The tricritical Lifshitz point on the phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ ferroelectrics

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The temperature dependence of the isobaric specific heat and permittivity of proper uniaxial $Sn_2P_2(Se_xS_{1-x})_6$ ferroelectrics whose T–x-diagram contains a Lifshitz point is investigated. With increasing selenium concentration the $T_0(x)$ line of the ferroelectric phase transitions from the paraelectric to the ferroelectric phases at $x_L \approx 0.28$ splits cleanly into $T_i(x)$ and $T_c(x)$ lines bounding the incommensurate phase. It is established that when S is replaced with Se the transitions on the $T_0(x)$ line approach the tricritical point, although they become first order transitions only for $x > 0.6$ where they are already virtual transitions. An analysis of experimental data in the mean field approximation suggests that when $Sn_2P_2S_6$ is under hydrostatic compression a change in the nature of the ferroelectric phase transition line precedes the triple point at which the paraelectric, ferroelectric and incommensurate phases converge: The tricritical point and the triple point are attained successively on the T–p-diagram at $x = 0$, while the Lifshitz point is a virtual point. The range of the T–p–x-diagram of $Sn_2P_2(Se_xS_{1-x})_6$ containing the tricritical Lifshitz point is determined; this point represents the intersection of the lines of the Lifshitz points and the tricritical points. The values of the critical indices for the order parameter and specific heat of the test ferroelectrics confirm that the phase transitions occur within these ferroelectrics close to such a higher-order point.

INTRODUCTION

In addition to second order phase transitions (PT), which are second-order critical points, phase diagrams of substances may also contain higher-order (polycritical) points. Such points include, specifically, third-order (tricritical) and fourth-order points.[1] The diagrams become visibly more complex when incommensurate phases are present. Triple points (TP) may then exist; these points represent the convergence of the high-symmetry phase, its commensurate low-symmetry phase and the incommensurate phase with a spatially-modulated order parameter. The Lifshitz points (LP) play a special role among such points; as the Lifshitz points are approached, the wave vector of modulation of the incommensurate phase continuously tends to zero.[2,3] Lines of tricritical points (TCP) and lines of LP are realized by varying certain variables that are not symmetrically conjugate to the order parameter on, for example, a temperature–pressure–composition (T–p–x) diagram. These lines may converge at a higher-order point: the tricritical Lifshitz point (TCLP) (Ref. 4).

There is extensive information on experimental observations of TCP.[5] Lifshitz points have been found on the temperature-magnetic field diagram of MnP (Ref. 6) and on the T–x-diagram of $Sn_2P_2(Se_xS_{1-x})_6$ proper ferroelectrics.[7,8] At the same time there are no examples of reliable identification of the TCLP. The only available data indicate that the critical behavior near the TCP induced by compression in $RbCaF_3$ (Ref. 9), NH_4Cl (Ref. 10), and in NbO_2 (Ref. 11) crystals is similar to that expected for the TCLP. However incommensurate phases whose existence would allow direct identification of Lifshitz points and establishment of the existence of the TCLP have not yet been detected on the phase diagrams of these substances.

An LP is found on the T–x-diagram of $Sn_2P_2(Se_xS_{1-x})_6$ when $x_L \approx 0.28$ (Ref. 8). In these mixed crystals the line of the second-order phase transition from the paraelectric phase to the ferroelectric phase, $T_0(x)$ when $x > x_L$ splits into the second order transition line $T_i(x)$ and the first-order transition line $T_c(x)$ that bound the incommensurate phase. The temperature width of this phase diminishes continuously as $x \to x_L$, which is the primary indicator for the phase boundaries in the vicinity of the LP (Ref. 2). Splitting of the ferroelectric PT in $Sn_2P_2S_6$ into second- and first-order transitions is also detected from hydrostatic compression of the crystal.[12] However the $T_i(p)$ and $T_c(p)$ lines converge at the triple point on the T–p-diagram of $Sn_2P_2S_6$ at a finite angle, which excludes the possibility of interpreting this point as a Lifshitz point. Applying an electrical field to $Sn_2P_2(Se_xS_{1-x})_6$ crystals with $x > x_L$ along the axis of spontaneous polarization diminishes the temperature range of the incommensurate phase, while a TP is achieved on the T–E-diagram of these crystals, above which a first-order phase transition directly from the paraelectric phase to the ferroelectric phase occurs.[13] This fact suggests that the substitution S → Se at a certain value of $x > x_L$ will change the nature of the $T_0(x)$ line of the existing virtual phase transitions from second-order to first-order, i.e., the LP in $Sn_2P_2(Se_xS_{1-x})_6$ is close to a TCP.

