Infinite Lifshitz point in incommensurate type-I dielectrics

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The phenomenological analysis of the pressure-temperature (P-T) phase diagram of $[N(CH_3)_4]_2CuCl_4$ (TMATC-Cu) crystals is presented. It is shown that serious disagreement between the experimental results and theory may be removed assuming that the coefficient of the Landau free energy expansion κ at the gradient term $(dq/dz)(dq^*/dz)$ changes the sign in the experimental range of pressures. The phase diagram in the α-κ phase plane is characterized by infinite Lifshitz point (at $\kappa\rightarrow\infty$) in which both lines of the phase transitions into the incommensurate phase merge together, whereas the incommensurate wave vector approaches its zero value. The triple point ($P_K\approx 55$ MPa, $T_K\approx 304$ K) observed in these crystals may be considered as an artificial point, which results from the limitation of experimental resolution. Therefore, even above P_K there still exist two very close (unresolved) lines of the incommensurate phase transitions. [S0163-1829(99)12221-5]

It is well known that external influences (electric field, mechanical stress, hydrostatic pressure, etc.) essentially distort the structure of incommensurate (IC) phases of ferroelectric and ferroelastic crystals. In many cases they lead to the appearance of triple points in phase diagrams, where the two lines of the IC phase transitions [referred usually as normal (N)-IC and IC-commensurate (C) transitions, respectively] merge into the one line of direct transitions from the N to C phase. In the IC dielectrics of type I (according to Bruce-Cowley classification[1]) the phase transformation from N to C phase is usually associated with a two-component complex order parameter (q_1,q_2). The symmetry of the N phase allows the existence of Lifshitz invariant $i\delta(q_1dq_2/dz - q_2dq_1/dz)$. In the plane wave approximation it gives the linear (with respect to wave vector k) contribution to the soft mode dispersion, which near commensurate point k_C is presented as

$$\omega^2(k)=\alpha+2\,\delta(k-k_C)+\kappa(k-k_C)^2. \tag{1}$$

The minimum $\omega^2(k)$, thus, corresponds to point $k_i=k_0-k_C=-\delta/\kappa$. Therefore if just only $\delta\neq 0$, the direct second order phase transition N-C phase is impossible. Particularly, before it should take place at $\alpha=0$, the second order phase transition into the inhomogeneous IC phase occurs at $\alpha_i=A_0(T_i-T_0)=\delta^2/\kappa>0$. In fact this is the simplified presentation of one of the well known general principles of the Landau theory – the so-called Lifshitz condition. Therefore, in the case of scalar (nonsymmetry breaking) external influences the Lifshitz point, which has been introduced initially for IC system II (Refs. 2, 3) appear to be symmetry forbidden in the IC system I. In this case two kind of multicritical points are expected to occur.

(i) The condition $\alpha=\delta=0$ defines the isolated point of direct second order phase transition in the $\alpha-\delta$ phase plane from the N to C phase. Such a point appears in the intersection of two lines of phase transitions into the IC phase, i.e., it is tetracritical point.[4]

(ii) In principal, a direct first order phase transition from N to C phase is possible. The corresponding phase diagram has been considered by Sannikov.[5,6] The direct first order N-C transition appears at $\alpha=a_{nc}$ for $\beta<0$ if $\alpha_{nc}=\beta^2/4\gamma>\alpha_i$ (where γ is coefficient at six-order term in the free energy), thus, the condition $\alpha_{nc}=\alpha_i$ defines the coordinates of the triple point in the phase diagram. This point, however differs from the Lifshitz point, since the wave vector of the IC modulation, as well as the angle between the tangents to the lines of IC phase transitions are finite in the triple point. Instead of this, only the lines of the first order transitions $\alpha_{nc}(\sigma)$ and $\alpha_{ic}(\sigma)$ $(\sigma=\beta^2/4\gamma-\delta^2/2\kappa)$ have common tangent in the triple point.

Although the model of triple point in the IC dielectric I (Refs. 5, 6) seems to be fairly reliable, some recently obtained experimental results are not likely explicable within this model. One such result has been obtained for the improper incommensurate ferroelastic $[N(CH)_3)_4]_2CuCl_4$ (TMATC-Cu). The triple point separating the N, IC, and C phase in the pressure-temperature phase diagram has been found in previous studies by optical birefringence and acoustical methods.[7] One must remember that this crystal at atmospheric pressure undergoes several successive phase transitions, including two IC transitions at $T_i=298$ K and $T_C=292$ K.[8] At $T=T_i$ the high-temperature orthorhombic N phase (space group $Pmcn$) loses its stability at the wave vector $k_0=c^*(1/3-\xi)$, where $\xi\approx 0.007$ and is nearly temperature independent in the IC phase. At $T=T_C$ the wave number $\xi\rightarrow 0$ and the monoclinic improper ferroelastic C phase (space group $P12_1/c1$, $k_C=c^*/3$) appears. Following the symmetry consideration, the transition from N to C phase in TMATC-Cu is associated with the two-component order parameter and the Lifshitz invariant is allowed.[9] Therefore, the direct second order phase transition from the N into C phase is symmetry forbidden, which contradicts the experimental results.

