Critical behavior of $Sn_2P_2(Se_xS_{1-x})_6$ uniaxial ferroelectrics near the Lifshitz point

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A study is made of the temperature dependence of the parameters of the optical indicatrix, specific heat, and Raman scattering at high and low frequencies for the proper uniaxial ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$, the phase diagram of which exhibits a Lifshitz point separating the phase transitions to commensurate and incommensurate phases. It is found that the approach of the system to the Lifshitz point is accompanied by a change in the character of the temperature dependence of the order parameter, a growth in the amplitude and temperature interval of the corrections to the Landau-theory behavior of the specific heat, and an increase in the intensity of the light-scattering near the phase transition. The experimental results, which possibly reflect an enhancement of the role of order-parameter fluctuations near the Lifshitz point, agree with the estimate of the temperature width of the fluctuation region: The Ginzburg-Levanyuk parameter for $Sn_2P_2Se_6$ lies in the range 10^{-1}–10^{-2}.

On changes in the composition of mixed crystals of the proper uniaxial ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$ the second-order phase transition, with change of symmetry $P2_1/c \rightarrow Pc$ (in $Sn_2P_2S_6$ the phase transition from the paraphase to the ferrophase occurs at $T_0 = 339$ K), splits into first-order and second-order transitions bounding an intermediate incommensurate phase (in $Sn_2P_2Se_6$ the phase transitions from the paraphase to the incommensurate phase and from the incommensurate phase to the ferrophase occur at $T_i = 221$ K and $T_c = 193$ K, respectively).[1] The Lifshitz point, which separates the transitions from the paraelectric to the ferroelectric and incommensurate phases[2,3] occurs at $x_L \approx 0.28$ on the concentration phase diagram. For compositions with $x < x_L$ the Lifshitz point can also be reached by increasing the power of the laser radiation illuminating the sample.[4]

The phase diagram of the given compounds and the anomalies of their physical properties near the Lifshitz point were considered in Ref. 5, where, in particular, it was pointed out that the specific heat anomaly at the line of second-order transitions increases as the Lifshitz point is approached. This fact and also the shape of the temperature dependence of the specific heat (λ anomaly)[6] disagree with the predictions of Landau theory. It has also been found that the light-scattering intensity in the crystal $Sn_2P_2S_6$ increases as the temperature approaches the phase transition near the Lifshitz point.[7]

The aforementioned critical anomalies of the static and dynamic properties of $Sn_2P_2(Se_xS_{1-x})_6$ crystals may be due to the growth of order-parameter fluctuations near the phase transition. It is known,[8–10] however, that fluctuation effects are substantially suppressed in uniaxial ferroelectrics; moreover, deviations from Landau theory can be caused by defects,[11] so that the experimental identification of fluctuational anomalies is a very complex problem. The Lifshitz point has the distinctive property that the correlation length for order-parameter fluctuations decreases sharply near it. Therefore, as the Lifshitz point is approached, the role of defects can be diminished and that of fluctuations enhanced. This conclusion follows from the results of Ref. 11 and is discussed in detail below. The ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$ thus offer a convenient possibility for revealing the fluctuational anomalies; this is the goal of the present study.

EXPERIMENTAL RESULTS

Mixed crystals of $Sn_2P_2(Se_xS_{1-x})_6$ were subjected to temperature studies of the parameters of the optical indicatrix and the intensities of the high-frequency modes in the Raman scattering spectra that become inactive in the centrosymmetric phase. These studies permit one to follow the temperature dependence of the order parameter at the transition through the Lifshitz point. The temperature dependence of the specific heat[6] was analyzed. The intensity of the light-scattering in the low-frequency region 5–120 cm^{-1} and its temperature dependence at fixed frequencies (isofrequency Raman scattering)[12] were studied both for samples of different compositions and as a function of the power of the exciting radiation at a fixed composition. The purpose of these studies was to obtain information about changes in the relative intensity of one-phonon and two-phonon scattering as the Lifshitz point is approached.

