
On the critical exponent of order parameter in $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals

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Abstract. We have determined critical exponents of the order parameter in ferroelectric $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals at the atmospheric pressure. They are equal to 0.29 ± 0.02 for $\text{Sn}_2\text{P}_2\text{S}_6$ and 0.24 ± 0.02 for $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$. These values suggest that, with changing selenium concentration from $x = 0$ up to $x = 0.28$, the solid solutions $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ approach the conditions of tricritical point, which is realised in the vicinity of $x = 0.28$. The conclusion agrees well with the results of our recent works derived with the other techniques.

Keywords: optical birefringence, ferroelectric phase transition, spontaneous strain, critical exponent

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1. Introduction

$\text{Sn}_2\text{P}_2\text{S}_6$ crystals represent a well-known ferroelectric material that undergoes a proper ferroelectric, second-order phase transition at 337 K [1]. The transition is accompanied by the point symmetry group change $2/mFm$ and by appearance of spontaneous electric polarisation, which is almost parallel to the crystallographic axis a . Many authors have noticed that the phase transition in $\text{Sn}_2\text{P}_2\text{S}_6$ is close to a number of specific polycritical points on the (x, T) -phase diagram of $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ solid solutions, namely a tricritical point (see, e.g., the recent work [2–5]), a Lifshitz point [1, 3, 6], or a tricritical Lifshitz point [7]. The results of our recent work [5] have testified that, at $x = 0.28$, the tricritical point should occur on the (x, T) -phase diagram of $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ rather than the Lifshitz one, whereas the triple point characterised by the appearance of incommensurately modulated phase should occur at some higher concentrations of selenium (e.g., at $x \geq 0.4$).

It is known that, according to the mean-field theory of phase transitions, the behaviour of physical properties of crystals can be characterised by a number of critical exponents, which acquire different values for different polycritical points on the phase diagram. For example, the classical value of the critical exponent β governing the temperature behaviour of the order parameter for uniaxial ferroelectrics is equal to 0.5 and this exponent should be 0.25 for the case of the tricritical point (see, e.g., [8]). The same β value, though with some logarithmic corrections [9], is predicted for the uniaxial ferroelectrics manifesting the tricritical Lifshitz behaviour. On the other hand, the β parameter should be 1/3 for the uniaxial ferroelectrics with the Lifshitz point or even lower (0.25) for a Lifshitz-type or a uniaxial tricritical Lifshitz-type phase transition. A similar behaviour takes place if one considers the critical exponent of heat

capacity for the uniaxial Lifshitz-type systems: the α value is then predicted to be $1/6$ [6, 9], whereas for the Lifshitz-type and uniaxial tricritical Lifshitz-type systems the critical exponent α should be equal to 0.25 and 0.5, respectively. Hence, the critical exponents can help in ascertaining which kind of a special polycritical point appears at the phase diagram.

The critical exponent β governing the behaviour of the order parameter in $\text{Sn}_2\text{P}_2\text{S}_6$ crystals has been determined to be equal to 0.42 [1], while for the solid solutions with $x \approx 0.3$ it has been found that $\beta = 0.2$ [10]. These values have been obtained on the basis of temperature behaviour of optical indicatrix rotation. On the other hand, the same authors have clarified [6, 11] the critical exponent for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals, following from optical measurements associated with the temperature dependence of optical birefringence. It has also been stated in the literature (see [11]) that the critical exponent β is temperature dependent and decreases from 0.5 down to 0.3 for the temperatures distant enough from the Curie point. Notice that such a temperature behaviour of β is quite unusual. The careful recent studies for the thermal diffusivity [2] have shown that the critical exponent α derived from these data amounts to 0.5 for all the temperature range outside the region of critical fluctuations. Moreover, it has also been demonstrated that anomalous part of the thermal diffusivity in the ferroelectric phase is well described in the frame of the mean-field theory outside the critical fluctuation region [2]. The same value α has been obtained on the basis of ultrasonic velocity measurements [12]. According to our recent data concerned with the temperature evolution of thermal expansion coefficients [13], the α parameter determined for the ferroelectric phase is equal to 0.52 ± 0.08 , thus agreeing well with the results [2, 12]. This α value is peculiar for the temperature behaviours of both the heat capacity and the thermal expansion coefficients for the crystals that stay under conditions close to the tricritical point on their phase diagram and, moreover, it does not agree with the value $\beta = 0.42$.