The present study carries out an investigation of the temperature dependences of the specific heat and permittivity of $Sn_2P_2(Se_xS_{1-x})_6$ crystals and analyzes their physical parameters in order to determine the position of the TCLP on the T–p–x-diagram and to determine the nature of the critical behavior of these proper ferroelectrics under phase transitions from their proximity to the TCLP.

EXPERIMENTAL RESULTS

An adiabatic calorimeter with a relative error of less than 1% (Ref. 14) was used for measuring the temperature dependence of the specific heat $c_p(T)$ of the $Sn_2P_2(Se_xS_{1-x})_6$ crystals. Single crystal specimens grown by gas transport reactions[7] were investigated. The $c_p(T)$ relation of the $Sn_2P_2S_6$ ferroelectric was obtained by analyzing one single crystal 1.0215 g in weight. Several (three to five)

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single crystals with a total mass of approximately 1.5 g were placed in the calorimeter for measuring $c_p(T)$ of solid solutions with $x = 0.2$; 0.25 and 0.30. The $c_p(T)$ relation was obtained in heating conditions from 80–100 K. In the vicinity of the phase transition the value of c_p was determined in temperature increments of 0.1–0.3 K. The measurement results for $c_p(T)$ were processed by the least squares method and by approximating the regular section with a fourth-degree polynomial.

Measurements of the temperature dependences of the permittivity were carried out at 1 kHz using an R 5058 bridge. An indium-gallium paste was used as the contact material on $2\times2\times3$ mm^3 polar single-crystal faces.

A second-order ferroelectric phase transition occurs in $Sn_2P_2S_6$ at $T_0\approx337$ K$(P2_{1/c}\rightarrow P_c)$ without altering the number of lattice constants in the elementary cell. The transverse polarization wave period in the incommensurate phase of $Sn_2P_2Se_6$ is about 12 elementary cells at $T_i\approx221$ K and grows to 14 cells when cooled to $T_c\approx193$ K (Ref. 15). The growth of the temperature width of the incommensurate phase in $Sn_2P_2(Se_xS_{1-x})_6$ with increasing distance from the LP with coordinates $T_L\approx295$ K, $x_L\approx0.28$ satisfies the relation $T_i - T_c = 45.8(x - x_L)^2$ (Ref. 16). This relation is shown in Fig. 1.

The coordinates of the TP on the T–p-diagram of $Sn_2P_2S_6$ corresponds to $T_{TP}\approx295$ K, $p_{TP}\approx0.18$ GPa (Refs. 12, 17). The triple point line on the T–p–x-diagram of $Sn_2P_2(Se_xS_{1-x})_6$ passes through the Lifshitz point on the T–x-diagram. This suggests that the intermediate phase on the T–p-diagram of $Sn_2P_2S_6$ is also an incommensurate phase. The change in its temperature width $T_i - T_c$ with increasing distance from the TP and with increasing pressure is also shown in Fig. 1 (based on Ref. 12). The concentration and baric dependences of the width of the incommensurate phase are determined in these composition and compression ranges. At the same time these relations have a qualitatively different form. The width of the incommensurate phase when S is substituted with Se increases in accordance with a square law which satisfies the primary criterion for the LP (Ref. 2). Upon compression of $Sn_2P_2S_6$, $T_i - T_c$ grows linearly in $p - p_{TP}$ (Fig. 1). This indicates that the TP on the T–p-diagram of $Sn_2P_2S_6$ is not a Lifshitz point. In such a case the line of triple points on the T–p–x-diagram of $Sn_2P_2\cdot(Se_xS_{1-x})_6$ becomes a line of Lifshitz points with increasing x. Analysis of the specific heat was carried out in order to confirm this assumption.

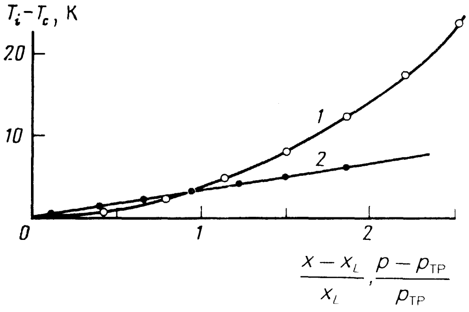

FIG. 1. Concentration dependence of the temperature range of the incommensurate phase $Sn_2P_2(Se_xS_{1-x})_6$ at atmospheric pressure (1) and its baric dependence in $Sn_2P_2S_6$ (2).

