Comparison of critical fluctuations in $Sn_2P_2S_6$ and $Sn_2P_2(Se_{0.28}S_{0.72})_6$ crystals

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Abstract

We report on the quantitative parameters of fluctuation effects observed in the birefringence and linear thermal expansion of $Sn_2P_2(Se_xS_{1-x})_6$ crystals with $x = 0$ and 0.28. These parameters, including the Ginzburg number that governs the temperature width of the scaling region, are found to be of the same order of magnitude. The relevant implications concerned with the influence of structural defects and multicritical points on the phase diagram are discussed.

Keywords: $Sn_2P_2(Se_xS_{1-x})_6$ crystals, phase transitions, critical fluctuations, multicritical points

1. Introduction

Single crystals based on $Sn_2P_2(Se_xS_{1-x})_6$ solid solutions are known for their structural phase transformations and availability of multicritical points on their temperature–concentration–pressure phase diagram (see, e.g., [1]). They also reveal characteristics very promising for practical applications [2]. Recently there has been an upsurge in the interest of researchers in those crystals, which has included studies by more refined experimental techniques and re-examination of some obscure points concerned with their phase diagram (see the works [3–7], among many examples).

It is generally believed [1] that a specific multicritical point, a so-called Lifshitz point, exists on the phase diagram at the atmospheric pressure, which has the coordinates $T_{LP} \approx 283$ K and $x = 0.28$. At $x < 0.28$ one deals with a proper, second-order ferroelectric phase transition (PT) at T_0, which separates paraelectric (the point group 2/m) and ferroelectric (the group m) phases. At $x > 0.28$ an intermediate incommensurate phase appears, confined by a first-order PT point T_C and a second-order point T_i. Moreover, the PTs in the $Sn_2P_2(Se_xS_{1-x})_6$ family should not be far from a common tricritical point and a special virtual tricritical Lifshitz point [1]. However, too few convincing results have still been reported in the literature for the crucial selenium concentrations $0.2 < x < 0.6$, and this concerns, in the first place, the most reliable and decisive structural

data (see [8]). This is why we deem any further experimental investigations on the solid solutions $Sn_2P_2(Se_xS_{1-x})_6$ to be desirable.

It is known that the tricritical point and the Lifshitz point differ essentially in relation to critical thermal fluctuations observed near the critical temperature. If any multicritical points were absent, the order parameter fluctuations in the proper uniaxial ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$ would have been suppressed by long-range interactions and weak logarithmic corrections to the Landau theory would have been unobservable, except for extremely narrow scaling region around the Curie point [9]. The fluctuation phenomena should be very weak in the vicinity of the tricritical point, though they become strongly enhanced near the Lifshitz point (see, e.g., [1]). In other words, one can obtain some important, though indirect, information about the nature of multicritical point, which influences the physical properties of $Sn_2P_2(Se_xS_{1-x})_6$ crystals most of all, issuing from the size of critical fluctuations observed in reliable experiments.

In this brief report we compare the fluctuation phenomena for the cases of pure sulphur crystals ($x = 0$, $T_0 \approx 283$ K) denoted as SPS and solid solutions with $x = 0.28$ ($T_0 \approx 337$ K; denoted as SPSeS), employing an optical birefringence technique, which is very sensitive to structural transformations [10], and a supplementary linear thermal expansion technique. Although those techniques have earlier been applied to the crystal family under test long ago (see, e.g., [11–14]), the corresponding results are not detailed enough.

2. Results

The birefringence of SPS and SPSeS crystals grown with a vapour transport technique at the Uzhgorod National University was studied [15, 16] at the wavelength $\lambda = 632.8$ nm of a He–Ne laser with a standard Senarmont technique (the accuracy not worse than $(1 \div 2) \times 10^{-5}$). Relative elongations $\Delta d / d$ of samples due to the thermal expansion were measured [4, 17] using an automated quartz dilatometer (the accuracy $\sim 2 \times 10^{-6}$).

