Lifshitz point on the state diagram of ferroelectrics

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An analysis is made of the shape of the phase diagrams of substances in the neighborhood of the Lifshitz point, which separates the second-order phase transitions going from the initial phase to a commensurate and to an incommensurate phase. The conclusions of the thermodynamic theory in the mean field approximation and in a treatment including the effects of the interaction of well-developed fluctuations are compared. The possible complication of the phase diagram by a crossing of the line of Lifshitz points with a line of tricritical points and the possible existence of a tricritical Lifshitz point are discussed. The changes in the character of the critical behavior in the neighborhood of the Lifshitz point are discussed in reference to the results of experimental studies of the transformation of anomalies of the thermodynamic characteristics, principally for the proper uniaxial ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$.

1. INTRODUCTION

Long-period structures have been receiving considerable attention of late in condensed-matter physics. Structures of this kind include charge-density waves in metals, magnetic structures of the spin-wave type, helicoidal phases in liquid crystals, concentration modulation in intercalculated compounds, and the long-period phases arising in phase transitions on surfaces and in structural phase transitions. If the wavelength of the modulation is not a multiple of the lattice period of the initial high-symmetry phase, then an incommensurate (IC) phase occurs. The problem of the change in the translational symmetry at a phase transition was first considered by Lifshitz.[1] Development of a theory of IC phases in crystals was begun by Dzyaloshinskiĭ[2,3] for the particular case of long-period magnetic structures. Its extension to ferroelectrics started with the papers by Levanyuk and Sannikov.[4,5]

Hornreich[6] examined the state diagram of a substance having an IC phase and noted that it can have a triple point, viz., the Lifshitz point (LP), which separates the phase transitions occurring directly from the high-symmetry phase to a low-symmetry commensurate phase from transitions occurring to the IC phase. The Lifshitz point is the most obvious feature of the thermodynamics of phase transitions involving the formation of modulated structures in ferromagnets or in proper ferroelectrics. Near the LP the period of the IC phase is large, and at the LP itself it goes to infinity. As the LP is approached, the decrease in the correlation length leads to expansion of the critical region of well-developed fluctuation effects and substantial deviations from Landau theory.

The Lifshitz point introduced in Ref. 6 has the property that as it is approached, the wave vector of the modulation continuously goes to zero ($q_0 \to q_c = 0$), i.e., the commensurate phase is ferromagnetic. In the general case a commensurate phase with $q_c \neq 0$ can exist. Therefore, other types of Lifshitz points are possible, on approach to which the wave vector q_0 of the IC structure continuously approaches a nonzero value $q_c \neq 0$.[7]

Phase diagrams can also exhibit triple points of the LP type.[8–11] However, as these are approached the period of the IC phase suffers a discontinuity, there is no modulation wave with an infinitely large period, and the critical fluctuations are of an ordinary order of magnitude.

Modulated structures of various types have been observed in many (about a hundred) magnetic crystals.[12] The existence of IC phases has been established in dozens of ferroelectric crystals. Of the proper ferroelectrics they have been studied most in $NaNO_2$ (Ref. 13), and of the improper ferroelectrics, in K_2SeO_4 (Ref. 14). At the same time, experimental information about LPs on phase diagrams is at present extremely limited. The LP has been investigated in magnets only for MnP (Refs. 15, 16) and in proper ferroelectrics only for crystals of the system $Sn_2P_2(Se_xS_{1-x})_6$ (Refs. 17–20). The point is also accessible in ferroelectric liquid crystals.[21] Triple points, at which a high-symmetry, an incommensurate, and a commensurate phase come together, have been observed on the state diagrams of the ferroelectrics $RbH_3(SeO_3)_2$ (Ref. 22) and Ag_3AsS_3 (Ref. 23), the improper ferroelastics $[N(CH_3)_4]_2MCl_4$ (M = Mn, Fe, Co, Zn; Ref. 24), $[N(CH_3)_4]_2CuBr_xCl_{4-x}$ (Ref. 25), and the proper ferroelastics $Cs_2HgCl(Br)$ (Ref. 26), in the magnetic solid solutions $NiBr_{2-x}I_x$ (Ref. 27), and in alloys of chromium with transition metals (Ref. 28).

Thus the experimental information on the critical behavior of solid substances near a true LP, on approach to which the modulation period increases without bound, is extremely limited—there are data only for MnP and $Sn_2P_2(Se_xS_{1-x})_6$. In addition to this, there is active theoretical research on systems with LPs on their state diagram.[29–33] The goal of the present review article is to analyze the main conclusions of the thermodynamic theory, in the mean field approach and also with the interaction of well-developed fluctuations taken into account, as to the shape of the phase diagrams of substances in the neighborhood of a

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Lifshitz point. The possible complication of the structure of the diagrams due to the role of nonlinearity[34] and due to a crossing of a line of Lifshitz points and a line of tricritical points and to the existence of a tricritical Lifshitz point[35] are discussed. The conclusions of the theory as to the transformation of the anomalies of the basic thermodynamic characteristics on transition through the LP are adduced. They are compared with the results of experimental studies, mainly for ferroelectrics of the system $Sn_2P_2S(Se)_6$, for the purpose of tracking the principal feature of the Lifshitz point—the growth of fluctuations of the order parameter as this point is approached.

2. STATE DIAGRAMS OF SUBSTANCES WITH INCOMMENSURATE PHASES

The existence of IC phases on the state diagrams of substances can be explained in the framework of Landau theory by considering the density of the nonequilibrium thermodynamic potential[2-5]

$$\Phi = \Phi_1[\eta_i(X_j)] + \Phi_2\left[\eta_i, \frac{\partial^n \eta_i}{\partial X_j^n}\right], \tag{1}$$

where Φ_1 has the form of the classical Landau expansion in the components of the order parameter $\eta_i(X_j)$, and Φ_2 depends on the components and their derivatives with respect to the spatial coordinates X_j. The principal features of the diagram are determined by the shape of the dispersion surface for the stiffnesses of the components of the order parameter (the coefficients of the invariants that are quadratic in the components of the order parameter) in the neighborhood of a symmetric Lifshitz point q_c of the Brillouin zone (the point q_c is where the wave vector of the modulation is fixed at the phase transition to the low-temperature ordered phase):

$$\alpha(\mathbf{q}) = \alpha_0(T, x) + \sum_n \alpha_n(T, x)(\mathbf{q} - \mathbf{q}_c)^n; \tag{2}$$

here x is an external parameter (pressure, field, composition of mixed crystals, etc.).

Depending on the symmetry of the system, two types of transitions to the IC phase are possible, and so there are two possible types of triple points on the state diagrams. Type I occurs for a two-component order parameter, when the thermodynamic potential (1) contains terms linear in the derivatives, i.e., Lifshitz invariants; this is equivalent to the presence of terms with odd powers of n in the dispersion relation (2).[33] In this case the transitions to the IC phase are symmetry-related.[1] This type of transition obtains, in particular, in improper ferroelectrics such as K_2SeO_4 (Ref. 14). The shape of the phase diagrams and the character of the possible triple points on them depend on the maximum order n_{max} of the terms included in the expansion of the dispersion relation (2) and the values of the coefficients α_n (Refs. 8, 11). For example, the state diagrams of ferroelectric crystals described by the space group C_4 or C_{4v}, whose order parameter transforms according to the two-dimensional irreducible representation E_4, can have a triple point (of the LP type) at which a line of second-order phase transitions from the paraelectric to the IC phase comes together with lines of first-order transitions from the IC to the ferroelectric phase and from the paraelectric to the ferroelectric phase.[9] The last two have a common tangent at the triple point. At such a point the wave vector of the modulation is discontinuous, and the critical fluctuations are of an ordinary order of magnitude. For two-dimensional representations E_n with arbitrary n there can also exist triple points at which three lines of second-order phase transitions between the paraelectric, IC, and ferroelectric phases come together. These lines do not have a common tangent at such a triple point of the LP type.[9]

The diversity of possible situations becomes richer when invariants cubic in the order parameter and linear in the wave vector (of the type $\eta_i\eta_j\partial\eta_k/\partial X$), which stabilize the IC phases,[8,10] are allowed. These are possible, for example, for the three-dimensional representation F_{2u} of the group Q_h and are relevant to the state diagrams of superconducting materials having phases with a charge-density wave.[36]

Type II transitions[33] occur in systems having a one-component order parameter, for which Lifshitz invariants are not allowed in expansion (1). In this situation the existence of IC phases is not dictated by symmetry (the Lifshitz condition[1] holds) but is due solely to the nature of the interatomic interactions in the particular system.[6,8] Here the dispersion relation (2) has only terms with even powers n. The phase diagrams are also extremely diverse and depend on the values of the coefficients α_n and the value of n_{max} (Refs. 8, 11). The simplest form of diagram is for $n_{max} = 4$, in which case the diagram contains a Lifshitz point with the coordinates $\alpha_0(T,x) = \alpha_2(T,x) = 0$ (Ref. 6). The main conclusions of the thermodynamic theory for this case will be the subject of the rest of this article.