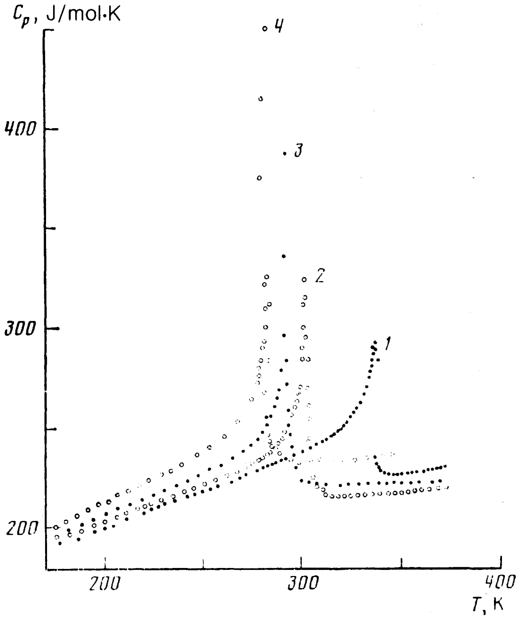

FIG. 2. The temperature dependences of the isobaric specific heat of $Sn_2P_2(Se_xS_{1-x})_6$ crystals in the vicinity of the phase transition: $x = 0$ (1), 0.20 (2), 0.25 (3), 0.30 (4).

The $c_p(T)$ relations of $Sn_2P_2(Se_xS_{1-x})_6$ crystals at $0\leqslant x\leqslant0.3$ are shown in Fig. 2. The peaks in the specific heat upon phase transitions grow noticeably with increasing x. No transition heat was detected up to $x = 0.25$, providing unambiguous confirmation of the second order phase transition line $T_0(x)$ for $x\leqslant0.25$. Transition heat is detected in the composition with $x = 0.3$ corresponding to a first-order transition from the incommensurate phase to the ferroelectric phase. The anomalous part of the specific heat is determined within the framework of the mean-field theory by the relation[18]

$$\Delta c_p(T) = \frac{T}{2\rho C_C^2}\left[\beta^2 - \frac{4(T-T_0)\gamma}{C_C}\right]^{-1/2}, \qquad (1)$$

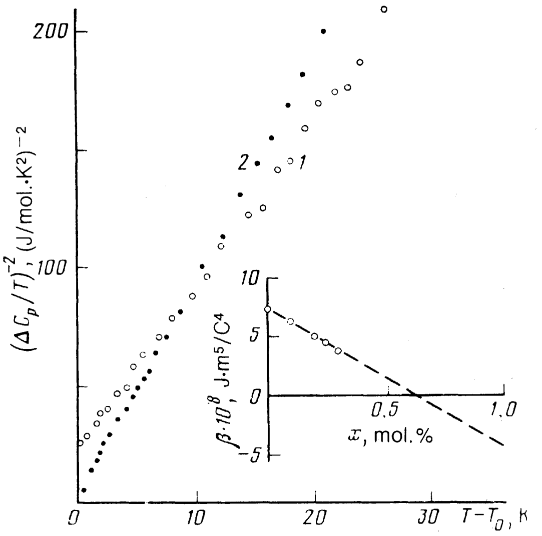

FIG. 3. Temperature dependences of $(\Delta c_p/T)^{-2}$ in the ferroelectric phase of $Sn_2P_2(Se_xS_{1-x})_6$ crystals at $x = 0$ (1), 0.25 (2). Insert: The concentration dependence of the coefficient β in expression (2).

TABLE I. Coefficients of the expansion of the thermodynamic potential.

Composition	α 10^6 J·m/C^2·K^1	β 10^8 m^5·J/C^4	γ 10^{10} m^9·J/C^6
$Sn_2P_2S_6$	1.6	7.42	3.5
$Sn_2P_2(Se_{0.2}S_{0.8})_6$	1.6	5.07	4.5
$Sn_2P_2(Se_{0.25}S_{0.75})_6$	1.6	4.54	4.82
$Sn_2P_2(Se_{0.3}S_{0.7})_6$	1.6	3.77	5.06

where ρ is the density of the material, C_C is the Curie-Weiss constant, and β and γ are the coefficients of expansion (2).

The influence of fluctuation effects which limit the applicability of this relation will be examined below. The coefficient β is determined from the jump in specific heat Δc_p with known ρ and C_C. The coefficient γ was determined by plotting $(\Delta c_p/T)^{-2}$ as a function of $T - T_0$ (Fig. 3). We see that β diminishes with increasing x, while the coefficient γ grows (see table). We note that the temperature behavior of the spontaneous polarization calculated with these values of β and γ is in agreement with the experimental data.