Let us now stress that the only parameter allowing direct determination of the critical exponent β for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals is the spontaneous polarisation or, at least, some secondary parameters directly induced by that polarisation. Unfortunately, there is the only one report in the literature regarding the temperature dependence of the spontaneous polarisation in $\text{Sn}_2\text{P}_2\text{S}_6$, which has been measured along a axis [1]. However, the mentioned data might not be reliable. Indeed, determination of the spontaneous polarisation in semiconductor materials represents a very complicated problem, due to screening effects and incomplete switching of domain structure. For instance, the critical exponent β evaluated from the data for the spontaneous polarisation [1] is equal to 0.75 for the temperature region close to the Curie temperature and it decreases down to 0.15 with decreasing temperature. The latter behaviour has no physical meaning from the viewpoint of classical Landau theory of second-order phase transitions. Thus, different critical exponents for $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ solid solutions disagree with each other or are determined with insufficient accuracy.

In our work [14] we have shown that determination of the critical exponent for the case of low-symmetry ferroelectric $\text{Sn}_2\text{P}_2\text{S}_6$ crystals, for which the spontaneous polarisation has two non-zero projections, P_1 and P_3 , represents a cumbersome problem. This is because the orientation angle of the spontaneous polarisation vector can be temperature dependent. The value of the critical exponent in the case of $\text{Sn}_2\text{P}_2\text{S}_6$ crystals obtained on the basis of spontaneous mechanical strains is close to $\beta = 0.24 \pm 0.02$ [13]. Notice that the mentioned value of β exactly corresponds

to the tricritical point. However, as shown in [4, 5], the tricritical point appears on the (x, T) -diagram at $x = 0.28$, while for the pure $\text{Sn}_2\text{P}_2\text{S}_6$ crystals we have that point on the (P, T) -diagram at $P = 4.3$ kbar and $T = 259$ K. Moreover, a reliable value of the critical exponent for $\text{Sn}_2\text{P}_2\text{S}_6$ obtained using the optical birefringence is equal to 0.3 [15]. The disagreement between the critical exponent and the coordinates of the tricritical point can be caused by the fact that the β value mentioned above has been obtained using the assumption that the angle between the a axis and the spontaneous polarisation vector is equal to 13 deg at the room temperature [16]. Notice that the angle value $\varphi = 13$ deg has been derived while searching for a spatial direction in which the dielectric constant reaches its maximum at the room temperature, although that direction can be somewhat different from the direction of the maximum spontaneous polarisation. Of course, temperature rotation of the spontaneous polarisation vector in the symmetry plane is permitted by symmetry. However, some other reasons can be responsible for the disagreement of the critical exponent data, too. In particular, as shown in [17], one cannot determine the exact phase transition point T_C taking into account a diffuse character of anomalies of different physical parameters (e.g., the optical birefringence) near T_C . As a consequence, the critical exponent could be estimated only roughly. Nonetheless, the study [17] has presented a method for evaluation of the critical exponent from diffuse anomalies obtained experimentally. On that basis the exact value of the critical exponent β has been determined, which is equal to 0.3 for $\text{Sn}_2\text{P}_2\text{S}_6$ crystals.

The goal of the present work is to analyse the temperature increments of the optical birefringence [15] and the relative mechanical elongations [13, 18] induced by the spontaneous polarisation and to determine in this way the critical exponent of the order parameter for both the $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals at the atmospheric pressure.