In the presence of a one-component order parameter ($\boldsymbol{\eta}\|X$) and a single modulation direction ($\mathbf{q}\|Z$), which is the situation for the systems that have been investigated experimentally (the ferromagnet MnP and the proper uniaxial ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$), the thermodynamic potential density (1) can be rewritten in the form[6,29]

$$\Phi = \Phi_0 + \frac{\alpha}{2}\eta^2 + \frac{\beta}{4}\eta^4 + \frac{\delta}{2}\left(\frac{\partial\eta}{\partial Z}\right)^2 + \frac{g}{2}\left(\frac{\partial^2\eta}{\partial Z^2}\right)^2; \tag{3}$$

here $\alpha = \alpha_T(T - T_0)$ and β, δ, and g are constants, with β and $g > 0$. After taking the Fourier transform and making use of the fact that the wave vector of the modulation is fixed at the Brillouin zone center ($q_c = 0$), we get

$$\Phi = \Phi_0 + \frac{1}{2}(\alpha + \delta q^2 + gq^4)\eta^2 + \frac{\beta}{4}\eta^4. \tag{4}$$

On the assumption that there is no dispersion of the effective mass of the ferroelectric sublattice ($\tilde{m} = \text{const}$), the dispersion of the stiffness of the order parameter is characterized by the form of the soft optical branch associated with the phase transition along the modulation direction:

$$\omega^2(q) \sim \alpha + \delta q^2 + gq^4. \tag{5}$$

If $\delta < 0$, then the minimum of this branch is shifted away from the center of the Brillouin zone (Fig. 1a). From the condition

$$\left.\frac{\partial\omega^2(q)}{\partial q}\right|_{T_i} = 0$$

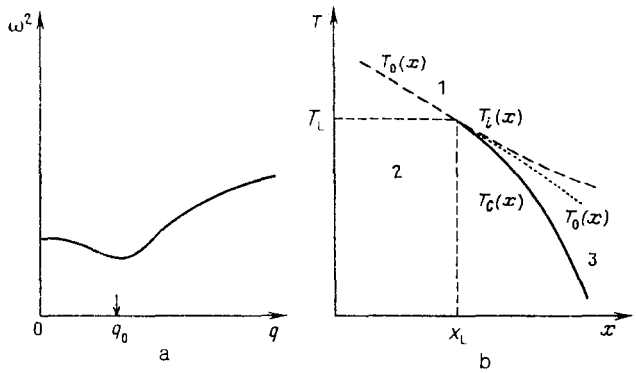

FIG. 1. Schematic of the soft optical branch (a) and the phase diagram (b) for compounds undergoing a phase transition to an incommensurate phase in the neighborhood of a Lifshitz point. *1)* Initial disordered phase, *2)* commensurate ordered phase, *3)* incommensurate phase. The dashed line is a line of second-order phase transitions; the solid line is a line of first-order phase transitions.

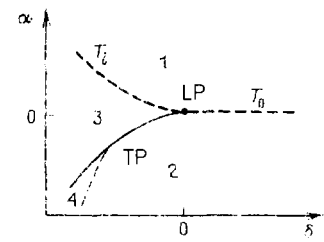

FIG. 2. Phase diagram of a system with the thermodynamic potential of Eq. (3) with allowance for the invariant $\mathbf{f}\,(\partial\eta/\partial Z)^4$ and the condition $\beta = \mathbf{g} = \mathbf{f} = 1$ (Ref. 32). *1)* Paraphase, *2)* commensurate phase, *3)* incommensurate phase, *4)* rippled state. The dashed lines are lines of second-order phase transitions; the solid line is a line of first-order phase transitions.

it follows that at the temperature

$$T_i = T_0 + \frac{\delta^2}{4g\alpha_T} \tag{6}$$

there occurs a phase transition to an IC phase with a modulation wave vector

$$q_0^2 = -\frac{\delta}{2g}. \tag{7}$$

The density of the thermodynamic potential of the IC and commensurate phases obtained by minimizing (4) with respect to the amplitude of the equilibrium value of the order parameter is described by the expression[5]

$$\Phi_{\rm IC} = \Phi_0 - \frac{(\alpha - \alpha_i)^2}{6\beta}, \quad \alpha_i = \alpha_T(T_i - T_0),$$

$$\Phi_{\rm c} = \Phi_0 - \frac{\alpha^2}{4\beta}.$$

When these potentials are equal, a first-order phase transition from the IC to the commensurate phase occurs at a temperature

$$T_{\rm c} = T_0 - \frac{\sqrt{2}}{\sqrt{3} - \sqrt{2}}\frac{\alpha_i}{\alpha_T},$$

from which one obtains the relation

$$\frac{T_0 - T_{\rm c}}{T_i - T_0} \approx 4.4. \tag{8}$$

At the Lifshitz point $(T_{\rm L}, x_{\rm L})$ on the phase diagram (Fig. 1b) the coefficients α and δ vanish simultaneously. If one assumes a linear dependence $\delta \sim (x_{\rm L} - x)$ and $g = \text{const}$ in the neighborhood of this point, it is expected that[29]

$$q_0^2 \sim (x - x_{\rm L}), \quad T_i - T_{\rm c} \sim (x - x_{\rm L})^2. \tag{9}$$

Consequently, on approach to the LP the critical wave vector should go continuously to zero, while the lines of second-order transitions $T_i(x)$ and first-order transitions $T_c(x)$ that bound the IC phase for $x > x_{\rm L}$ merge smoothly (parabolically) into a line of second-order transitions $T_0(x)$ for $x < x_{\rm L}$.

Another possible situation is when $\alpha_2 > 0$ and $\alpha_4 < 0$ in the dispersion relation (2), and it is necessary to take into account the term of sixth order in the wave vector, with a coefficient $\alpha_6 > 0$ (Ref. 8). Then, as the triple point, with coordinates $\alpha_0 = 0$, $\alpha_4 = 0$, is approached on the phase diagram, the period of the modulation wave in the IC phase remains finite, and the critical fluctuations are not as large as in the case of the LP considered above, with $\alpha_0 = 0$, $\alpha_2 = 0$ in (2) or $\alpha = 0$, $\delta = 0$ in (3).