The concentration dependence of β for $x \leqslant 0.3$ is close to linear (see insert in Fig. 3). Its extrapolation in the range $x > 0.3$ indicates a change of sign of β at $x \approx 0.6$. This suggests that direct phase transitions from the paraelectric phase to the ferroelectric phase with $x > 0.6$ are first-order transitions. Data from dielectric investigations of $Sn_2P_2(Se_xS_{1-x})_6$ also confirm that the second-order ferroelectric phase transition approaches a tricritical transition: With increasing x the $\varepsilon(T)$ ratio above and below T_0 grows from 2.5 at $x = 0$ to 8 at $x = 0.25$. Figure 4 compares the $\varepsilon^{-1}(T)$ relations in the paraphase of $Sn_2P_2S_6$ and $Sn_2P_2Se_6$ crystals obtained in cooling conditions. The $\varepsilon^{-1}(T)$ relation is extrapolated to zero for a second order phase transition in $Sn_2P_2Se_6$ and $T' = T_0 - 1$ K (the difference $T_0 - T'$ is dependent on the dimensions of the specimen and is likely determined by the effect of the surface layers[19]). For $Sn_2P_2Se_6$ this relation intersects the temperature axis substantially below T_c, the temperature of the phase transition from the incommensurate phase to the ferroelectric phase. This confirms the first-order nature of the virtual phase transition from the paraelectric phase to the ferroelectric phase for $Sn_2P_2Se_6$.

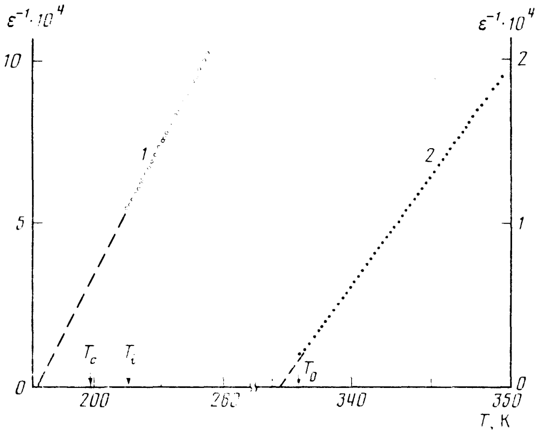

FIG. 4. Temperature dependences of the inverse permittivity of the paraelectric phase of $Sn_2P_2Se_6$ (1) and $Sn_2P_2S_6$ (2) crystals.

DISCUSSION OF RESULTS

For proper uniaxial ferroelectrics with one-dimensional modulation the expansion of the density of the thermodynamic potential in powers of the order parameter η and its spatial derivatives takes the form[18]

$$\Phi = \Phi_0 + \frac{\alpha}{2}\eta^2 + \frac{\beta}{4}\eta^4 + \frac{\gamma}{6}\eta^6 + \frac{\delta}{2}\left(\frac{d\eta}{dz}\right)^2 + \frac{g}{2}\left(\frac{d^2\eta}{dz^2}\right)^2 + \dots \quad (2)$$

We assume that $\alpha = \alpha_T(T - T_0)$, while the remaining coefficients are weakly temperature-dependent. We will consider the situation in which we have $\delta, \beta < 0$, while $\gamma, g > 0$ in (2). When the inequality

$$\delta^2/2g > 2\beta^2/16\gamma \quad (3)$$

is satisfied, there is a second-order phase transition from the paraelectric phase to the incommensurate phase; otherwise there is a first-order phase transition from the paraelectric phase to the ferroelectric phase. The incommensurate phase vanishes at the triple point, which is given by the equality in (3) (Ref. 20) and is not a Lifshitz point. The lines of the tricritical points and the Lifshitz points in the T-p-x-space may converge at the tricritical Lifshitz point determined by the condition $\alpha(T,p,x) = \beta(T,p,x) = \delta(T,p,x) = 0$. The line of the triple points determined above also converges on the TCLP. Figure 5 provides a schematic representation of the phase diagram in the space of the coefficients α-β-δ,