Fig. 1a shows the birefringence increments $\delta(\Delta n)_c$ for the SPS and SPSeS crystals calculated from the output optical Senarmont data in the assumption of invariable sample thickness. The $\delta(\Delta n)_c$ value is equal to the true birefringence Δn_c with the accuracy of an additive factor ($\delta(\Delta n)_c = \Delta n_c + \text{const}$). Therefore the shift of the $\delta(\Delta n)_c$ curves for different crystals on the ordinate scale (see Fig. 1a) has no strict physical meaning and is intended only for reducing overlap of those curves. In general, the main features of the $\delta(\Delta n)_c(T)$ dependences agree well with those found in the earlier studies [11, 12] for the concentrations $x = 0$ and 0.29.

One can see that the characters of the birefringence curves for the SPS and SPSeS are somewhat different near the PT point: we have an anomaly resembling a kink in the former case and a diffused, cusp-like anomaly in the latter. Temperature dependences of the relative elongations $(\Delta d / d)_c$ measured along the c axis are displayed in Fig. 1b. In

the close vicinity of the PT point the curves for the both crystals are qualitatively similar, with the same weak cusps. There is no evidence for the two successive PTs associated with existence of the incommensurate phase on the phase diagram (see Introduction), so that we will treat all the data considering that a single PT occurs at T_0.
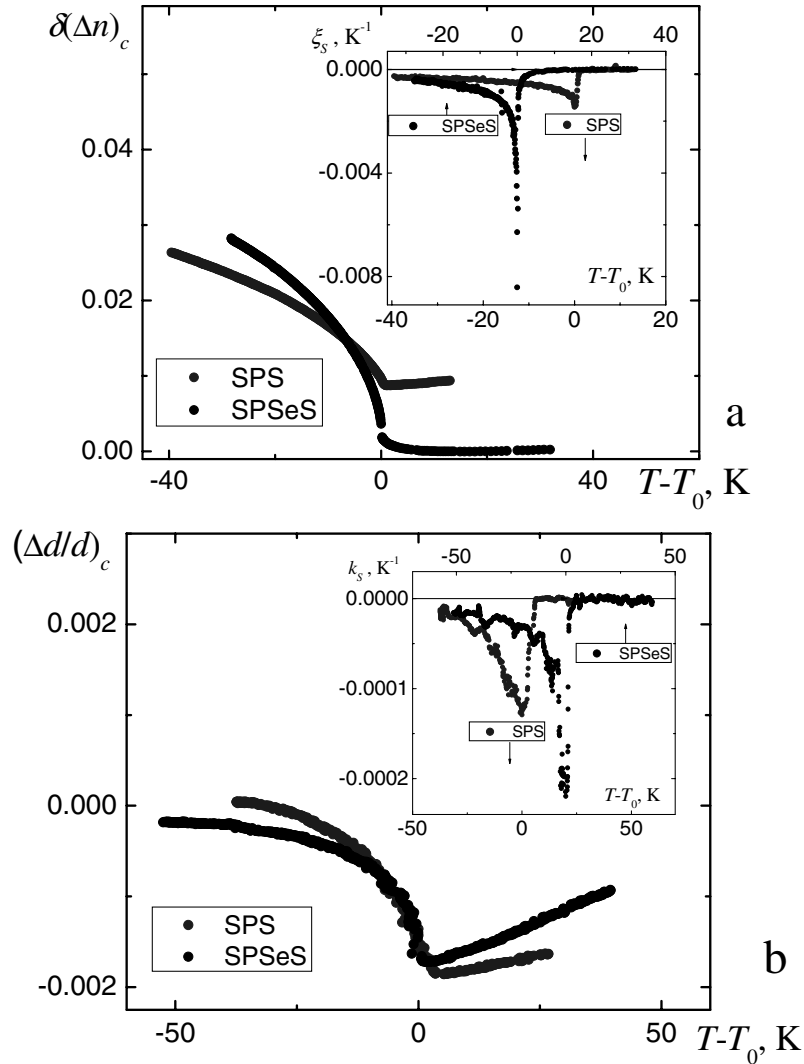

Fig. 1. (a) Temperature dependences of optical birefringence increments $\delta(\Delta n)_c$ for the light propagating along the crystallographic axis c in SPS ($\bullet$) and SPSeS ($\bullet$) crystals. The insert shows temperature derivative ξ_S of the spontaneous part of birefringence Δn_S. (b) Temperature dependences of relative elongations $(\Delta d / d)_c$ along the c axis for the SPS ($\bullet$) and SPSeS ($\bullet$) crystals. The insert shows anomalous part k_S of the linear thermal expansion coefficient calculated as temperature derivative of spontaneous relative elongations $(\Delta d / d)_S$. Notice that lower and upper abscissa scales in the both inserts correspond to the SPS and SPSeS, respectively.