The Raman-scattering studies were done on a DFS-24 spectrometer with a spectral resolution $\Delta\nu \approx 1$ cm^{-1}. The scattering was excited by polarized light from He–Ne (6328 Å) and Kr (6471 and 6764 Å) cw gas lasers. The laser power was determined with the aid of an IMO-2 calorimeter. The signal was detected by an OF-1L photon-counting system, and the spectral line shapes were analyzed on a computer. During the measurements of the optical constants and the Raman spectra the temperature was stabilized to within 0.1 K, and in the studies of isofrequency Raman scattering its rate of change was 0.2 K/min or less. X-ray oriented single-crystal samples with typical dimensions of $3\times4\times5$ mm^3 were grown by gas-transport reactions.[1] The composition of

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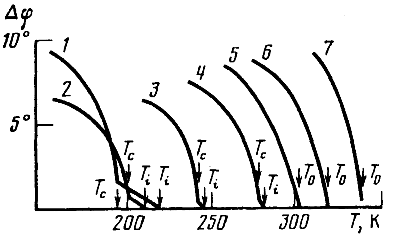

FIG. 1. Temperature dependence of the rotation angle of the plane of the optic axes in $Sn_2P_2(Se_xS_{1-x})_6$ crystals on cooling for various values of x: 1) 1, 2) 0.8, 3) 0.5, 4) 0.3, 5) 0.2, 6) 0.1, 7) 0. The rotation angle was measured from the linear extrapolation of the $\varphi(T)$ curve in the paraphase to the low-temperature region.

the samples was monitored by chemical analysis. The coordinate system was chosen with the Y axis perpendicular to the symmetry plane and the X axis along the [100] direction (in the unit cell of Ref. 13), which is close to the direction of the spontaneous polarization P_s.

The transformation of the temperature dependence of the rotation angle $\Delta\varphi$ of the plane of the optic axes in $Sn_2P_2(Se_xS_{1-x})_6$ under cooling is shown in Fig. 1. Below the temperatures of the transitions from the paraphase, i.e., in the ferrophase for $x < x_L$ and in the incommensurate phase for $x > x_L$, the temperature dependence of $\Delta\varphi$, which is proportional to η^2, yields information on the nature of the temperature dependence of the order parameter. Analysis of the dependence of $\Delta\varphi$ on $\tau \equiv (T_0 - T)/T_0 \equiv (T_i - T)/T_0$ on the assumption of power-law behavior of the order parameter $\eta \sim [T_0(T_i) - T]^\beta$ implies that the critical exponent β is equal to 0.42, 0.36, 0.33, 0.20, 0.28, 0.30, and 0.46 (with an uncertainty of ± 0.02) respectively for $x = 0$, 0.1, 0.2, 0.3, 0.5, 0.8, and 1, i.e., β decreases as the Lifshitz point is approached.

Figure 2 shows the temperature dependence of the high-frequency (≈ 550 cm^{-1}) bands in the Raman spectra. At the transition to the paraphase these bands become Raman-inactive; their intensity is proportional to the square of the order parameter.[7] Analysis of the spectroscopic data (the inset in Fig. 2) also shows that the critical exponent for the order parameter decreases strongly as the Lifshitz point is approached—from 0.44 at $x = 0$ to 0.18 at $x = 0.3$.

According to the data of calorimetric studies,[6] the anomaly of the isobaric specific heat C_p (the anomaly is measured with respect to the linear extrapolation of the specific heat in the paraphase) in $Sn_2P_2(Se_xS_{1-x})_6$ crystals on the line $T_0(x)$ of second-order phase transitions from the paraphase to the ferrophase increases as the Lifshitz point is approached for $x < x_L$. Here the anomalous temperature dependence of C_p below T_0, like that in the paraphase, becomes stronger. The behavior of the specific heat at the transition T_i from the paraphase to the incommensurate phase is closest to the "step" predicted by Landau theory for $Sn_2P_2Se_6$. However the height of the anomaly at T_i and also the height of the "tail" of $C_p(T)$ in the paraphase increase on approach to x_L.