Analysis of a thermodynamic potential of the form (3) with an added invariant $\mathbf{f}\,(\partial\eta/\partial Z)^4$ shows that for $\mathbf{f} > 0$ the state diagram can have another triple point besides the LP (Fig. 2); at this new triple point an IC and a commensurate phase coexist with a rippled state (polar IC phase).[34,37] Whereas in the ordinary IC phase the order parameter η oscillates about a zero mean and the amplitude of the oscillations decreases and the wave vector increases with increasing temperature, in the rippled state the order parameter oscillates about a nonzero mean. The amplitude of the oscillations increases with increasing temperature, while the average value of the order parameter and the wave vector decrease. At the first-order transition to the ordinary IC state the average value of η drops discontinuously to zero, and the amplitude and wave vector of the modulation also change discontinuously. With decreasing temperature the rippled state has a continuous (second-order) transition to the commensurate phase. At the triple point with coordinates $\alpha \approx -7.09$ and $\delta \approx -5.32$ (under the condition $\beta = \mathbf{g} = \mathbf{f} = 1$) the slope of the two lines of first-order phase transitions are expected to be equal. There is as yet no information concerning the experimental observation of the rippled state or of the triple point at which the rippled state vanishes.

As one moves away from the LP into the IC phase the growth in amplitude of the order-parameter wave causes nonlinear effects to become important, and the structure of the phase diagram can become substantially more complicated, with transitions between different types of incommensurate states (the so-called "devil's staircase").[38]

A substantially different phase diagram with a Lifshitz point (in comparison with the form shown in Fig. 1) will arise if $\beta < 0$ and the invariants $\gamma\eta^6$ and $\lambda\eta^2(\partial\eta/\partial Z)^2$ are taken into account in expansion (3), i.e., in the case when the direct phase transition from the paraelectric to the ferroelectric phase is first order. If $|-\delta| \to 0$, then the lines of transitions $T_i(x)$ and $T_c(x)$ will come together at a finite angle at the triple point, which is determined by the relation

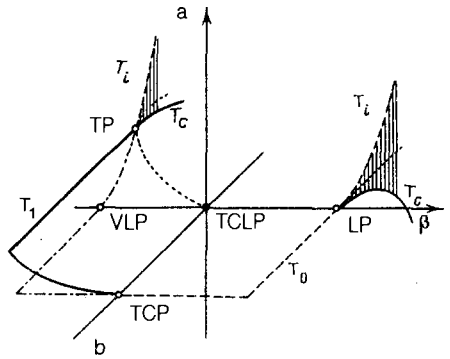

FIG. 3. Schematic phase diagram of a system with the thermodynamic potential of Eq. (10). The dashed lines are lines of second-order transitions from the paraphase to the ferrophase (T_0) or to the incommensurate phase (T_i); the solid lines are second-order transitions from the paraphase to the ferrophase (T_1) or from the incommensurate phase to the ferrophase (T_c). The regions of the incommensurate phase are shaded; the dotted lines in these regions are lines of virtual transitions T_0 for $\beta > 0$ and T_1 for $\beta < 0$. LP is a Lifshitz point, TCP is a tricritical point. TCLP is a tricritical Lifshitz point, VLP is a virtual Lifshitz point, and TP is a triple point. The line of triple points entering the TCLP is shown by a dotted line.

$\delta^2 = 3g\beta^2/8\gamma$ (Ref. 33). The LP is not reachable, i.e., it becomes virtual (Fig. 3).[40]

It is known that under the condition $\alpha = 0, \beta = 0$ there is a tricritical point (TCP), at which the phase transition from the high-symmetry phase to a low-symmetry phase commensurate with it changes from a second-order to a first-order transition.[41] The line of first-order phase transitions is determined by the relation

$$\alpha - \frac{3}{16}\frac{\beta^2}{\gamma} = 0.$$

On the state diagram with three "external" variables, e.g., temperature, pressure, and composition, there is a line of TCPs, specified by the conditions $\alpha(p,x) = \beta(p,x) = 0$ and $\delta > 0$. The relation $\alpha(p,x) = \delta(p,x) = 0$ for $\beta > 0$ specifies a line of Lifshitz points. These lines cross at the tricritical Lifshitz point (TCLP), for which $\alpha(p,x) = \beta(p,x) = \delta(p,x) = 0$ (Refs. 35, 40). A line of certain higher triple points also goes into the TCLP. Figure 3 shows a schematic illustration of the phase diagram in the space of coefficients α–β–δ on the assumption that the "temperature" α is not altered by the external "field". The existence regions of the IC phase for $\beta = \text{const} > 0$ and $\beta = \text{const} < 0$ are indicated by shading. The positive β semiaxis coincides with a line of LPs and the negative semiaxis with a line of virtual LPs. The axis $\delta > 0$ is a line of TCPs. In the neighborhood of the TCLP ($\beta = 0$) the line of first-order phase transitions α_c from the IC to the ferroelectric phase is determined by the equality of their thermodynamic potentials

$$\Phi_c = \frac{1}{3}\left(\frac{\alpha^3}{\gamma}\right)^{1/2}, \quad \Phi_{\text{IC}} = \frac{1}{3}\left[\frac{\alpha - (\delta^2/2g)^3}{5\gamma}\right]^{1/2}$$

and has the form

$$\alpha_c \approx -0.7\frac{\delta^2}{g}.$$

Thus in the mean field approximation the phase diagram in the neighborhood of the TCLP ($\beta = 0$) has qualitatively the same form as for the LP ($\beta > 0$): for $|-\delta| \to 0$ the lines of phase transitions bounding the IC phase come together parabolically in both cases. However for $\beta < 0$ these phase boundaries come together at a finite angle at a triple point.

3. CHANGE IN THE ANOMALIES OF THE THERMODYNAMIC PROPERTIES OF FERROELECTRICS ON TRANSITION THROUGH THE LIFSHITZ POINT

Lifshitz points have been observed on the state diagrams of the ferromagnet MnP (Ref. 15), liquid crystals (the NAC point; Refs. 21, 42), and the proper ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$ (Refs. 17–20). The temperature interval of the IC phase in the improper ferroelectric $RbH_3(SeO_3)_2$ decreases when an electric field is applied, and it has been conjectured that the triple point that can be reached in this way is also a Lifshitz point.[22] Studies of the proper ferroelectric $NaNO_2$ in a transverse electric field have shown[39] that the transitions to the IC phase in this compound are close to a tricritical Lifshitz point. It has been established in studies of the temperature–composition diagrams of liquid-crystal mixtures that different relative positions of the tricritical points and NAC point are possible, and, as a result, the latter can become a triple point or an end critical point.[42]

A sufficiently complete set of experimental data on the anomalies of the thermodynamic properties and their change over the phase diagram has been obtained only for the ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$. For this example it is possible to compare the experimental situation with the conclusions of the phenomenological theory.

The shape of the concentration phase diagram of $Sn_2P_2(Se_xS_{1-x})_6$ crystals was determined previously.[18,19] In $Sn_2P_2S_6$ there is a second-order ferroelectric phase transition at $T_0 \approx 338$ K ($P2_{1/c} \to Pc$) with no change in the number of formula units in the unit cell. As S is replaced by Se the line $T_0(x)$ for $x > 0.28$ splits smoothly into a line of second-order phase transitions $T_i(x)$ and a line of first-order phase transitions $T_c(x)$. For $Sn_2P_2Se_6$ one has $T_i \approx 221$ K and $T_c \approx 193$ K. The intermediate phase is incommensurate. The period of the transverse wave of spontaneous polarization in the IC phase of $Sn_2P_2Se_6$ is close to 12 unit cells at T_i and increases to 14 unit cells on cooling.[20] The temperature width of the IC phase in $Sn_2P_2(Se_xS_{1-x})_6$ increases with distance from the LP with coordinates $T_L \approx 295$ K, $x_L \approx 0.28$ in accordance with the relation $T_i - T_c = 45.8(x - x_L)^2$ (Ref. 43). This relation is plotted in Fig. 4. The wave vector of the modulation on the line $T_i(x)$ varies according to Eq. (9), i.e., $q_i^2 \sim x - x_L$ (Ref. 44).

Hydrostatic compression of $Sn_2P_2S_6$ also causes splitting of the second-order phase transition into second-order and first-order transitions.[45] The coordinates of the triple point on the T–p diagram of $Sn_2P_2S_6$ are $T_{TP} \approx 295$ K, $p_{TP} \approx 0.18$ GPa. The line of triple points 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 means that the intermediate phase on the T–p diagram of $Sn_2P_2S_6$ is also incommensurate. The change in its temperature width $T_i - T_c$ with distance from the triple point under increasing pressure, according to the data of Ref. 45, is also shown in Fig. 4.