2. Results of analysis

Accounting for diffuse characters of both the thermal expansion and the birefringence anomalies near T_C (see [13, 15, 18]), we cannot determine the exact T_C value. As a consequence, the critical exponent can be found only approximately. In solving this problem, we apply the approach developed in the work [19]. Namely, we consider a phase transition diffused due to some scalar inhomogeneity, e.g., scalar defects. The latter do not change the symmetry of crystalline matrix, though their existence causes some distribution of the Curie temperature over a sample (this model is similar to that described in [8]). Then the phase transition temperature should be distributed over our sample within some temperature region $\Delta T = T_{CN} - T_{Cl}$, where T_{Cl} and T_{CN} are respectively the lowest and the highest Curie temperatures.

Now let us divide the sample into N homogeneous elementary cells (in our simulation we have taken N to be equal to 10^6). The Curie temperature of the i th cell is determined as $T_{Ci} = T_{CN} - i \times \Delta T / N$. Therefore the temperature dependences of the optical birefringence and the relative elongation increments may be described as

$$\delta(\Delta n)_i = \frac{A}{N} \sum_{i=1}^N (T_{CN} - i \times \Delta T / N - T)^{2\beta}, \quad (1)$$

$$\delta(\Delta L / L)_i = \frac{B}{N} \sum_{i=1}^N (T_{CN} - i \times \Delta T / N - T)^{2\beta}, \quad (2)$$

respectively. Here A and B are proportionality coefficients which should be the same for all the

elementary cells. The temperature dependences of the increments of relative elongations for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals are presented in Fig. 1 (see [13]).

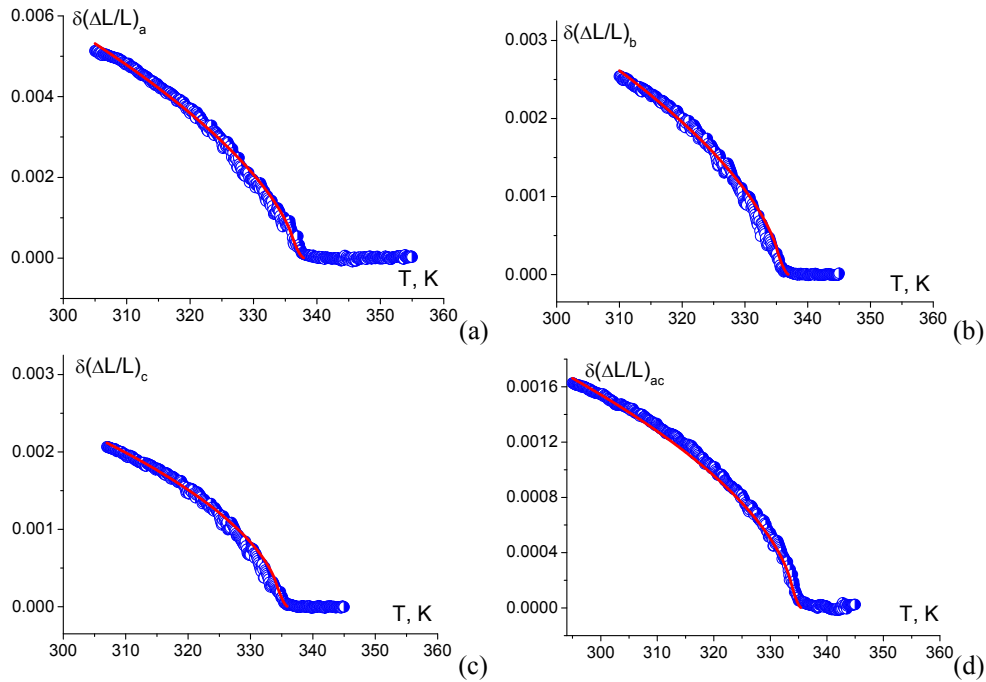


Fig. 1. Temperature dependences of relative elongation increments for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals (a) along a axis, (b) b axis, (c) c axis, and (d) bisector of a and c axes: circles denote experimental data and solid curves are fits based on Eq. (2).