The data shown in Fig. 3 for $x = 0$, 0.1, 0.2 indicate that the behavior of ΔC_p in a certain temperature interval can be compared with the logarithmic fluctuation corrections characteristic for uniaxial ferroelectrics[8]:

$$\Delta C_p \propto |\ln|\tau|^{-1}|\delta^{-3/2}.$$

Here the coefficient δ is a combination of the quantities δ_{ij} in the plane perpendicular to the direction of P_s. Because one of these quantities (namely that along the wave vector of the modulation) $\delta_0 \sim |x - x_L|$ (Ref. 14), the amplitude of the corrections and the temperature interval in which they are present should increase as the Lifshitz point is approached, in agreement with the experimental results (Fig. 3a).

It is known[15] that in the presence of strong fluctuations the two-phonon light-scattering is comparable in intensity to the one-phonon scattering. One can therefore obtain direct information on the growth of order-parameter fluctuations near the phase transition by studying the Raman scattering.

The integrated Raman intensity I for $Sn_2P_2S_6$ at frequencies 5–120 cm^{-1} in the $Z(XX)Z$ geometry, in which the soft optical mode associated with the phase transition is active for $T < T_0$, increases as the transition temperature is approached from either side (inset in Fig. 4). This correlates with the aforementioned behavior of the specific heat of this crystal[6] and disagrees with the step-like behavior predicted by Landau theory.

A convenient method of obtaining information on the behavior of the intensity ratio of one-phonon and two-phonon scattering is to study the isofrequency temperature dependence of the Raman intensity I_ω. Figure 4 shows the corresponding curves, normalized by the intensity of an individual high-frequency one-phonon band, for a frequency of 6 cm^{-1}. We see that the growth of the isofrequency intensity I_ω as the phase transition is approached from the paraphase is maximum for the composition with $x = 0.2$, which is closest to $x \approx 0.28$. This confirms the predominance of two-phonon scattering over one-phonon scattering at low frequencies near a transition close to the Lifshitz point.

It has been reported[4] that for a fixed composition, for example $x = 0.2$, the Lifshitz point can be induced by in-

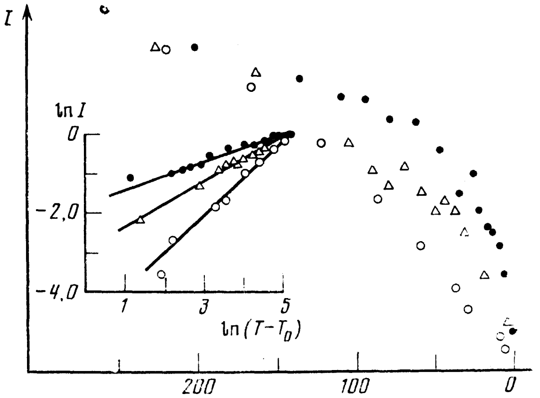

FIG. 2. Temperature dependence of the integrated intensities of the high-frequency (≈ 550 cm^{-1}) modes in $Sn_2P_2(Se_xS_{1-x})_6$ for $x = 0$ (○), 0.2 (△), and 0.3 (●). The intensities are normalized to unity at $T_0 - T = 220$ K. In logarithmic coordinates (inset) the curves are approximated by straight lines with slopes of 0.88, 0.54, and 0.36, respectively.