(i) Above $P_K \approx 55$ MPa the direct phase transition from N to C phase is observed. However, the variations of optical birefringence Δn_C and shear elastic constant C_{66} (Ref. 7) are quite continuous near T_0, therefore the corresponding phase transition is of the second order, but not of the first order, as it follows from the symmetry.

(ii) The magnitudes of the jumps of the optical birefringence $\delta(\Delta n_C)$ and of the elastic constant δC_{66} (Ref. 7) at the first order phase transition from the IC to C phase $(T = T_C)$ critically decrease at approaching to P_K, whereas the lines of the N-C and IC-C phase transitions do not have a common tangent in the triple point (P_K, T_K) that contradicts the prediction of the theory.[5,6]

A similar point has been also revealed in the *P-T* phase diagram of improper incommensurate ferroelectric NH_4HSeO_4.[10] For TMATC-Mn (Ref. 11) the appearance of such a triple point is expected in the region of negative hydrostatic pressure. In the vicinity of triple point all these crystals manifest the behavior rather close to this one, which is expected in the case of the Lifshitz point. However, the Lifshitz point is symmetry forbidden in the IC system I, as was already mentioned. Levanyuk[12] was the first to pay attention to this disagreement. However, this problem is still unsolved.

Considering the phase diagrams in IC systems I, the authors[5,6,9] have restricted the free energy expansion by the first order gradient terms of the order parameter. In this case only two types of policritical points are expected, which correspond to tetracritical or triple points. Within these theories it was assumed that coefficient κ^* at the gradient term $(dq_1/dz)(dq_2/dz)$ is positive and independent of the external influences. Obviously such an assumption restricts the behavior of IC systems and results in a reduction of a number of possible types of policritical points in their phase diagrams. In fact no physical reasons are found for such a restriction and the coefficient κ^* can takes negative values as well. Moreover, according to the group theory the product $(\epsilon/2)(dq_1/dz)(dq_2/dz)P$ (where P is scalar external parameter, which is associated in our case with the hydrostatic pressure) is also invariant to all operations of symmetry in the N phase and for this reason must be included in the free energy expansion. After a simple procedure of renormalization one obtains a new effective coefficient $\kappa = \kappa^* + \epsilon P$. Generally speaking, this coefficient is thus dependent on P and we can expect for some real systems that it may change the sign at experimental range of the applied pressures P. In order to stabilize the Landau free energy we must include in the expansion additional high order gradient terms. In our opinion it seems rather interesting then to consider the phase diagram also in the α-κ phase plane, which completes previous considerations of the phase diagram in the α-δ and α-σ phase planes. This phase diagram is rather unusual, since it contains infinity critical point, which appears when the value of coefficient κ tends to infinity. In this case the lines of N-IC and IC-C phase transitions merges at infinity, whereas the wave vector of the IC modulation continuously approaches its zero value. We shall refer to the infinite multicritical point as an infinite Lifshitz point, since all other properties of this point are the same as for usual (finite) Lifshitz point in IC system II. Although somewhat unusual at first glance, such a model is able to explain the main features experimentally observed. Particularly, as will be shown below, the experimentally observed ''finite'' triple point in the phase diagram may appear as result of limit experimental resolution, therefore even above P_K there always exists two very close lines of the incommensurate phase transitions. To make it more clear let us consider a partial case of the free-energy expansion for TMATC-Cu containing a sixth-order $(n=6)$ anisotropic invariant[9]