The concentration and pressure dependences of the width of the IC phase have been determined in comparable intervals of composition and compression. At the same time, the form of these dependences is qualitatively different. The

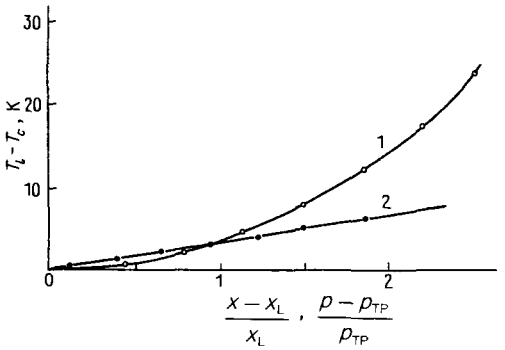

FIG. 4. Concentration dependence of the temperature interval of the incommensurate phase in $Sn_2P_2(Se_xS_{1-x})_6$ at atmospheric pressure (*1*) and its pressure dependence in $Sn_2P_2S_6$ (*2*).

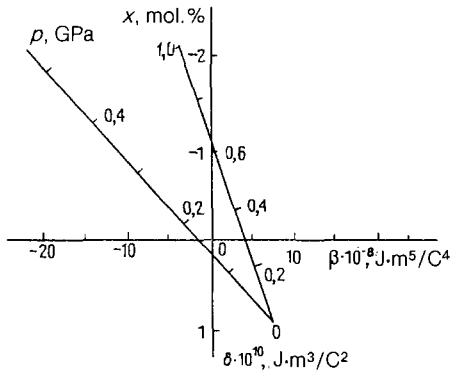

FIG. 5. Concentration and pressure "thermodynamic paths" in the δ, β plane (δ and β are the coefficients in Eq. (10)); these paths are followed through a change in the composition of the mixed crystals $Sn_2P_2(Se_xS_{1-x})_6$ and through hydrostatic compression of $Sn_2P_2S_6$, respectively.

width of the IC phase increases quadratically as S is replaced by Se, in fulfillment of the basic criterion for a Lifshitz point (9). Under compression, the width $T_i - T_c$ in $Sn_2P_2S_6$ increases linearly with $p - p_{TP}$ (Fig. 4). This indicates that the triple point on the T–p diagram of $Sn_2P_2S_6$ is not a Lifshitz point. In this case the line of triple points TP on the T–p–x diagram of $Sn_2P_2(Se_xS_{1-x})_6$ should go over into a line of Lifshitz points as x increases.

For proper uniaxial ferroelectrics with one-dimensional modulation in the IC phase we expand the density of the thermodynamic potential Φ in powers of the order parameter (the polarization P) and its spatial derivatives, following (3):

$$\Phi = \Phi_0 + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 + \frac{\delta}{2}P'^2 + \frac{g}{4}P''^2 + \frac{\lambda}{2}P^2P'^2 + \frac{c}{2}u^2 + kP^2u, \qquad (10)$$

where $\alpha = \alpha_T(T - T_0)$; the rest of the coefficients are assumed to be temperature independent. The last two terms in expansion (10) describe the energy of the elastic strain and the electrostriction interaction; here $c \equiv c_{ij}$ are the elastic stiffness constants, k is the electrostriction coefficient, $u \equiv u_{ij}$ is the strain tensor. It is assumed that the coefficients g, λ, c, and k do not depend on the composition of the mixed crystals.

Using data on the temperature dependence of the isobaric specific heat c_p (Refs. 40, 46) and of the spontaneous polarization P_s and the permittivity ε (Ref. 40) of $Sn_2P_2(Se_xS_{1-x})_6$ crystals, and also information on their thermal expansion[46] and elastic constants c_{ij} (Refs. 18, 47, 48) and on the temperature dependence of the wave vector q_0 of the modulation of the IC phase[20] and the effect of hydrostatic compression on the phase transition temperature,[45] we determined the thermodynamic paths in α–β–δ space on compression of the $Sn_2P_2S_6$ crystal or on changes in the chemical composition in the system $Sn_2P_2(Se_xS_{1-x})_6$. According to estimates[40] of the pressure dependences of β and δ, as the pressure is increased on the T–p diagram of $Sn_2P_2S_6$, first the tricritical point is reached (the order of the ferroelectric phase transition changes from second to first) and then, at the triple point, the first-order ferroelectric phase transition splits into second-order and first-order transitions bounding an IC phase (Fig. 5). In this case the Lifshitz point is virtual.

As the selenium content is increased on the concentration diagram of $Sn_2P_2(Se_xS_{1-x})_6$ at atmospheric pressure, first the Lifshitz point ($x_L \approx 0.28$) is reached and then the virtual tricritical point ($x_{VTCP} \approx 0.6$)—the expected direct phase transitions from the paraphase to the ferrophase for $x > 0.6$ are first order.

Thus the T–x diagram of $Sn_2P_2(Se_xS_{1-x})_6$ has a Lifshitz point, while the T–p diagram of $Sn_2P_2S_6$ has a triple point. Both thermodynamic paths, the concentration path and the pressure path, pass side by side toward the tricritical Lifshitz point TCLP (see Fig. 5). Here the virtual ferroelectric phase transition is more first order for $x = 0$ and $p = 0.5$ GPa than for $x = 1$ and atmospheric pressure. The fact that the expected direct phase transition from the paraelectric to the ferroelectric phase is increasingly first order causes the temperature interval in which the IC phase exists to become narrower.[40,49]

The fact that the coefficients δ and β in the neighborhoods of the LP and TCP are much smaller than their "atomic" values justifies taking additional terms of higher order into account in expansion (10), e.g., the term $(\lambda/2)P^2P'^2$, which characterizes the biquadratic coupling of the order parameter with its spatial derivative. Because of this coupling, and also on account of the homogeneous and inhomogeneous elastic strains, the coefficient of the P^4 term in expansion (10) is renormalized. For the paraelectric–ferroelectric transition the renormalization of the coefficient β is due to the interaction of the order parameter with the homogeneous strain,

$$\beta^0 = \beta - \frac{k^2}{2c}.$$

(The thermodynamic "paths" shown in Fig. 5 actually correspond to values of β^0.) In the IC phase the inhomogeneous distribution of the order parameter induces inhomogeneous strains; because of this, a "gap" Δ between the homogeneous and inhomogeneous strains forms on account of the long-range elastic forces. Then

$$\beta^* = \beta^0 + \Delta + \frac{2}{3}\lambda q^2.$$

The gap, which remains nonvanishing right to the LP, is given by

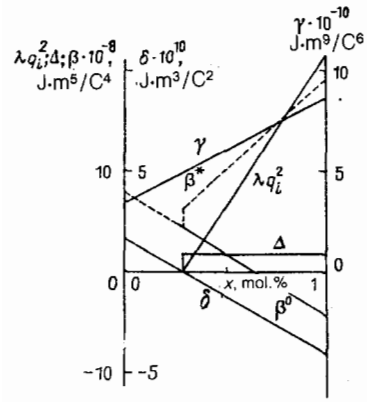

FIG. 6. Concentration dependence of the coefficients of the thermodynamic potential (10) of $Sn_2P_2(Se_xS_{1-x})_6$ crystals.

$$\Delta = \frac{4}{3}(K - \tilde{K}),$$

where (in the isotropic approximation)

$$K = \frac{k^2}{2\varkappa}, \quad \tilde{K} = \frac{k^2}{2[\varkappa - (4\mu/3)]},$$

and $\varkappa$ and μ are the bulk and shear moduli, respectively.