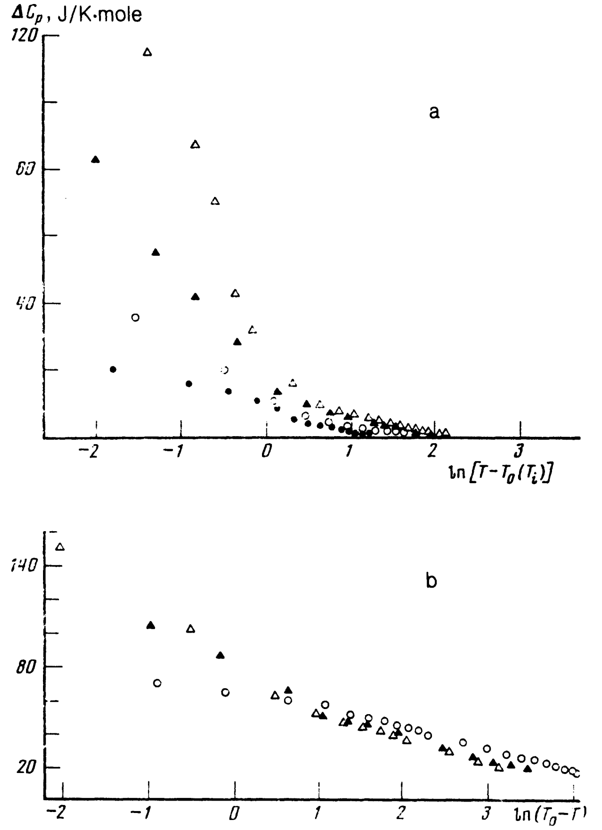

FIG. 3. Temperature dependence of the anomalous part of the specific heat of $Sn_2P_2(Se_xS_{1-x})_6$ crystals in the paraphase (a) and ferrophase (b) for $x=0$ (○), 0.1 (▲), 0.2 (△), and 1 (●).

creasing the power of the laser radiation on the sample. One can get closer to the Lifshitz point by a smooth change in the power than by a discrete change in the chemical composition of the samples. In fact, as the Lifshitz point was approached by increasing the power of the radiation exciting the Raman scattering from 0.05 to 0.2 W (the waist diameter was 0.2 mm), the maximum intensity of the isofrequency scattering at the phase transition increased substantially (Fig. 4). This agrees with the changes in $I_\omega(T)$ as the Lifshitz point is approached by changing the concentration and also indicates that fluctuation effects play an important role near the Lifshitz point.

DISCUSSION OF THE RESULTS

The condition for applicability of Landau theory is the Ginzburg-Levanyuk criterion, which ensures that the fluctuations are sufficiently small and which can be written[15,16]

$$\tau \gg T_0\beta^2/\alpha_T\delta^3 \equiv \mathrm{Gi}, \qquad (1)$$

where Gi is the Ginzburg number, α_T, β, and δ are the coefficients in the expansion of the thermodynamic potential in the order parameter:

$$\Delta\Phi=\alpha_T(T-T_0)\eta^2+\beta\eta^4+\delta(\nabla\eta)^2+g(\nabla^2\eta)^2. \qquad (2)$$

For the phase transition to the incommensurate phase in a uniaxial ferroelectric with one-dimensional modulation, the Ginzburg-Levanyuk criterion is of the form[17]

$$\tau' \gg T_i\beta^2/\alpha_T\delta_a{}^2\delta_0, \qquad (3)$$

if it is assumed that the components of the tensor δ_{ij} in the directions orthogonal to the modulation vector in reciprocal space are of the usual "atomic" order δ_a.

In uniaxial ferroelectrics the long-range dipole-dipole interaction substantially limits the phase volume occupied by critical fluctuations in momentum space. Because of this, the temperature dependence of the thermodynamic quantities as $\tau\to 0$ is described by the Landau relations with logarithmic fluctuation corrections.[8–10] At the same time, in the immediate neighborhood of the phase transition the contribution of defects to the anomalies in the physical quantities has a stronger temperature dependence than does the contribution from order-parameter fluctuations.[11] The latter contribution can dominate only quite far from the phase transition. However, on a decrease in the coefficient δ [analogous to a decrease in the correlation length ($r_c^2\sim\delta$)] at fixed τ, the fluctuation contribution can increase and the defect contribution decrease. This is seen from the expressions for the corrections to the specific heat due to the fluctuation contribution $\Delta C_{\mathrm{fl}}\propto\delta^{-3/2}$ and, for example, quenched random defects $\Delta C_{\mathrm{def}}\propto\delta^{3/2}$ (Ref. 11). Such a situation is possible near the Lifshitz point, on approach to which one of the components δ_{ij} (namely δ_0) goes to zero. It is natural to assume that upon transition through the Lifshitz point the change in the order parameter at a defect is insignificant, being determined by its short-range interaction with the atoms of the crystal lattice. As we have mentioned, $\delta_0\sim|x-x_L|$ for the ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$. Therefore, a study of the mixed crystals $Sn_2P_2(Se_xS_{1-x})_6$ can reveal the critical fluctuational anomalies.