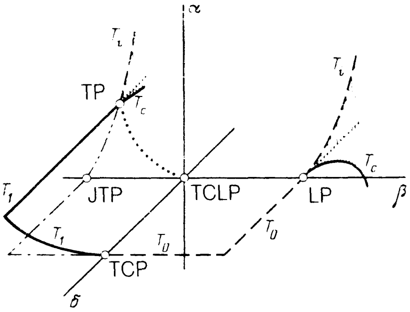

FIG. 5. Schematic phase diagram of a system with thermodynamic potential (2). Dashed curves: Second order transitions from the paraelectric phase to the ferroelectric phase (T_0) or to the incommensurate phase (T_i); solid curves: First order transitions from the paraelectric phase to the ferroelectric phase (T_1) or from the incommensurate phase to the ferroelectric phase (T_c). The incommensurate phase regions are shaded; the dotted lines in these areas represent the lines of the virtual transitions T_0 for $\beta > 0$ and T_1 for $\beta < 0$. The dot and dash curve represents the projection of the T_1 line onto the β-δ plane; the double dot-dash line represents the line of virtual transitions T_i at $\beta < 0$; the solid circles represent the line of triple points terminating at the TCLP; the VTP is the virtual Lifshitz point.

assuming that the "temperature" α is not altered by the external "field." The range of the incommensurate phase when $\beta = \text{const} > 0$ and $\beta = \text{const} < 0$ is identified. The positive semiaxis β coincides with the line of Lifshitz points, while the negative semiaxis coincides with the line of virtual Lifshitz points. The axis $\delta > 0$ lies on the line of tricritical points.

We will analyze the phase diagram on which an external field is used to exert uniform compression. We add an elastic part to the expansion (2) which appears as

$$\Phi_{\text{el}} = \frac{c}{2}u^2 + qu\eta^2 + \frac{\lambda}{2}u^2\eta^2 + \frac{\varkappa}{2}u\left(\frac{d\eta}{dz}\right)^2 - up. \qquad (4)$$

Here $u \equiv u_{ij}$ is the deformation tensor, $c \equiv c_{ijkl}$ is the tensor of elastic moduli, the coefficients q, λ and k are positive, and $p \equiv \sigma_{ii}$ is the elastic force conjugate to deformation u. Minimizing (4) and adding Φ_{el} to (2) we obtain a new expression for the thermodynamic potential:

$$\Phi - \Phi_0 = \left(\frac{\alpha}{2} + \frac{qp}{c} + \frac{\lambda p^2}{2c^2}\right)\eta^2 + \left(\frac{\beta}{4} - \frac{q^2}{2c} - \frac{\lambda qp}{c^2}\right)\eta^4 + \gamma^*\eta^6 + \left(\frac{\delta}{2} + \frac{\varkappa p}{c}\right)\left(\frac{d\eta}{dz}\right)^2 + g^*\left(\frac{d^2\eta}{dz^2}\right)^2 + \ldots, \qquad (5)$$

in which the renormalized coefficients γ^* and g^* in the expression are independent of pressure. It is clear from (5) that hydrostatic compression can alter the signs of both the coefficient β and the coefficient δ, thereby inducing TCP or LP. Analysis of the concentration dependence of the coefficients β and δ, where new variables—the concentration and chemical potential—are considered in place of u and p, yields analogous results.

In the vicinity of the TCLP δ changes when $\beta = 0$. For this condition the thermodynamic potential of the ferroelectric phase takes the form

$$\Phi_F = \frac{\alpha}{2}\eta^2 + \frac{\gamma}{6}\eta^6.$$

For the incommensurate phase where the order parameter satisfies $\eta = \eta_k \cos(kz)$ in the single harmonic approximation we have

$$\Phi_{\text{in}} = \frac{\alpha(k)}{4}\eta_k^2 + \frac{5\gamma}{96}\eta_k^6, \qquad \alpha(k) = \alpha + \delta k^2 + gk^4.$$

Using the minimization conditions

$$\frac{\partial\Phi}{\partial\eta} = \frac{\partial\Phi}{\partial\eta_k} = \frac{\partial\Phi}{\partial k} = 0$$

we find the expression for the thermodynamic potentials of the ferroelectric and incommensurate phases:

$$\Phi_F = -\frac{1}{3}\left(\frac{\alpha^3}{\gamma}\right)^{1/2}, \qquad \Phi_{\text{in}} = -\frac{1}{3}\left[\frac{(\alpha - \delta^2/2g)^3}{5\gamma}\right]^{1/2}. \qquad (6)$$

There will be a second-order phase transition from the paraelectric phase to the incommensurate phase along the line

$$\alpha_i - \delta^2/2g = 0, \qquad (7)$$

where δ is a function of presssure and composition. The first-order phase transition from the incommensurate phase to the ferroelectric phase also forms the line α_c which we will find from equality of the potentials (6):

$$\alpha_c \approx -0.7\delta^2/g. \qquad (8)$$

We note that in the vicinity of an LP far from a TCP the temperature of this phase transition is determined by the relation[18]

$$\alpha_c \approx -2.2\delta^2/g.$$

In the mean-field approximation the form of the phase diagram in the vicinity of the TCLP ($\beta = 0$) does not differ qualitatively from the phase diagram for the LP ($\beta > 0$). The phase transition lines bounding the incommensurate phase converge parabolically in both cases as $\delta \to 0$. However, when $\beta < 0$ these phase boundaries converge at a finite angle on the TP, determined by the equality in (3).