$$F = \int_{-L/2}^{L/2} \phi(z)\,dz,$$

$$\begin{aligned}\phi(z) = {}& \frac{\alpha}{2} qq^* + \frac{\beta}{4}(qq^*)^2 + \frac{\gamma_1}{6}(qq^*)^3 - \frac{\gamma_2}{12}(q^6 + q^{*6}) \\ &+ f(q^3 + q^{*3})U_0 + \frac{1}{2}C_{55}^o U_0^2 + \frac{i\delta}{2}\left(q^* \frac{dq}{dz} - q\frac{dq^*}{dz}\right) \\ &+ \frac{\kappa}{2}\frac{dq}{dz}\frac{dq^*}{dz} - \frac{i\mu}{2}\left(q^*\frac{d^3q}{dz^3} - q\frac{d^3q^*}{dz^3}\right) \\ &+ \frac{\lambda}{2}\frac{d^2q}{dz^2}\frac{d^2q^*}{dz^2},\end{aligned} \tag{2}$$

where $\alpha = A_0(T - T_0)$ and $\beta, \delta, \gamma_1, \gamma_2, \mu$, and λ are assumed to be positive. The free energy density functional $\phi(z)$ in Eq. (2) differs from Refs. 5, 6, 9 only by a presence of the two last terms, which contain third and second order derivatives of the inhomogeneous two-component order parameter $[q(z), q^*(z)]$. For simplicity we consider here only one gradient invariant (μ term) which produces the contribution to the free energy proportional to $(k - k_C)^3$ (see below). Indeed, the free energy is stabilized by a λ term. A trivial minimization procedure applied to Eq. (2) (see, e.g., Refs. 13, 14) leads us to the following expressions for the free energy in the IC and C phases.

IC phase:

$$\begin{aligned}F_{IC} = {}& \frac{\alpha_k}{2} q_k q_k^* + \frac{\beta}{4}(q_k q_k^*)^2 + \frac{\gamma_1}{6}(q_k q_k^*)^3 \\ &- \frac{\gamma_2}{2}(q_k^5 Q_{K''} + q_k^{*5} Q_{K''}^*) + f(q_k^3 U_{K'} + q_k^{*3} U_{K'}^*) \\ &+ C_{55}^o(K') U_{K'} U_{K'}^* + \frac{\alpha_Q(K'')}{2} Q_{K''} Q_{K''}^*;\end{aligned}$$

$$\alpha_k = \alpha + 2\delta(k - k_C) + \kappa(k - k_C)^2 + 2\mu(k - k_C)^3 + \lambda(k - k_C)^4;$$

$$q_k = q e^{i(k-k_c)z}, \quad q_k^* = q^* e^{-i(k-k_c)z},$$

$$K' = c^* - 3k, \quad K'' = 2c^* - 5k. \tag{3}$$

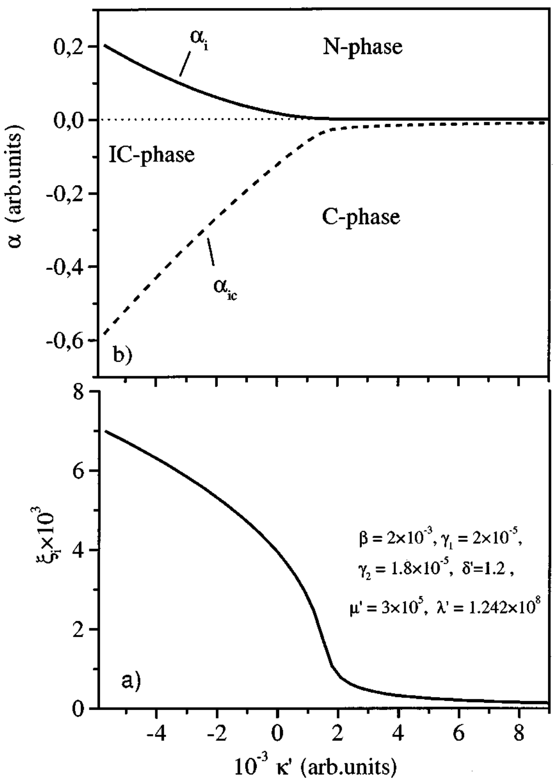

FIG. 1. The equilibrium wave number ξ_i of the incommensurate wave on the α_i line calculated via Eq. (6)(a) and calculated phase diagram in the α-κ' coordinate plane (b).