Figure 6 shows the concentration dependence of thermodynamic potential (10), as determined in Ref. 49 from the experimental data for $Sn_2P_2(Se_xS_{1-x})_6$. The effective value of the coefficient β^* decreases linearly like β^0 as x increases from 0 to x_L, and then at x_L it jumps upward by the value of the gap Δ and subsequently increases linearly. It is important to note that for $Sn_2P_2S_6$ the expected direct phase transition from the paraelectric to the ferroelectric phase is first order ($\beta^0 < 0$), whereas the observed phase transition from the paraelectric to the IC phase is second order ($\beta^* > 0$).

To illustrate the reliability of the estimates of the coefficients, in Fig. 7 we compare the experimental concentration dependence of the discontinuity in the specific heat on the line of phase transitions $T_i(x)$ with the values calculated from the formula $\Delta c_p = \alpha_T T_i / 3\beta^*$. The good agreement indicates that the phase transitions in mixed crystals $Sn_2P_2(Se_xS_{1-x})_6$ can be described with the help of potential (10) with allowance for the closely spaced Lifshitz and tricritical points.

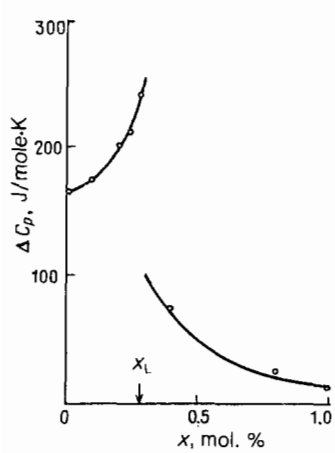

FIG. 7. Concentration dependence of the jump in the specific heat of $Sn_2P_2(Se_xS_{1-x})_6$ crystals on the line $T_0(x)$ for $x < x_L$ and on the line $T_i(x)$ for $x > x_L$. The points are experimental and the continuous lines, theoretical.

However, there are features of the anomalies in the physical properties of the $Sn_2P_2(Se_xS_{1-x})_6$ crystals that do not admit a phenomenological description in the mean field approximation. These include, for example, the fact that the anomalies of the temperature dependence of the specific heat,[50] coefficient of thermal expansion,[46] and velocity of ultrasound[18] extend deeper into the paraelectric phase as the composition approaches x_L, and also the low value of the critical exponent for the order parameter.[50] Possible causes of these deviations from mean field theory are the onset of appreciable fluctuation effects and the influence of defects.

4. THE ROLE OF FLUCTUATIONS IN THE NEIGHBORHOOD OF THE LIFSHITZ POINT. MANIFESTATION OF PROXIMITY TO THE TRICRITICAL LIFSHITZ POINT

As we have said, the principal feature of the Lifshitz point is that the wavelength of the modulation in the IC phase approaches infinity on account of the decrease in the coefficient δ in (3) as $x \to x_L$. This is analogous to a decrease in the correlation length ($r_c^2 \sim \delta$) and it promotes the growth of fluctuations of the order parameter.[6] The widening of the critical region can be estimated with the help of the Ginzburg–Levanyuk criterion.[51,52] For a transition to an IC phase with one-dimensional modulation, this criterion has the form[53]

$$\tau_{\mathrm{GI}} \equiv \frac{T_0(T_i)\beta^2}{\alpha_T \delta_a^2 \delta},$$

where

$$\tau \equiv \frac{T - T_0(T_i)}{T_0(T_i)},$$

if it is assumed that with respect to directions of reciprocal space that are orthogonal to the modulation vector, the coefficients of the quadratic term in dispersion relation (5) have the ordinary "atomic" value δ_α.

The critical behavior of substances near the Lifshitz point have been studied theoretically in a number of papers (see the review by Hornreich[7]). Particular attention has been paid to the analysis of systems with short-range interaction, in application to magnets. Here, in a d-dimensional space one singles out a sector of dimension m in which the wave vectors of the modulation lie.[6] The system is assumed isotropic in the m and $(d-m)$-dimensional spaces. The upper critical dimensionality, above which classical behavior is expected, is determined by the condition

$$d_{\mathrm{I}}(m) = 4 + \frac{m}{2}$$

with $m \leqslant 8$, and it is equal to 4 in the ordinary situation (for $m = 0$). Thus the regions of (d,m)-space in which classical or nonclassical critical behavior occur are divided by a line of critical dimensionality $(d_{\mathrm{I}}, m_{\mathrm{I}})$. The critical exponents for the system associated with the point (d,m) in the nonclassical region have been calculated by the renormalization-group method by expanding in the small quantities

$\varepsilon_\alpha = m_1 - m$ and $\varepsilon_\beta = (d_1 - m_I) - (d - m)$. It has been shown[6] that to lowest order in a ε_α and ε_β, all the critical properties depend only on the linear combination

$$\varepsilon_l = \frac{\varepsilon_\alpha}{2} + \varepsilon_\beta = 4 - d + \frac{m}{2}. \tag{11}$$

A distinctive feature of the Lifshitz point is the anisotropic nature of the correlation function for the order parameter. Fluctuations with wave vectors whose components lie in the m-dimensional space are characterized by a pair of exponents $\nu_L^{\parallel}$ and $\eta_L^{\parallel}$, while fluctuations with wave vectors in the $(d\text{-}m)$-space correspond to the pair $\nu_L^{\perp}$ and $\eta_L^{\perp}$. It is found that

$$\nu_L^{\parallel} = \frac{\nu_L^{\perp}}{2} = \frac{1}{4}\left[1 + \frac{(n+2)}{2(n+8)}\varepsilon_l\right] + O(\varepsilon_l^2), \qquad \eta_L^{\parallel}, \eta_L^{\perp} = 0 + O(\varepsilon_l^2), \tag{12}$$

where n is the number of components of the order parameter. Consequently, the critical exponents for the correlations of the order parameter in the directions along which the modulation wave arises differ by a factor of 2 from those for the other directions.

It is important to determine the lowest critical dimensionality d_l. Fluctuations prevent the formation of an ordered state for $d \leqslant d_l$, and therefore the phase transition temperature as a function of the dimensionality d goes to zero as $d \to d_l$. For the Lifshitz point $d_l = 2 + (m/2)$ (Ref. 35). Since $d_l = 4$ for the isotropic case $(m = d)$, an isotropic Lifshitz point cannot exist in real three-dimensional space. Only the uniaxial Lifshitz point $(m = 1)$ is experimentally accessible: $d_l = 2.5 < 3$. The temperature of the biaxial Lifshitz point $(m = 2)$ is 0 K, since for it $d_l = 3$.

Let us examine the effect of fluctuations on the form of the phase diagram near the Lifshitz point. In the neighborhood of this point the disordered phase is separated from the two ordered phases by a critical line with two branches, which cross at $T = T_L$ and $x = x_L$. In ferroelectrics, for example, these are lines of phase transitions from the paraelectric to the ferroelectric phase at $T_f(x)$ for $x < x_L$ $(\delta > 0)$ and to the incommensurate phase at $T_i(x)$ for $x > x_L$ $(\delta < 0)$. According to renormalization-group calculations, to zeroth order in ε_l the shape of the critical branches is given by the expression[54]

$$\tau_f \sim a\varepsilon\delta + A_f(\delta^{1/\Phi} - \delta^2) + b\varepsilon\delta^2 \quad \text{for } \delta > 0,$$
$$\tau_i \sim a\varepsilon\delta + A_i(|\delta|^{1/\Phi} - \delta^2) + \left(\frac{1}{4} + c\varepsilon_l\right)\delta^2 \quad \text{for } \delta < 0, \tag{13}$$

which in the limit $\delta \sim x_L - x \to 0$ take the form

$$\tau_f \sim A_f\delta^{1/\Phi}(\delta > 0), \quad \tau_i \sim A_i|\delta|^{1/\Phi}(\delta < 0); \tag{14}$$

here $\tau_f = [T_f(\delta) - T_L]/T_L$, $\tau_i = (T_i(\delta) - T_L)/T_L$; $a,b,c = O(\varepsilon_l)$. The crossover exponent Φ and the amplitude ratio A_i/A_f are universal quantities that do not depend on the details of the interaction in the system. It has been found[6,54] that

$$\Phi = \frac{1}{2} + \frac{n+2}{4(n+8)}\varepsilon_l + O(\varepsilon_l^2), \tag{15}$$

$$A_f = -\frac{m}{8} + O(\varepsilon_l), \quad A_i = -\left(1 - \frac{2}{m}\right)\frac{m}{8} + O(\varepsilon_l). \tag{16}$$

It follows from (16) that

$$\frac{A_i}{A_f} = \left(1 - \frac{2}{m}\right) + O(\varepsilon_l).$$

For example, for a one-component order parameter and a one-dimensional modulation in three space, formulas (15) and (16) give $\Phi \approx 0.625$, $A_f \approx -1/8$, $A_i \approx 1/8$, $A_i/A_f \approx -1$. We note that in the approximation used, the amplitude ratio is independent of the number of components of the order parameter.