We will consider the role of fluctuation effects with a phase transition in the vicinity of the TCLP. For this it is important to determine the upper critical dimensions d_u above which the behavior of the system satisfies the conclusions of mean-field theory and the lower critical dimensions d_l where the temperature of the critical point as a function of the dimensions d tends toward 0 K as the lower critical dimensions d_l are approached. According to Ref. 4 a uniaxial TCLP can be achieved in a space with $d = 3$ and a substantial role of fluctuation effects may be anticipated in its vicinity: $d_l = 2.5 < d < d_u = 3.5$.

We will compare the values of the critical indices for the specific heat (α'), the susceptibility (γ') and the order parameter (β') obtained by renormalized calculations[2,5,21,22] using an expansion in the small parameter $\varepsilon' = d_u - d$ for a system with a single-component order parameter η and a uniaxial anisotropy in the hardness dispersion for fluctuations of η:

ФП второго рода $\alpha' \approx 0{,}17$, $\gamma' \approx 1{,}17$, $\beta' \approx 0{,}33$;

TCP $\alpha' = 0.50$, $\gamma' = 1.00$, $\beta' = 0.25$;

LP $\alpha' \approx 0.25$, $\gamma' \approx 1.25$, $\beta' \approx 0.25$;

TCLP $\alpha' \approx 0.66$, $\gamma' \approx 1.07$, $\beta' \approx 0.14$.

These values of the indices are quite approximate since the parameter ε' is not sufficiently small; for example, for the LP, $\varepsilon' = 1.5$. More exact molecular-dynamic calculations[23] for the LP yield the following values:

$\alpha' \approx 0.3$, $\gamma' \approx 1.4$, $\beta' \approx 0.2$.

The renormalized data allow, however, identification of the following trends in the changes of critical indices following the phase diagram in the vicinity of the TCLP. The index $\beta' \approx 0.33$ therefore corresponds to normal critical Ising behavior (the area on the α–β–δ diagram shown in Fig. 5 for $\delta > 0$ and $\beta > 0$). This index diminishes when both the TCP and the LP are approached. The index β' continues to diminish along the line of tricritical points or the line of Lifshitz points towards the TCLP and achieves its minimum value at the TCLP. The index α' is maximized at the TCLP.

The long-range Coulomb forces in uniaxial ferroelectrics substantially damp fluctuation effects. This can be taken into account by increasing the dimensionality of space to 4. Here $d = d_u$ for a second-order phase transition and the critical behavior satisfies theoretical conclusions in the mean-field approximation ($\alpha' = 0$, $\gamma' = 1$, $\beta' = 0.5$) with weak multiplicative fluctuation corrections.[18] In this case, $d_u > d$ for the TCP. For uniaxial ferroelectrics $d_u > d$ at the

LP as well, i.e., the fluctuation effects continue to play a significant role. However there are no theoretical calculations for this case. Obviously the interaction of order-parameter fluctuations will diminish as the TCLP is approached along the line of LP. In uniaxial ferroelectrics $d_u < d$ for the TCLP. This supports the possibility of using formula (1) in its vicinity for analyzing the temperature dependences of the specific heat.