C phase:

$$F_C=\frac{\alpha}{2}qq^*+\frac{\beta}{4}(qq^*)^2+\frac{\gamma_1'}{6}(qq^*)^3-\frac{\gamma_2'}{12}(q^6+q^{*6}),$$

$$q=re^{i\psi},\quad q^*=re^{-i\psi},\quad \psi=m\pi/3,\quad m=0,1,2\ldots,$$

$$\gamma_1'=\gamma_1-6f^2/C_{55}^o,\quad \gamma_2'=\gamma_2+6f^2/C_{55}^o. \tag{4}$$

The N-IC transition occurs at $\alpha_i=A_0(T-T_i)=\alpha_k(k_i)=0$. The equilibrium value of incommensurate wave vector $k_i=|k_0-k_C|=\xi_i c^*$ at this second order phase transition corresponds to the absolute minimum of α_k in Eq. (3), therefore it should be found from the condition

$$\partial\alpha_k/\partial k=\delta+\kappa(k-k_C)+3\mu(k-k_C)^2+2\lambda(k-k_C)^3=0. \tag{5}$$

The analytical solution of Eq. (5) is rather complicated, therefore we solve it numerically for the case of TMATC-Cu crystals. It is convenient to use the normalized coupling constants $\delta'=\delta c^*$, $\kappa'=\kappa c^{*2}$, $\mu'=\mu c^{*3}$, and $\lambda'=\lambda c^{*4}$ presenting thus the incommensurate modulation by the dimensionless wave number ξ. The N-IC transition occurs at $T=T_i$ when the absolute minimum of $\alpha(\xi_i)$ tends zero. Determined in such a way dependences $\alpha_i(\kappa')$ and $\xi_i(\kappa')$ are presented in Figs. 1(b) and 1(a), respectively. We see that the IC wave number $\xi_i(\kappa')$ is characterized first by a fast decreasing when parameter κ' arises to its certain value (which depends on chosen values for δ' and λ') and then gradually

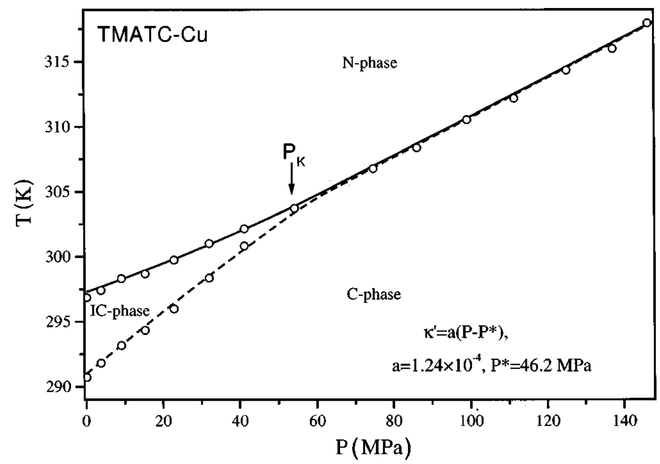

FIG. 2. The phase diagram [Fig. 1(b)] presented in the P-T coordinate plane (solid and dashed lines correspond to second and first order transitions, respectively); ○, experiment (Ref. 7).

approaches zero in the infinity ($\kappa'\rightarrow\infty$). The phase transition point $\alpha_{ic}=A_0(T-T_C)$ from the IC to C phase can be approximately estimated using the condition $F_{\mathrm{IC}}(\alpha_{ic})=F_{\mathrm{C}}(\alpha_{ic})$.[13] We will neglect in the IC phase the contribution due to the anisotropic γ_2 term in Eq. (3). In the IC phase the invariant $(q^6+q^{*6})\rightarrow(q_{k_0}^5 Q_{2c^*-5k_0}+\text{c.c.})$, so it induces a fifth harmonic $Q_{2c^*-5k_0}\propto\langle q_{k_0}\rangle^5$. Hence the γ_2 term is actually of the order of $(qq^*)^5$ and for this reason can be disregarded. However, this term remains important for the C phase, where it represents its lock-in energy. Another f term is of the order of $(qq^*)^3$, therefore it must be taken into account. In general, this term causes the temperature changes of the equilibrium value of the IC wave vector due to the dispersion of $C_{55}^o(k)$.[13] The fact, that the wavelength of IC modulation remains nearly constant in whole region of the IC-phase of TMATC-Cu crystal[8] means that dispersion of $C_{55}^o(k)$ is weak enough in the vicinity of $k_C\pm k_i$. For this reason the minimization of F_{IC} can be essentially simplified, i.e., we can restrict it to the amplitude of the modulation only. From Eqs. (3) and (4) we get

$$6(\alpha_{ic}-\alpha_i)r_o^2+3\beta r_o^4+2\gamma_1' r_o^6=6\alpha_{ic}r_c^2+3\beta r_c^4+2(\gamma_1'-\gamma_2')r_c^6, \tag{6}$$

where the equilibrium values of the order parameter amplitudes in the IC phase ($r_o^2\equiv|q_k|^2$) and in the C phase ($r_c^2\equiv qq^*$) are given by

$$r_o^2=[-\beta+\sqrt{\beta^2-4(\alpha-\alpha_i)\gamma_1'}]/2\gamma_1' \tag{7}$$

$$r_c^2=[-\beta+\sqrt{\beta^2-4\alpha(\gamma_1'-\gamma_2')}]/2(\gamma_1'-\gamma_2').$$