For $\varepsilon_l \to 0$ formulas (13) and (15) yield the form of the branches of the critical line in the mean field approximation:

$$T_f - T_0 = 0 \quad (\delta > 0), \quad T_i - T_0 = \frac{\delta^2}{4} \quad (\delta < 0).$$

In this approximation $\Phi = 0.5$, $A_i > 0$, and $A_f = 0$, in agreement with relation (9). Figure 8 shows the shapes of the critical lines in the neighborhood of a Lifshitz point according to mean field and renormalization-group calculations.

Thus fluctuations can have a substantial effect on the shapes of the phase boundaries in the neighborhood of the LP. For example, without fluctuations the branch $T_f(x)$ coincides with the line $T_0(x)$ as $x \to x_L$, and the branch $T_i(x)$ deviates quadratically from this line. When fluctuations are taken into account, e.g., for the case $m = n = 1$, both branches $T_f(x)$ and $T_i(x)$ converge smoothly with the tangent to the phase boundary at x_L, with curvatures that are equal in magnitude but opposite in sign, i.e., the LP coincides with an inflection point of the critical line.

Mean field calculations also give a line of first-order transitions $T_c(x)$ from the IC phase to an ordered commensurate phase (8).[29] Renormalization-group calculations do not give any information about this line. Nevertheless, the generalized scaling approach is assumed to be valid for this line also.[54,55] Consequently, the shape of the line $T_c(x)$ as $x \to x_L$ is determined by the same crossover exponent as for the line $T_i(x)$.

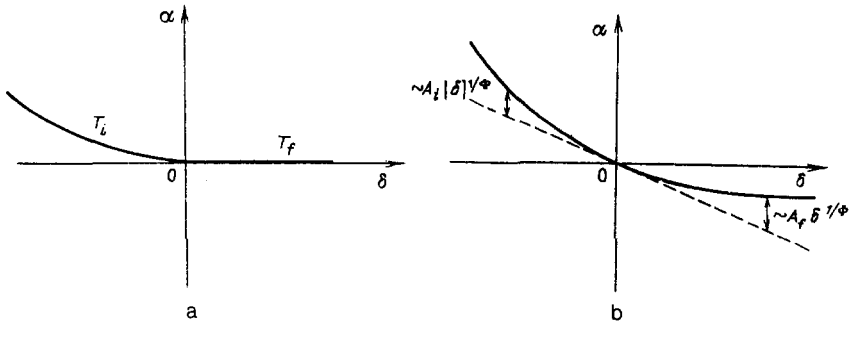

FIG. 8. The shape of the branches of the critical line in the neighborhood of Lifshitz points separating the paraelectric phase from the incommensurate phase $T_i(x)$ and from the commensurate phase $T_f(x)$ in the mean field approximation (a) and according to the renormalization-group calculation of Ref. 54 (b).

The region of validity of the scaling laws, e.g., for the order parameter $\eta \sim |\bar{\tau}|^{\beta'}$ or for the susceptibility $\chi \sim \bar{\tau}^{-\gamma'}$, is largest for the optimum choice of linear scaling axes $\bar{\tau}$ and $\bar{x}$. At a certain point of the critical line the orientation of the $\bar{\tau}$ axis can be chosen parallel to any direction in the (T,x) plane except the direction tangent to this line. The same asymptotic behavior is expected in all nontangential directions. The optimum direction is determined from renormalization-group calculations. One assumes[55] that the $\bar{\tau}$ axis is perpendicular to the critical line at the LP (then the value of $\bar{\tau}$ is determined by the "distance" to the critical line in the (T,x) plane), while the $\bar{x}$ axis is tangent to it. If the dependence of the phase transition temperature on the variable x in the neighborhood of the LP is found to be weak, then the scaling axes $\bar{\tau}$ and $\bar{x}$ are close to the axes T and x, respectively. In such a case the temperature width of the IC phase on approach to the LP can be described by a power law: $T_i - T_c \sim (x - x_L)^{1/\Phi}$.

For the LP one introduces[6] a new critical exponent β_q, which characterizes the change in the wave vector of the modulation on the line $T_i(x)$:

$$q_i \sim (x - x_L)^{\beta_q} \beta_q = \frac{\nu_L^{\parallel}}{\Phi}. \tag{17}$$

In mean field theory $\beta_q = 0.5$ (see Eq. (9)).[29] Fluctuation effects can alter this value of β_q, just as they do the shape of the phase boundaries near the LP. However, according to renormalization-group studies[6,7] there is no correction to the classical value of β_q to first order in ε_l.

For a Lifshitz point, because of the two correlation lengths, there are new scaling relations:[6]

$$m\nu_L^{\parallel} + (d-m)\nu_L^{\perp} = 2 - \alpha'_L,$$
$$\nu'_L = (4 - \eta''_L)\nu''_L = (2 - \eta^{\perp}_L)\nu^{\perp}_L. \tag{18}$$

The three-exponent relation

$$2\beta'_L = 2 - \alpha'_L - \gamma'_L \tag{19}$$

remains unchanged. Formulas (11), (12), (18), and (19) can be used to calculate the exponents for the correlation length (ν), specific heat (α'), susceptibility (γ'), and order parameter (β'). In Landau theory $\alpha' = 0$, $\gamma' = 1$, $\beta' = 0.5$, and $\nu = 0.5$. Renormalization-group calculations for a three-dimensional space in the case of a one-component order parameter and a one-dimensional modulation give the following values of the critical exponents for the LP:[6] $\beta'_L \approx 0.25$ and $\gamma'_L \approx 1.25$. However, these values are not exact, since for real space the parameter ε_l is equal to 1.5, as follows from (11), and cannot be considered small. The values $\beta' = 0.19 \pm 0.02$, $\gamma' = 1.4 \pm 0.06$, and $\alpha' \approx 0.2$ have been obtained[32] for this case by the method of statistical modeling. These effective values are expected in the temperature interval $10^{-2} < \tau < 2 \cdot 10^{-1}$.

The degree of deviation from the conclusions of mean field theory depends on the force of interaction between fluctuations, i.e., on the value of the coefficient β of the fourth-degree invariant η^4 in (3). On approach to a tricritical point $\beta \to 0$, and its upper critical dimensionality $d_I = 3$. Consequently, in the neighborhood of a TCP the behavior of the system conforms to the conclusions of mean field theory with weak fluctuational corrections. As one moves along the line of LPs toward the tricritical Lifshitz point (TCLP) the size of the fluctuation effects also decreases, but they remain important: for a uniaxial ($m = 1$) TCLP one has $d_I = 3.5$ (Ref. 36). The lower critical dimensionality in this case is $d_l = 2.5$, i.e., the uniaxial TCLP can exist in real space. Renormalization-group calculations[56,57] give $\beta' \approx 0.14$ and $\gamma' \approx 1.07$ for the TCLP. Although such calculations give only approximate results, they do reveal the tendency of the critical exponents to change as one moves around on the phase diagram in the neighborhood of the TCLP. For example, normal Ising-like behavior corresponds to an exponent $\beta' \approx 0.33$. This exponent decreases as one approaches both the TCP and the LP. As one moves along the line of TCPs or along the line of LPs toward the TCLP, the exponent β' continues to decrease, reaching its minimum value at the TCLP.