To proceed with a quantitative analysis of our experimental data, we have determined spontaneous parts of birefringences (Δn_S) and relative elongations (($\Delta d / d)_S$) attributed to the effect of the PT. This can be done in a standard manner after subtracting thermooptic (or lattice) contributions from the initial $\delta(\Delta n)(T)$ (or $(\Delta d / d)(T)$) dependences. These contributions can be found from linear fittings of the data inside the paraelectric phase. Neglecting rotation of spontaneous polarisation vector with temperature in the symmetry plane [6, 15], on the basis of symmetry considerations (see the well known analysis [18]) one arrives at

$$\Delta n_S \propto \left\langle P^2 \right\rangle, \ (\Delta d / d)_S \propto \left\langle P^2 \right\rangle, \tag{1}$$

where $\left\langle P^2 \right\rangle$ is the equilibrium mean squared order parameter of the PT (i.e., spontaneous polarisation). According to Eqs. (1), we should have zero Δn_S and $((\Delta d / d)_S$ in all the paraelectric phase, i.e. the experimental dependences $\delta(\Delta n)(T)$ and $(\Delta d / d)(T)$ should be perfectly linear there. However, this is not so, in particular in the vicinity of the PT where clear precursor 'tails' are present (see Fig. 1). It is obvious that nonzero spontaneous birefringence and relative elongation in the paraelectric phase close to the Curie point are due to intrinsic (thermal) and/or extrinsic (defect-induced) fluctuations (see, e.g., [19, 20]).

Table 1. Parameters concerned with fluctuation effects in the vicinity of PT in the SPS and SPSeS crystals as obtained from the optical birefringence and linear thermal expansion (see explanations in the text).

Crystal	SPS		SPSeS	
Experimental data	Birefringence	Thermal expansion	Birefringence	Thermal expansion
$G \ (10^{-2})$	1.1	6.1	3.8	4.6
ΔT_{fluct} (K)	3.7	11.4	5.4	10.2
$\Delta n_S^{\text{fluct}}$ at $T = T_0$ (10^{-3}) or $(\Delta d / d)_S^{\text{fluct}}$ at $T = T_0$ (10^{-4})	1.1 –	– 6.1	3.8 –	– 4.6
$\mid \xi_S \mid$ maximum $(10^{-3} \ \text{K}^{-1})$ or $\mid k_S \mid$ maximum $(10^{-4} \ \text{K}^{-1})$	1.4 –	– 1.3	8.4 –	– 2.2

The main purpose of this study is to derive and compare quantitative parameters of those fluctuations in the SPS and SPSeS. The first parameter is quite natural: this is the values of the fluctuation tails just at the PT point, i.e. $\Delta n_S^{\text{fluct}}$ at $T = T_0$ and $(\Delta d / d)_S^{\text{fluct}}$ at $T = T_0$ (see Table 1). The other parameters may be found after differentiating numerically and smoothing the $\Delta n_S(T)$ and $(\Delta d / d)_S(T)$ dependences. The temperature

derivatives ξ_S and k_S of the spontaneous birefringence and relative elongations, respectively, are shown in the inserts of Fig. 1. Notice that k_S represents anomalous part of the linear thermal expansion coefficient. It is known [10, 21, 22] that the both derivatives should behave similarly to the heat capacity and can be described, at least qualitatively, by power-law relationships like

$$\xi_S \text{ (or } k_S) = A + B_- \mid \tau \mid^{-\alpha} \text{ (} \tau < 0 \text{),}$$

$$\xi_S \text{ (or } k_S) = B_+ \mid \tau \mid^{-\alpha} \text{ (} \tau > 0 \text{),} \tag{2}$$

where $\tau = (T - T_0)/T_0$ is the reduced temperature, A denotes a jump that follows from the Landau theory, $B_\pm$ the critical amplitudes for the parent ($\tau > 0$) and ferroelectric ($\tau < 0$) phases, and α the critical index determined by both the thermal fluctuations and the influence of structural defects [23].