As one can see from Fig. 1, the dependences mentioned are well fitted by Eq. (2), so that the power law $\delta(\Delta L/L)_i \sim (T_C - T)^{2\beta}$ is fulfilled. Indeed, since the increments of the relative elongation are induced by the spontaneous polarisation, due to electrostriction effect, they should be proportional to the square of the spontaneous polarisation, whereas the critical exponent describing the spontaneous polarisation itself should be equal to β . The same considerations remain true for the birefringence increment, which is again induced by the spontaneous polarisation, due to a quadratic Kerr effect. As seen from Table 1, the mean value of the critical exponent β is equal to 0.29 ± 0.02 , i.e. it is the same as obtained by us in the work [17] from the birefringence data. Since the values of the critical exponent obtained from different physical parameters for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals agree well, it is quite probable that the temperature dependence

Table 1. Critical exponents of the order parameter for the $\text{Sn}_2\text{P}_2\text{S}_6$ crystals.

Physical parameter under analysis	Critical index β	Parameter B , K^{-1}	Temperature T_{CN} , K	Coefficient of determination R^2
$\Delta L_a/L_a$	0.31	0.00062	338	0.997
$\Delta L_b/L_b$	0.30	0.00037	337	0.990
$\Delta L_c/L_c$	0.27	0.00035	336	0.990
$\Delta L_{ac}/L_{ac}$	0.28	0.00022	335.5	0.997
Mean value	0.29 ± 0.02		336.6 ± 1.1	

of spatial orientation of the spontaneous polarisation vector in the plane ac does not play an important part in determination of the β value.