We will use available experimental data to establish the thermodynamic paths in the space α–β–δ (Fig. 5) for an $Sn_2P_2S_6$ crystal under compression or with changes in the chemical composition in the $Sn_2P_2(Se_xS_{1-x})_6$ series, i.e., we will determine projections of the p and x axes onto the β–δ plane. For $Sn_2P_2S_6$ the Curie-Weiss constant $C_C \approx 0.7\cdot 10^5$ K^{-1} (Fig. 4), consequently $\alpha_T = 1/C_c\varepsilon_0 = 1.6\cdot 10^6$ J·m/C^2, where ε_0 is the permittivity. From calorimetric data $\beta_S = 7.4\cdot 10^8$ J·m^5/C^4, $\gamma_S = 3.5\cdot 10^{10}$ J·m^4/C^6, so their "atomic" values are equal to $\beta_{aT} \sim \alpha_T T_0/\eta_s{}^2 \approx 2\cdot 10^{10}$ J·m^{5}C^4, $\gamma_{aT} \sim \alpha_T T_0/\eta_S{}^4 \approx 2\cdot 19^{12}$ J·m^{9}C^6, where $\eta_S = 0.15$ C/m^2 is the spontaneous polarization in saturation. We have $\beta_{Se} \approx -4\cdot 10^8$ J·m^5/C^4 assuming β is linearly dependent on x (Fig. 3) for $Sn_2P_2Se_6$, which is also substantially below the "atomic" value. Therefore the ferroelectric phase transitions throughout the entire $Sn_2P_2(Se_xS_{1-x})_6$ series can be assumed to be close to the TCP. It follows that relation (8) is useful for determining the coefficients δ and g in (2). Recalling that, consistent with the x-ray data,[15] the wave vector of the incommensurate structure of $Sn_2P_2Se_6$ at T_i is $k_0 \approx 4.2\cdot 10^8$ m^{-1}, and using the relation $k_0^2 = \delta/2g$ we find

$$\delta_{Se} \approx -2.2\cdot 10^{-10}\ \mathrm{J\cdot m^3/C^2},\ g_{Se} \approx 1\cdot 10^{-27}\ \mathrm{J\cdot m^5/C^2}.$$

Assuming that $\delta \sim |x - x_L|$ in the vicinity of the LP, we find for $Sn_2P_2S_6$ the result $\delta_S \approx 1\cdot 10^{-10}$ J·m^3/C^2.

Figure 6 shows the concentration axis x on the β–δ plane using the values of the coefficients β and δ given above for $x = 0$ and 1.

We consider the effect of pressure. According to Ref. 12 the baric rate of the temperature drop of the phase transition is $dT_0/dp \approx 220$ K/GPa for $Sn_2P_2S_6$. Upon attainment of the TP ($p_{TP} \approx 0.18$ GPa) the temperature drops by approximately 44 K. According to (5) the linear component of the baric temperature shift of the phase transition $\Delta T = 2qp/c\alpha_T$ is responsible for a temperature drop of the phase transition of approximately 45 K. This estimate accounts for the fact that the electrostriction coefficient for $Sn_2P_2S_6$ is $q = q_{el}c_{11} = 4.8\cdot 10^9$ J·m/C^2, where $q_{el} = 0.2$ C/m^2 (Ref. 14). A value of $c_{11} = 2.4\cdot 10^{10}$N/m^2, equal to the average longitudinal elastic modulii was used. If we assume that the pressure-squared term in (5) shifts T_0 by less than 5 K, the coefficient $\lambda \sim c^2\alpha_T/p^2 = 1.4\cdot 10^{11}$ J·m/C^2 ($\lambda_{aT} \sim 10^{12}$ J·m/C^2). Using this value of λ we employ (5) to determine that compression of $Sn_2P_2S_6$ will reduce β to zero at $p \approx 0.15$ GPa, while at the TP this coefficient has already dropped below zero and is equal to $-0.3\cdot 10^8$ J·m^5/C^2.

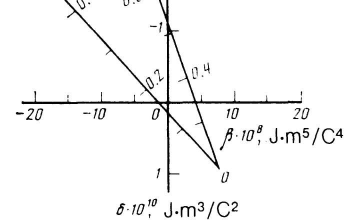

FIG. 6. The concentration and baric thermodynamic "paths" on the δ–β-plane (δ and β are the coefficients in (2)) implemented from changes in the composition of mixed $Sn_2P_2(Se_xS_{1-x})_6$ crystals and from hydrostatic compression of $Sn_2P_2S_6$, respectively.

We will use the "atomic" value of the coefficient δ to estimate renormalization of the coefficient χ with compression of $Sn_2P_2S_6$ using relation (5). To within an order of magnitude $\chi_{aT} \approx q/k_0^2 \approx 3\cdot 10^{-8}$. Then we have $\delta \approx -10^{-10}$ J·m^3/C^4 at the TP, i.e., it is already negative at $p = 0.18$ GPa.

According to these estimates of the baric relations of β and δ the TCP is first achieved with increasing pressure on the T–p-diagram of $Sn_2P_2S_6$ (the ferroelectric phase transition changes from a second-order transition to a first order transition), and at the TP the first-order ferroelectric phase transition then splits into first- and second-order transitions that bound the incommensurate phase. The LP is a virtual point in this case.