The peak values of the derivatives detected in our experiments characterise indirectly 'strength' of the critical divergences given by Eqs. (2) and so they can be chosen as another parameter of the fluctuation effects near the critical point (see Table 1). The most important, parameter describing the fluctuation effects is the Ginzburg number G. It governs the temperature width of fluctuations so that the fluctuation-dominated scaling region and the region where the mean-field approach is valid are expected to be given respectively by the inequalities $\mid \tau \mid << G$ and $\mid \tau \mid >> G$, while at the temperatures $\mid \tau \mid \sim G$ a crossover between those regions region occurs. The G parameter can be defined as a reduced temperature at which the fluctuation-driven changes of the heat capacity are equal to the jump of the latter predicted by the Landau theory [24]. Since the temperature dependence of the derivatives ξ_S and k_S should be similar to that of the heat capacity, one can obtain the average Ginzburg numbers from the data presented in the inserts of Fig. 1 (see Table 1). Finally, recalculation of the G data to the absolute temperature scale results in the regions ΔT_{fluct} of notable fluctuations around the PT point, which are also shown in Table 1.

3. Discussion

Let us analyse the results obtained above. The most prominent effect seen in the birefringence near the T_0 point for the SPSeS crystals is a sharp ξ_S singularity, with the peak value 6.0 times larger than that observed for the SPS (see Fig. 1a and Table 1). The corresponding ratio for the k_S peaks is essentially less (1.7). However, the relative accuracy for the thermal expansion is lower than that for the birefringence (cf. the noises seen in the experimental curves of Fig. 1a and Fig. 1b) (cf. the noises seen in the experimental curves of Fig. 1a and Fig. 1b). Moreover, typical temperature variation rates used in Refs. [4, 17] have been higher than those used in Refs. [15, 16], thus hindering achieving a true thermodynamically equilibrium behaviour of the thermal expansion. We suppose the latter to be closely associated with the fact that the G and ΔT_{fluct} parameters

derived from $k_S(\tau)$ are appreciably larger than those derived from the $\xi_S(\tau)$ dependences. Strictly speaking, some part of the Ginzburg number obtained from experiments should be referred to deviations from the equilibrium conditions rather than the fluctuations themselves. As a result, the quantitative parameters derived on the basis of $\delta(\Delta n)(T)$ dependences seem to be more reliable. In spite of all these considerations, we are also to remind that manifestations of the fluctuation effects can, in principle, differ for different physical quantities [25].

It is our experience that the peaks of the birefringence derivative or the thermal expansion coefficient represent rather vague parameters, when compare to the fluctuation-induced spontaneous parameters $\Delta n_S^{\text{fluct}}$ or $(\Delta d / d)_S^{\text{fluct}}$ at the PT point. Indeed, the derivatives include additional errors associated with extra mathematical processing, including a necessary smoothing. Besides, the functions $\Delta n_S(T)$ and $(\Delta d / d)_S(T)$ are continuous in the critical point, unlike the functions $\xi_S(T)$ and $k_S(T)$. Therefore the $\Delta n_S^{\text{fluct}}$ or $(\Delta d / d)_S^{\text{fluct}}$ values can be found by simple interpolation in case if the temperature $T = T_0$ is not exactly reached in the experiments, though this is not the case for the peak ξ_S and k_S values. In other terms, the ratios of $\Delta n_S^{\text{fluct}}$ and $(\Delta d / d)_S^{\text{fluct}}$ values for the SPSeS and SPS represent more reliable parameters for comparison of the fluctuation effects. They are equal to 3.5 and 0.8 for the birefringence and thermal expansion, respectively.