Let us estimate the Ginzburg number Gi for the crystals under study. The experimental data on the dielectric constant yield the expansion coefficients α_T and β for the crystals $Sn_2P_2S_6$ and $Sn_2P_2Se_6$. For $Sn_2P_2S_6$ we have $\alpha_T=12.6\cdot10^{-5}$ K^{-1}, $\beta=0.14\cdot10^{-12}$ esu, and transition temperature $T_0=339$ K, while for $Sn_2P_2Se_6$ we have $\alpha_T=17.6\cdot10^{-5}$ K^{-1}, $\beta=0.2\cdot10^{-12}$ esu, and $T_i=221$ K. We find the coefficient δ_0 from the relation $T_i-T_c=1.1\delta_0^2/g\alpha_T$, from which we eliminate the coefficient g in (2), knowing that the wave vector $\mathbf{q}_0$ of the modu-

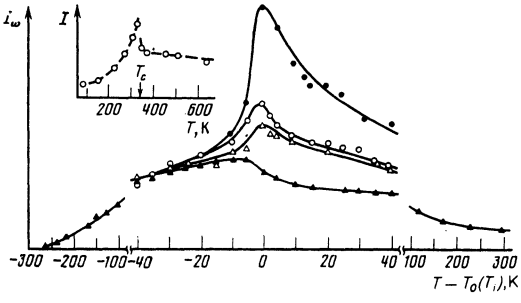

FIG. 4. Temperature dependence of the Raman intensity at a frequency of 6 cm^{-1} in the $Z(XX)Z$ geometry for $Sn_2P_2(Se_xS_{1-x})_6$ crystals with $x=0$ (▲), 0.2 (○), and 0.4 (△) at a laser radiation power $P=0.05$ W ($\lambda=6471$ Å) and for a crystal with $x=0.2$ (●) at $P=0.2$ W. The inset shows the temperature dependence of the integrated light-scattering intensity from the $Sn_2P_2S_6$ crystal in the range 5–150 cm^{-1} for the $Z(XX)Z$ geometry ($P=0.05$ W).

lation of the incommensurate phase is related to g by $q_0^2 = -\delta_0/2g$ and is equal to $\approx 10^7$ cm^{-1} (Ref. 18). For the crystal $Sn_2P_2Se_6$, in which the width $T_i - T_c$ of the incommensurate phase is 28 K, we obtain $|\delta_0| \sim 10^{-16}$ cm^2. Using relation (3), we obtain for the Ginzburg number $\mathrm{Gi} \approx 2 \cdot 10^{-2}$, assuming that $\delta = \delta_0$ along the direction of the modulation wave vector $\mathbf{q}_0$ and that $\delta = \delta_a \sim 10^{-17}$ cm^2 in the two orthogonal $\mathbf{q}$ directions. For $Sn_2P_2S_6$ the value of the parameter Gi is over twice as large. Consequently, in this crystal the strong-fluctuation region is more than twice as wide as in $Sn_2P_2Se_6$. As we see from criterion (3), the region in which Landau theory applies gets larger as the Lifshitz point is approached, since $\delta_0 \rightarrow 0$. The incommensurate phase of $Sn_2P_2(Se_xS_{1-x})_6$ crystals is probably found in the fluctuation region.

The Lifshitz point has been the subject of many theoretical studies (see, e.g., Refs. 2, 19, and 20). It was shown in these studies that as the Lifshitz point is approached, the critical exponent of the order parameter decreases substantially, while the exponents of the specific heat and susceptibility increase relative to their values from Landau theory. However, those studies considered a situation in which the form of the dispersion relation of the stiffness for the order parameter was not subject to renormalization by fluctuation corrections. In the case of $Sn_2P_2(Se_xS_{1-x})_6$ crystals, because of their low symmetry, fluctuations can alter the form of the soft dispersional branch, i.e., it becomes temperature dependent. Such a situation is similar to that in quartz[21,22] and has previously not been considered in relation to the Lifshitz point. It is therefore impossible to make a detailed comparison of the observed and theoretical asymptotic temperature behavior in the critical region of the proper uniaxial ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$ near the Lifshitz point.