Figure 6 shows the projection of the pressure axis p onto the β–δ plane. We expect that when compression is applied to the $Sn_2P_2S_6$ crystal the thermodynamic path runs close to the TCLP–TCP path and the TP is located close by on the p–T-diagram when $x = 0$. Such an assumption is consistent with the fact that to within experimental accuracy[12] compression of $Sn_2P_2S_6$ causes the phase transition to enter the ferroelectric phase with the intermediate phase appearing simultaneously.

The set of experimental results therefore indicates that an LP appears on the T–x-diagram of $Sn_2P_2(Se_xS_{1-x})_6$, while a TP appears on the T–p-diagram of $Sn_2P_2S_6$. Both the concentration and baric thermodynamic paths pass close by the TCLP (Fig. 6). The lower rate of broadening of the incommensurate phase on the T–p-diagram at $x = 0$ compared to the T–x-diagram for $p \approx 0$ (see Fig. 1) then becomes clear. We have $\beta \approx -17\cdot 10^8$ J·m^5/C^4 for $Sn_2P_2S_6$ at $p = 0.5$ GPa, which equals approximately $4\beta_{Se}$. Consequently the virtual ferroelectric phase transition is a stronger first-order transition for $x = 0$ and $p = 0.5$ GPa than for $x = 1$ at atmospheric pressure. First-order enhancement of the anticipated phase transition directly from the paraelectric phase to the ferroelectric phase narrows the temperature range of the incommensurate phase.[20]

From (7) and (8) we have

$$T_i - T_1 = \delta^2/2g\alpha_T - 3\beta^2/16\gamma\alpha_T. \tag{9}$$

If we recall that the value of the coefficient δ is near its value in $Sn_2P_2Se_6$ ($\approx -2\cdot 10^{-10}$ J·m^3/C^2) for $Sn_2P_2S_6$ at 0.5 GPa, we find by employing (9) that the temperature difference $T_i - T_1$ is within 5–10 K. The width of the incommensurate phase $T_i - T_c$ will also be close to this value since T_c rises to T_1 with growth of $|-\beta|$, and the inequality $T_1 - T_c \ll T_i - T_1$ holds. The experimentally observed value of $T_i - T_c = 7$ K in $Sn_2P_2S_6$ at 0.6 GPa is consistent with this estimate; this is approximately four times smaller than the width of the incommensurate phase in $Sn_2P_2Se_6$.

The critical index β' for the order parameter in $Sn_2P_2(Se_xS_{1-x})_6$ drops from 0.42 ± 0.02 for $x = 0$ to

0.19 ± 0.02 for $x = 0.3$, according to analyses of the optical properties.[24] Pyrocurrent studies indicate that β' diminishes with compression of the $Sn_2P_2S_6$ crystal and that it too equals 0.19 ± 0.02 at 0.18 GPa, corresponding to the TP (Ref. 25). Molecular-dynamics calculations at the LP for systems with a single-component order parameter and uniaxial modulation yield $\beta' \approx 0.20$ (Ref. 23). Fluctuations are substantially suppressed in uniaxial ferroelectrics, however, due to dipole-dipole interaction.[18] Although no theoretical calculations exist for this case, β' for the the LP will undoubtedly be much lower than 0.20. The observed low value of β' can be attributed to the proximity of the LP to the TCLP in $Sn_2P_2(Se_xS_{1-x})_6$. This also applies to the value of β' in the vicinity of the TP on the *T–p*-diagram of $Sn_2P_2S_6$. The proximity of the LP to the TCLP on the *T–x*-diagram is also consistent with the fact that the temperature dependence of the specific heat approaches a power law in the ferroelectric phase with the index $\alpha' \approx 0.5$ as $x \to x_L$ (Fig. 2).

Figure 6 clearly indicates that the TCLP can be attained on the *T–p*-diagram of mixed $Sn_2P_2(Se_xS_{1-x})_6$ crystals with $x < 0.28$. Since β' is minimized for the TCLP it appears likely that determination of its changes along the line of Lifshitz points in the *T–p–x*-space as x decreases from 0.28 will allow precise determination of the coordinates of the TCLP.

Finally we note that in analyzing anomalies in the thermodynamic functions in any experimental implementation of a TCP or LP it is important to account for their proximity to the higher order point, the TCLP. The $Sn_2P_2(Se_xS_{1-x})_6$ ferroelectrics are likely to be the first system for which a TCLP has been reliably proven to exist in rather easily attained experimental conditions. This makes possible a comprehensive analysis of such a polycritical point.

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