As for the principal parameter, the Ginzburg number, we have $G_{\text{SPSeS}} / G_{\text{SPS}} \approx 1.7$ according to the birefringence and $G_{\text{SPSeS}} / G_{\text{SPS}} \approx 1.1$ according to the thermal expansion data (see Table 1). Notice also that our G values correlate fairly well with those reported in the literature ($G \sim 4 \times 10^{-2}$ for $Sn_2P_2S_6$ [12] and $G \sim 10^{-2}$ for $Sn_2P_2Se_6$ [13, 14]), especially if we consider that all the estimations are order-of-magnitude only [21]. Summing up, the fluctuation effects in the birefringence of SPSeS may be regarded as only two times larger than in SPS and almost the same in the thermal expansion.

Let us now recall that in the most of practical cases it is hardly possible to separate the intrinsic and defect-induced contributions to all of the fluctuation parameters under analysis, e.g., the Ginzburg number. It is important in this respect that all of the $Sn_2P_2(Se_xS_{1-x})_6$ crystals are less perfect than, say, crystals grown from aqueous solutions. As a theoretical analysis shows [20, 26], apart from smearing out the anomalies near the critical points, structural defects can induce enhancement of apparent fluctuation phenomena and give rise to sharper critical divergences of different physical parameters in this temperature region. Moreover, when comparing the data for the SPS and SPSeS, one has to keep in mind that the substitution atoms distort a crystalline lattice and create additional point structural defects. Therefore, structural perfection of any solid solution, especially the one with comparable contents of selenium and sulphur, must be lower, or essentially lower, than that of the pure crystals ($x = 0$ or 1). As a consequence, the defect

concentrations typical of the SPSeS crystals should almost certainly exceed those of the SPS. This is why we have some grounds or, at least, cannot exclude that somewhat larger 'total' fluctuation parameters obtained for the SPSeS crystals originate from the defects. Then a 'virtual' comparison of the fluctuations in defect-free SPS and SPSeS would have shown approximately the same quantitative parameters or even would have given evidence concerning stronger thermal fluctuations in SPS. Of course, these considerations need thorough experimental verification.

In conclusion, a comparison of $Sn_2P_2(Se_xS_{1-x})_6$ crystals with $x = 0$, 0.28 and 1, involving both the birefringence and thermal expansion results and the earlier data on the birefringence [11–13], indicates that the crystals with the x values close or equal to 0.28 do not differ too much by the fluctuation parameters, when compare with all the other selenium concentrations. At the same time, the Lifshitz point at the concentration $x \approx 0.28$ should reveal much more striking fluctuation effects in different physical characteristics, when compare with the other concentrations x, including $x = 0$. In other words, there should have been a drastic difference between the quantitative fluctuation parameters obtained for the SPS and SPSeS, which has not been observed in the present studies. We therefore infer that the presence of the Lifshitz point on the phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ crystals affects the properties of the crystals with $x = 0$, 0.28 and 1 in a similar manner.

A presence of the common tricritical point not too far from $x = 0.28$ also cannot be excluded as an explanation of our experimental results. On the other hand, the situation can be even more complicated when the fluctuation effects are a result of 'superposition' of the Lifshitz point and the tricritical point. In order to derive more decisive information regarding the influence of multicritical points of different kinds on the properties of $Sn_2P_2(Se_xS_{1-x})_6$ solid solutions, more detailed and versatile studies are needed, which should involve the other physical characteristics and self-consistent consideration of the critical indices. The corresponding analysis will be the subject of a forthcoming paper.

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Анотація. *У роботі наведено кількісні параметри флуктуаційних ефектів, які спостерігаються в двозаломленні та лінійному термічному розширенні кристалів $Sn_2P_2(Se_xS_{1-x})_6$ із x = 0 and 0.28. Виявлено, що ці параметри, включно з числом Гінзбурга, яке обумовлює температурну ширину діапазону скейлінгу, за порядком величини однакові. Обговорено відповідні наслідки, пов'язані із впливом структурних дефектів та існуванням полікритичних точок на фазовій діаграмі.*