The line $\alpha_{ic}(\kappa')$ [Fig. 1(b)] has been calculated solving the Eq. (6) numerically. The magnitudes of the coupling constants used in our calculation were found using the ratio $\alpha_{ic}/\alpha_i\approx 3$, being determined from the experimental phase diagram.[7] As κ' arises both the lines of N-IC and IC-C phase transitions approach [Fig. 1(b)] and merge at $\kappa'\rightarrow\infty$. It is evident, that at infinity these lines have a common tangent, whereas the wave vector of IC modulation k_i approaches

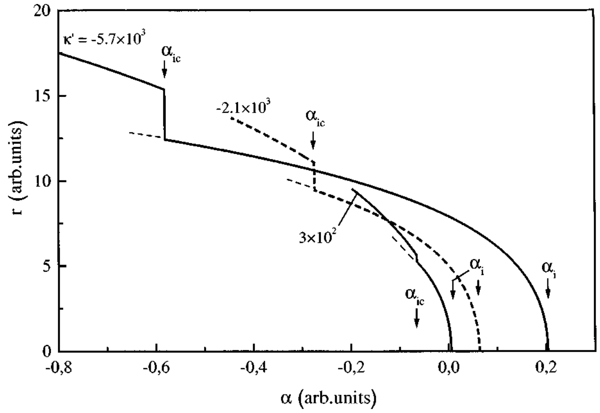

FIG. 3. The equilibrium order parameter amplitude r calculated via Eq. (7) at various values of coefficient κ'.

zero value. Thus the infinite critical point in its physical meaning is equivalent to the Lifshitz point.

The unusual phase diagram considered above does not contain any finite triple point, which indeed is observed in experiment.[7] The appearance of this point in the experiment we attribute to the limitation of experimental resolution. There is always a certain limit up to which both N-IC and IC-C lines can be observed separately. It immediately becomes obvious if we present the phase diagram in P-T coordinate plane (Fig. 2), which has been obtained assuming that the free energy coefficients $\beta,\gamma_1,\gamma_2,\lambda',\delta',\mu',f$ are nearly pressure independent. Some justification for such an assumption follows from the fact that the pressure behavior of these coefficients at least is not critical in the experimental range of pressures. Otherwise, the appearance of the policritical points of other types would be inevitable. The size of experimental points in Fig. 2 nearly corresponds to the limit of resolution, which has been estimated as 0.5 K. Above 55 MPa the lines of N-IC and IC-C phase transitions are separated by a temperature interval less than 0.5 K, so they cannot be experimentally resolved. Thus, the triple point in the phase diagram[7] can be considered as an artificial point.

Once more confirmation follows from the qualitative comparison of experimental results for temperature behavior of the optical birefringence Δn_C and elastic constant C_{66} (Ref. 7) with the temperature dependences of order parameter amplitudes r in the IC and C phase (Fig. 3) being calculated using Eq. (7). It should be kept in mind that anomalous changes $\delta(\Delta n_C)$ and δC_{66} are proportional in these phases to r^2[7]. The magnitude of a jump of the order parameter amplitude at the first order IC-C transition decreases nearly proportionally to the width of the IC phase (Fig. 3). In the region close to $\kappa'\to 0$ $(P\to P^*)$, which corresponds to the limit of experimental resolution (Fig. 2), the jump of the order parameter amplitude Δr at $T=T_C$ $(\alpha=\alpha_{ic})$ becomes negligibly small with respect to its initial value at $\kappa'=-5.7\times 10^3$ attributed to $P=$ 0.1 K as regards TMATC-Cu. Therefore, in the high pressure region it cannot be experimentally detected and the changes of the order parameter amplitude seem to be continuous which is in good agreement with experimental data.[7]

In conclusion we have presented here a phenomenological analysis of the pressure-temperature phase diagram of TMATC-Cu crystals. A serious disagreement between the experimental results and theory can be removed assuming that TMATC-Cu shows the P-T phase diagram with an infinite Lifshitz point. Observed experimentally finite triple point ($P_K\approx 55$ MPa, $T_K\approx 304$ K) (Ref. 7) should be considered as an artificial point, which appears as a result of the limit of experimental resolution. Therefore, even above P_K there are two very close (unresolved) lines of the incommensurate phase transitions.

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