In uniaxial ferroelectrics fluctuations are suppressed by the long-range Coulomb forces; this can be taken into account by increasing the dimensionality of the space to four.[58] The critical behavior of uniaxial ferroelectrics corresponds to mean field theory with logarithmic corrections. At the same time, for antiferroelectrics, in spite of the long-range dipole interaction, the critical behavior is the same as for the corresponding Ising system with short-range forces. In other words, mean field theory is sufficiently accurate only in the limit of a homogeneous long-range Coulomb interaction.[59]

A theoretical analysis of the critical behavior has been carried out for a "dipole" LP–a system with two modulation axes and a dipole interaction directed perpendicular to the plane of the modulation axes.[60,61] For such a system one expects quasi-one-dimensional critical behavior, since fluctuations are correlated only along the "long-range" axis. The temperature of the "dipole" LP goes to 0 K. It is noteworthy that for a "dipole" LP the critical exponents for the correlation length in the plane of the modulation axes ($\nu^{\parallel}$) and in the direction of the polarization axis ($\nu^{\perp}$) differ by a factor of three.[61]

It is important to note that uniaxial ferroelectrics, like the uniaxial LP in a system with short-range forces, has critical fluctuations characterized by two correlation lengths with different critical exponents ν. Therefore, the uniaxial LP in a uniaxial ferroelectric is characterized by three correlation lengths and in this sense is a most complex system. In spite of the fact that $d = 4$ in uniaxial ferroelectrics, for a Lifshitz point in them $d < d_I$, and fluctuation effects remain important. For a TCLP here $d > d_I$, and in the neighborhood of such a point one expects classical tricritical behavior.

As we mentioned in the introduction, the LP has been investigated experimentally in the magnet MnP (Refs. 15, 55) and in the proper ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$ (Refs. 17, 40). On the T–H diagram (temperature versus magnetic field perpendicular to the ferromagnetic axis) of MnP the line of second-order phase transitions from the paramagnetic phase to an IC phase with a modulated (fan) ordering of the spins and the line of first-order transitions from the IC phase to the ferromagnetic phase merge smoothly into a line of second-order transitions directly from the paramagnetic to the ferromagnetic phase. As the system approaches the triple point with coordinates $T_L \approx 121$ K, $H_L \approx 16.5$ kOe at which a second-order phase transition occurs, the wave vector of the modulation of the IC phase goes continuously to zero. It has been established by careful experiments that the crossover exponent for the phase diagram of MnP in the neighborhood of the LP is $\Phi = 0.64 \pm 0.04$. This value is in good agreement

with the value expected from renormalization-group calculations for such a case ($m = n = 1$), viz., $\Phi \simeq 0.625$ (Ref. 55). In addition, the triple point coincides with an inflection point of the critical line. Thus the data on the triple point on the T–H diagram of MnP are in complete agreement with the theoretical conclusions about the LP. However, there is no information in the literature as to the critical exponents for the thermodynamic parameters nor on the influence of tricriticality in this compound.

It has been reported that the critical behavior at TCPs induced by compression in crystals of the type $RbCaF_3$ (Ref. 62) and NH_4Cl (Ref. 63) and in NbO_2 (Ref. 64) is close to that expected for the TCLP. In particular, a value $\beta' \approx 0.19$ has been found for the critical exponent of the order parameter, which is substantially smaller than the value $\beta' = 0.25$ characteristic for a TCP. The fact that the soft branch associated with structural phase transitions in these substances is quite gently sloping[63] also indicates that the TCP and LP that they have will be close together. However, doubt has been cast[62] as to whether the higher-order critical point reached in these cases can be interpreted unambiguously as a TCLP. For example, the value of β' can be decreased by logarithmic fluctuational corrections. It also decreases on approach to a fourth-order critical point, in which case $\beta' \approx 0.17$.[65] Most importantly, no IC phases have been observed on the state diagrams of the substances mentioned, which, if present, would permit immediate identification of the LP and would establish the existence of a TCLP.

The anomalies of the thermodynamic characteristics in the mean field approximation have been investigated and analyzed most fully for the crystals $Sn_2P_2(Se_xS_{1-x})_6$, whose concentration phase diagram has not only a Lifshitz point at $x_L \simeq 0.28$ but also a "virtual" tricritical point at $x_{VTCP} \approx 0.06$ (Ref. 49). Information about the positions of the multicritical points on the state diagram permits interpretation of the complicated nature of the critical behavior of the thermodynamic functions. As the system approaches the second-order ferroelectric phase transition one should observe a change in its behavior (crossover) from tricritical to critical. Furthermore, another type of crossover is possible in the critical region—a transition from classical behavior, conforming with the conclusions of mean field theory, to fluctuational behavior. The region in which the latter type of crossover appears and its particular properties are determined by the dimensionality of the system and the number of components of the order parameter. For uniaxial ferroelectrics, as we know,[58] the effective spatial dimensionality is $d = 4$, which is equal to the upper critical dimensionality d_1 for a second-order phase transition. However, for a first-order Lifshitz point ($L = 1$, i.e., the coefficient of the q^2 term in the expansion of the stiffness for fluctuations of the order parameter in even powers q^{2L} is equal to zero) with a single modulation direction one has $d < d_1 = 4.5$. The critical behavior corresponding to a Lifshitz point in principle is intermediate between the critical behavior for the d-dimensional and $(d-1)$-dimensional cases (the latter is identical to a Lifshitz point of infinite order, $L \to \infty$). This is manifested in a widening of the fluctuation region as the LP is approached, and also in a change of the critical exponents.

Whereas for $x < x_L$ the second-order transition on the line $T_0(x)$ is characterized by a one-component order parameter (the eigenvector of the nondegenerate optical phonon at the Brillouin zone center is $q = 0$), for $x > x_L$ the second-order phase transition from the paraelectric to the IC phase on the line $T_i(x)$ has a two-component order parameter ($n = 2$)—the dynamic instability of the lattice is characterized by a two-pronged star of wave vectors. Consequently, as x increases away from the LP one observes a crossover to Heisenberg behavior.

Thus, in analyzing the experimental data one must take into account the possible presence of four types of crossover:

1. From tricritical behavior to critical behavior;
2. From classical critical behavior to fluctuational;
3. From fluctuational in the d-dimensional case to fluctuational in the nearly $(d-1)$-dimensional case;
4. From fluctuational Ising-like ($n = 1$ for $x < x_L$) to fluctuational Heisenberg-like ($n = 2$ for $x > x_L$).

Let us examine the change in the effective values of the critical exponents for the specific heat (α') and for the order parameter (β') as determined from the thermooptical data for $Sn_2P_2(Se_xS_{1-x})_6$ crystals[66] by the Senarmont method. This method was used to measure the change in the angle of rotation of the polarization of light, φ, which is proportional to the birefringence Δn. As we know, in the region of weak fluctuational corrections $\Delta n \sim n^2 \sim \tau^{2\beta'}$. In addition, throughout the temperature interval we have $d\Delta n/dT \sim \Delta c_p \sim \tau^{-\alpha'}$.

