsilon(T)$ dependence for paraphase of $Sn_2P_2S_6$ crystal, however, we can not state the adequacy of such function with the observed critical behaviour.

Let us discuss the results of experimental data analysis. The second-order PT in $Sn_2P_2S_6$ is close to multicritical points on a state diagram temperature-composition-compression, i.e. to LP, TCP and TCLP. In uniaxial ferroelectric at cooling to TCP it is expected absolute fulfillment of Curie-Weiss law—$\gamma = 1$. For LP—$\gamma = 1(1/6) \approx 1.17$.[14] For TCLP Curie-Weiss law is modified by a logarithmic factor with unknown power index.[14] In case of the second-order PT distant from the above multicritical points, the $(\log\tau)^{1/3}$ correction is expected.[13] The lack for $Sn_2P_2S_6$ of a distinct linear section on $\{(\varepsilon - \varepsilon_0)/[C/(T - T_0)]\}^{1/b} = f[\log(\tau)]$ dependence (Figure 7) is probably due to the presence of crossover between two types of critical behaviour—the power Lifshitz behaviour and the logarithmic one.

## CONCLUSION

The field transformation of dielectric permittivity temperature anomalies which is caused by the second order PT in proper uniaxial ferroelectric $Sn_2P_2S_6$ confirms the nearness of this transition to TCP. However, for ferroelectrics-semiconductors, to which belong $Sn_2P_2S_6$ crystals, the character of critical behaviour strongly depends on the degree of nonequilibrium of electronic subsystem. Thus, at the decreasing of the cooling rate of the sample or at long duration temperature stabilization on the vicinity of PT in paraphase, the intermediate obviously incommensurate phase arising can be observed. Thus, the coordinates of Lifshitz point on phase diagram, and probably tricritical point too, depend on condition of temperature at measurings.

For uniaxial ferroelectrics the PT nearness to LP and TCP in total with suppressing the order parameter fluctuation by dipole-dipole long-range interaction allow to assume the presence of crossovers between different type of critical behaviour. Experimentally in paraphase on $Sn_2P_2S_6$ crystals for dielectric susceptibility the deviation from Curie-Weiss law was observed, which satisfactorily can be described by logarithmic multiplicative correction. However for reliable identification of critical behaviour of uniaxial ferroelectrics in the vicinity of tricritical Lifshitz point it is necessary to carry out additional investigations on the possible influence of crystal lattice defects.

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