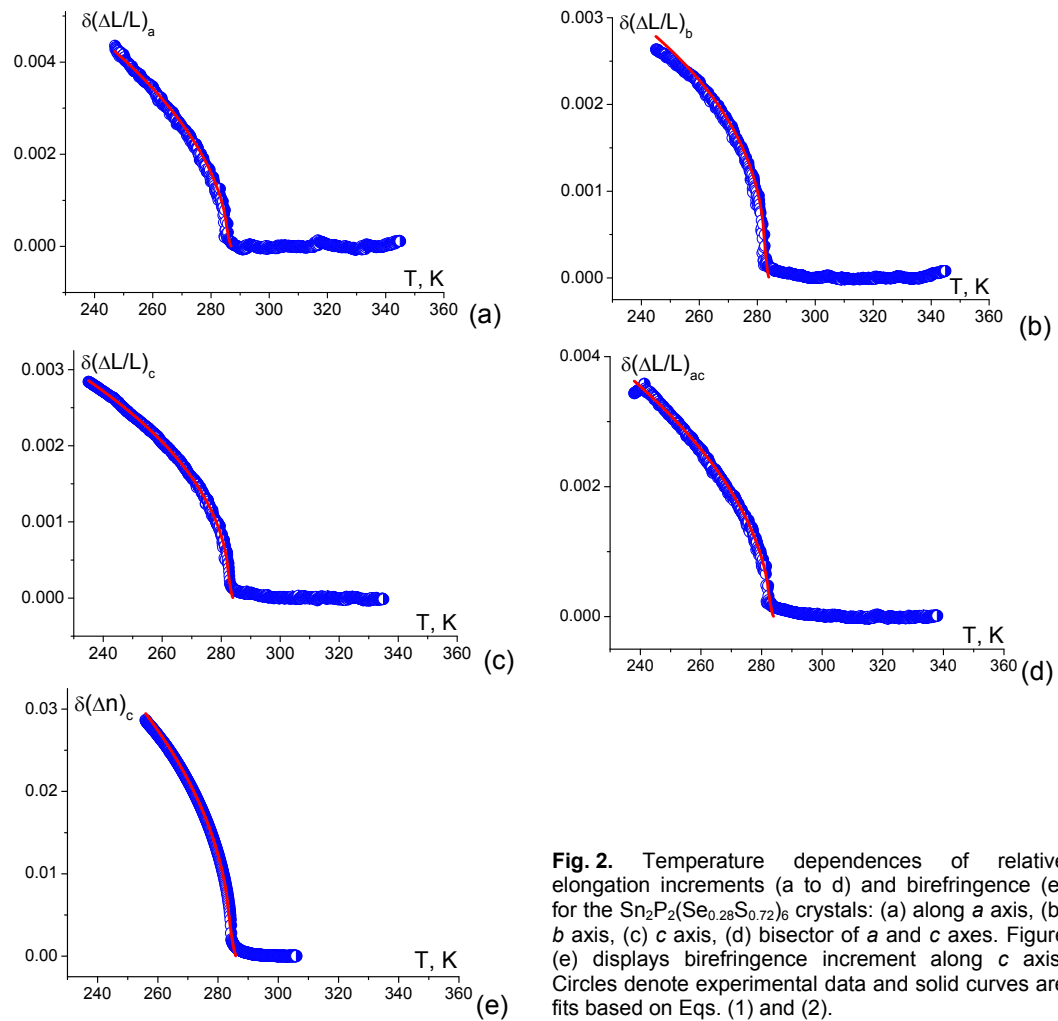


Fig. 2. Temperature dependences of relative elongation increments (a to d) and birefringence (e) for the $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals: (a) along a axis, (b) b axis, (c) c axis, (d) bisector of a and c axes. Figure (e) displays birefringence increment along c axis. Circles denote experimental data and solid curves are fits based on Eqs. (1) and (2).

Table 2. Critical exponents of the order parameter for the $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals.

Physical parameter under analysis	Critical index β	Parameters A or B, K^{-1}	Temperature T_{CN} , K	Coefficient of determination R^2
$\delta(\Delta n)_c$	0.24	0.0061	286	0.999
$\Delta L/L_a$	0.26	0.00063	287	0.998
$\Delta L/L_b$	0.21	0.0065	284	0.996
$\Delta L/L_c$	0.23	0.0005	284	0.999
$\Delta L/L_{ac}$	0.26	0.00052	284	0.998
Mean value	0.24 ± 0.02		285.0 ± 1.5	

The mean value of the critical exponent β for $\text{Sn}_2\text{P}_2(\text{Se}_{0.72}\text{S}_{0.28})_6$ has been evaluated from all the dependences presented in Fig. 2. It is equal to 0.24 ± 0.02 (see Table 2). This value

corresponds to the conditions of the tricritical point and agrees well with the conclusions drawn in our earlier work [5]. We have shown (see [5]) that a change in the phase transition order from the second-order one (at $x < 0.28$) to the first-order one (at $x > 0.28$) should occur in the solid solutions with $x = 0.28$.

3. Conclusions

Following from the results presented above, we conclude that the main reason for disagreement among the values of the critical exponent of the order parameter in $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ obtained in different works is a diffuse character of anomalies of the physical parameters measured in the vicinity of T_C . As demonstrated in our recent work [17], this diffuse character of the anomalies is caused by too high temperature change rates in the region of the phase transition. Of course, the temperature rotation of the spontaneous polarisation vector in the ac plane also can affect the accuracy of determination of the critical exponent, though this effect is probably quite small.

As a result, we have determined the critical exponents of the order parameter for the both $\text{Sn}_2\text{P}_2\text{S}_6$ and $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ crystals at the atmospheric pressure. These exponents are found to be equal 0.29 ± 0.02 for $\text{Sn}_2\text{P}_2\text{S}_6$ and 0.24 ± 0.02 for $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$. This suggests that the $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ solid solutions approach the conditions of the tricritical point when the selenium concentration changes from $x = 0$ up to $x = 0.28$. Then the tricritical point should appear somewhere in the vicinity of $x = 0.28$. This conclusion agrees perfectly with the results of our earlier study [5].

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***Анотація.** В даній роботі визначені критичні індекси параметру порядку для сегнетоелектриків $\text{Sn}_2\text{P}_2\text{S}_6$ і $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$ при атмосферному тиску. Вони дорівнюють 0.29 ± 0.02 для $\text{Sn}_2\text{P}_2\text{S}_6$ і 0.24 ± 0.02 для $\text{Sn}_2\text{P}_2(\text{Se}_{0.28}\text{S}_{0.72})_6$. Дані значення свідчать про те, що при зміні концентрації селену від $x = 0$ до $x = 0.28$, тверді розчини $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ прямують до умов трикритичної точки, яка реалізується в околі $x = 0.28$. Цей висновок узгоджується з результатами наших попередніх робіт.*