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[1] Yu. M. Vysochanskiĭ, M. I. Gurzan, M. M. Maĭor, *et al.*, Fiz. Tverd. Tela (Leningrad) **27**, 858 (1985) [Sov. Phys. Solid State **27**, 525 (1985)].

[2] R. M. Hornreich, M. Luban, and S. Shtrikman, Phys. Rev. Lett. **35**, 1678 (1975).

[3] T. A. Aslanyan and A. P. Levanyuk, Fiz. Tverd. Tela (Leningrad) **20**, 804 (1978) [Sov. Phys. Solid State **20**, 466 (1978)].

[4] Yu. M. Vysochanskiĭ, V. G. Furtsev, M. M. Khoma, *et al.*, Zh. Eksp. Teor. Fiz. **89**, 939 (1985) [Sov. Phys. JETP **62**, 540 (1985)].

[5] M. M. Khoma, M. M. Maĭor, Yu. M. Vysochanskiĭ, and V. Yu. Slivka, Kristallografiya **31**, 734 (1986) [*sic*].

[6] M. M. Maĭor, B. M. Koperles, B. A. Savchenko, *et al.*, Fiz. Tverd. Tela (Leningrad) **25**, 214 (1983) [Sov. Phys. Solid State **25**, 117 (1983)].

[7] A. A. Grabar, Yu. M. Vysochanskiĭ, V. G. Furtsev, *et al.*, Ukr. Fiz. Zh. **31**, 908 (1986).

[8] A. P. Levanyuk, Izv. Akad. Nauk SSSR Ser. Fiz. **29**, 879 (1965).

[9] V. G. Vaks, A. I. Larkin, and S. A. Pikin, Zh. Eksp. Teor. Fiz. **51**, 361 (1966) [Sov. Phys. JETP **24**, 240 (1967)].

[10] A. I. Larkin and D. G. Khmel'nitskiĭ, Zh. Eksp. Teor. Fiz. **56**, 2087 (1969) [Sov. Phys. JETP **29**, 1123 (1969)].

[11] A. P. Levanyuk, V. V. Osipov, A. S. Sigov, and A. M. Sobyanin, Zh. Eksp. Teor. Fiz. **76**, 345 (1979) [Sov. Phys. JETP **49**, 176 (1979)].

[12] V. S. Gorelik and S. V. Ivanova, Kratk. Soobshch. Fiz., No. 11, 18 (1981).

[13] G. Dittmar and H. Schöfer, Z. Naturforsch. **296**, 312 (1974).

[14] A. Michelson, Phys. Rev. B **16**, 577 (1977).

[15] A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **36**, 810 (1959) [Sov. Phys. JETP **9**, 571 (1960)].

[16] V. L. Ginzburg, Fiz. Tverd. Tela (Leningrad) **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1961)].

[17] Yu. M. Sandler and K. S. Aleksandrov, Fiz. Tverd. Tela (Leningrad) **25**, 3554 (1983) [Sov. Phys. Solid State **25**, 2045 (1983)].

[18] T. K. Parsamyan, S. S. Khasanov, V. Sh. Shekhtman, *et al.*, Fiz. Tverd. Tela (Leningrad) **27**, 3327 (1985) [Sov. Phys. Solid State **27**, 2003 (1985)].

[19] R. M. Hornreich, M. Luban, and S. Strikman, Phys. Rev. B **19**, 3799 (1979).

[20] K. Kasi and W. Selke, Phys. Rev. B **31**, 3128 (1975).

[21] T. A. Aslanyan and A. P. Levanyuk, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 76 (1978) [JETP Lett. **28**, 70 (1978)].

[22] T. A. Aslanyan, A. P. Levanyuk, M. Vallade, and J. Lajzerowicz, J. Phys. C **16**, 6705 (1983).

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