Figure 9 shows the temperature dependence of the effective exponents β' and α' for the ferroelectric phase of $Sn_2P_2S_6$, as obtained by processing the data on $\varphi(T)$. As τ decreases, β' increases from 0.3 to 0.5 and then decreases somewhat in the immediate neighborhood of T_0. This is consistent with a crossover from tricritical behavior ($\beta' = 0.25$) to classical critical behavior ($\beta' = 0.5$). The temperature of this crossover, as obtained from the relation $\alpha = \beta^2/4\gamma$ with the values of the coefficients of potential (10) from Fig. 6 corresponds to $T_0 - T \approx 4$ K for $Sn_2P_2S_6$. It should be noted that the number Gi defined according to Ref. 51 corresponds to approximately the same temperature distance to T_0. Consequently, for $Sn_2P_2S_6$ and also for mixed crystals with composition close to x_L, the crossover from tri-

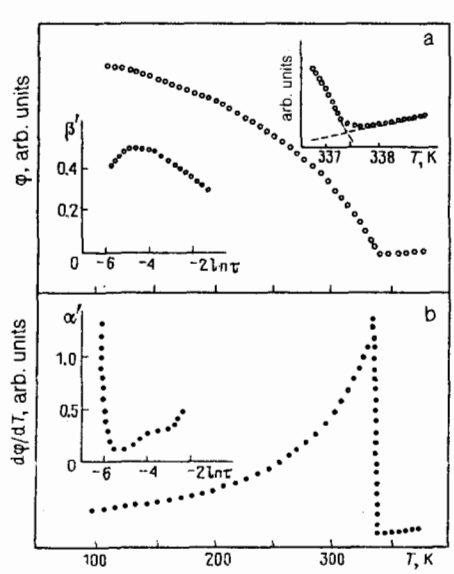

FIG. 9. Temperature dependence of the birefringence (a) and its derivative (b) for the $Sn_2P_2S_6$ crystal. The insets show the temperature dependence of the critical exponents of the order parameter (β') and specific heat (α').

critical behavior to critical behavior is actually a crossover from tricritical behavior to fluctuational behavior.

The temperature dependence of the exponent α' agrees with the above: it decreases from 0.5 to 0.1 as the temperature is raised. As T_0 is approached, at $\ln \tau \leqslant -6$, the value of α' increases, tending toward the value 1.5, which is characteristic for behavior governed by defects.[67] Consequently, in the immediate vicinity of T_0 the critical behavior of the $Sn_2P_2S_6$ crystal is probably governed by defects.

For the sample with $x = 0.29$, which is closest to the LP ($x_L \approx 0.28$), the exponent is $\beta' = 0.20 \pm 0.02$ throughout the temperature interval. The critical exponent α' varies somewhat about the value 0.5 (Ref. 66). According to an estimate based on the values shown in Fig. 6 for the coefficients of the thermodynamic potential (10), for compositions near x_L one should observe tricritical behavior all the way to a fraction of a degree from T_0. This reflects the proximity of the LP on the state diagram to the TCLP (Fig. 5). However, the experimental value of β' is clearly lower than the classical tricritical value, which should obtain near a TCLP in the case of one-dimensional modulation in a uniaxial ferroelectric ($d_I = 3.5 < d = 4$). The probable reason for such a low value of β' is crossover to the critical behavior characteristic for a biaxial TCLP, for which $d_I = 4$. That this system is close to a state with two-dimensional modulation is indicated by calculations of the lattice dynamics of $Sn_2P_2(Se_xS_{1-x})_6$ crystals in the rigid-ion model,[68] according to which the dispersion of the soft optical branch is insignificant along both axes (z and y) perpendicular to the direction of the spontaneous polarization ($\mathbf{P}_s$ is close to the Cartesian axis x).

For states with $x > x_L$ Heisenberg-like critical behavior is expected on the line of transitions $T_i(x)$ from the paraelectric to the IC phase. The most convenient crystal for analysis of the critical exponents is $Sn_2P_2Se_6$, which has the largest temperature width of the IC phase. According to Fig. 6 (see Ref. 49), the second-order phase transition at T_i is quite far from the TCP. In the IC phase near T_i one finds $\beta' = 0.35 \pm 0.01$ and $\alpha' = 0.0 \pm 0.1$ (Ref. 66). These values agree with the results of calculations[69] for the two-component three-dimensional Heisenberg model.

On the whole, the results of the analysis of the critical behavior of the ferroelectrics $Sn_2P_2(Se_xS_{1-x})_6$ indicate that when IC phases are present on the state diagram, it is necessary to take into account the possibility of a complicated combination of crossovers involving tricriticality, the character of the spatial anisotropy of the order-parameter fluctuations, and changes in the number of components of the order parameter.

Another remarkable finding is the similarity of the critical behavior of quasi-two-dimensional systems such as $RbCaF_3$ and $BaMnF_4$ and that of $Sn_2P_2(Se_xS_{1-x})_6$ crystals. In principle it is possible to trace the evolution of the tricritical Lifshitz behavior as the symmetry of the crystal lattice changes: tetragonal (uniaxially compressed $RbCaF_3$) to rhombic ($NaNO_2$) to monoclinic ($Sn_2P_2(Se_xS_{1-x})_6$).

In conclusion we note that the relationships established by studying substances in the neighborhood of the LP are useful for analyzing the thermodynamic properties at phase transitions in different compounds. In addition, the results that have been obtained to date indicate that substances in states near LPs on the phase diagrams are softer than normal. This promotes strong nonlinearity of their physical properties, e.g., the high optical cubic nonlinearity in the IC phase near the LP in $Sn_2P_2(Se_xS_{1-x})_6$ (Ref. 70). In the neighborhood of the LP the width of the IC phase can change not only under "conventional" influences such as mechanical compression, a change in the chemical composition, or a static electric or magnetic field which is not conjugate to the order parameter, but also in the field of an electromagnetic wave,[70] the creation of a metastable population of the energy levels in semiconducting materials by illumination or a rapid change in temperature.[71]

In this review we have not discussed the results of studies (see, e.g., Refs. 72 and 73) of the changes in the shape of the phase diagrams of ferroelectrics in the neighborhood of the LP in a static electric field conjugate to the order parameter (the E–T–x diagrams). Such studies are of interest for the purpose of establishing the evolution of the shape of the E–T–x diagrams upon a change in the distance to the TCLP, of searching for polar IC phases and observing fourth-order points (at which polar IC phases vanish) on the E–T–x diagrams.[74]

The evolution of the shape of the modulation wave on cooling toward the low-temperature boundary of the IC phase in proper ferroelectrics must be handled separately. An urgent problem is to extend the results of theoretical studies[75–78] to the description of phase transitions from the IC to the ferrophase with allowance for higher harmonics of the modulation, nonlinearities, and coupling with strains, in order to explain how the anomalies of the thermodynamic properties, in particular the dielectric susceptibility, change along the line $T_c(x)$ at various distances for the LP and TCLP.

The microscopic mechanisms for the onset of IC phases and the presence of LPs on the state diagrams have been analyzed in other reviews.[79,80] For $Sn_2P_2(Se_xS_{1-x})_6$ compounds some experimental results on the lattice dynamics and an analysis of the microscopic mechanisms for the phase transitions and the reasons for the presence of the LP on the concentration diagram are given in Refs. 68 and 81. From the standpoint of studying microscopic models it is assuredly of interest to develop an understanding of the conditions for the presence of a TCLP on the state diagrams.

For analysis of the experimental data in the neighborhood of the LP it is particularly important to continue the research (not discussed in this article) on the effects of metastability of the IC phases. Finally, there is an urgent need to study the kinetic properties and to elucidate the features of the dynamic critical phenomena in the neighborhood of LPs.

5. CONCLUSION

The critical behavior of the majority of crystals in the neighborhood of phase transitions differs from the behavior predicted for the corresponding universality classes. One can see that the relative disparity between the observed and standard values of the critical exponents for the thermodynamic functions are correlated with the anisotropy of the dispersion of the stiffness for fluctuations of the order parameter. One manifestation of this anisotropy is the Lifshitz point, which separates on the state diagram the second-order transitions going from the initial phase to commensurate and incommensurate phases. Another decisive factor is the interaction between fluctuations, with a force proportional to the distance

to the tricritical point on the state diagram. It follows from the present review that the identification of such higher-order critical points is an important prerequisite for determining the mechanisms governing the anomalies of the phenomenological properties of substances at phase transformations.

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