Fluctuation theory of the smectic-*A*–crystal phase transition

A. R. Muratov

M. V. Lomonosov State University, Moscow

(Submitted 13 January 1988)
Zh. Eksp. Teor. Fiz. **94**, 105–111 (June 1988)

The smectic-*A*–crystal phase transition is investigated in the case when it is a first-order transition that is almost second-order. The analysis is performed using the Landau expansion in the order parameter associated with the short-wavelength density modulation. Effects induced by fluctuations are taken into account. The form of the phase diagram of the system is found for the case of an anisotropic four-point scattering vertex in the Landau expansion.

The liquid-crystalline state of matter is distinctive in that, as a rule, a whole series of phase transitions occurs in the system in a small range of temperatures. Among the liquid-crystalline phases are the nematic phases, which are translationally invariant, and phases with modulated density. The latter include smectic and diskotic phases, possessing one-dimensional and two-dimensional lattices, respectively. The strongly layered true crystals that are known as smectics *B*, *E*, *F*, *G*, and *H* are also usually regarded as liquid crystals. The point is that it is difficult to distinguish these phases experimentally from smectics (the smectics *B* also include true smectics).

Transitions from a smectic state to a strongly layered crystal are always first-order. However, these transitions can also be regarded as almost second-order. Evidence for this is provided both by the weakness of the modulation in the layer and by the small experimentally observed heat of transition. In the present paper we construct a theory of the smectic-*A*–crystal transition, based on the Landau expansion.[1] A smectic *A* is a layered structure in which each layer can be regarded as a two-dimensional isotropic liquid. As the temperature is lowered, density modulation arises within the smectic layer as well, i.e., the smectic *A* crystallizes. To study this transition we shall use the Landau expansion of the energy density E in the short-wavelength field $\varphi(\mathbf{r})$:

$$E=\frac{\tau}{2}\varphi^2+\frac{\alpha}{8q_0^2}[(\nabla^2+q_0^2)\varphi]^2+\frac{\alpha_\parallel}{2}(\nabla_\parallel\varphi)^2 +\frac{\mu}{6}\varphi^3+\frac{\lambda}{24}\varphi^4. \tag{1}$$

Here τ vanishes near the transition point: $\tau\sim T-T_0$, where T is the temperature and the quantity T_0 is close to the transition temperature but does not coincide with it. The isotropic gradient term in (1) has the same form as in the liquid. The quantity q_0 in it determines the fundamental period of the density modulation. The presence of smectic order leads to the appearance in (1) of anisotropic terms, one of which (with coefficient $\alpha_\parallel$) has been retained in (1). In it, $\nabla_\parallel \equiv \mathbf{n}\cdot\nabla$, where $\mathbf{n}$ is the unit vector along the normal to the layers. We shall assume that in equilibrium the layers are perpendicular to the z axis, i.e., $\mathbf{n}$ is the unit vector along this axis.

In Eq. (1) there is a term cubic in the field φ, and this leads to the result that, even in the mean-field approximation, a transition describable by this energy becomes a first-order transition. However, as Brazovskiĭ showed,[2] in the theory of weak crystallization a large role is played by fluctuations of the field φ. The character of these fluctuations depends in an essential way on the relative magnitudes of the isotropic and anisotropic terms in the energy (1). The crystallization of an isotropic liquid was investigated in Ref. 3. The changes that arise when weak anisotropy is taken into account, for both signs of $\alpha_\parallel$, were considered in Ref. 4. In Refs. 3 and 4 it was assumed that fluctuations of the field φ with wave vectors $\mathbf{q}$ close to the surface of a sphere of radius q_0 in reciprocal space are strongly developed. For strong anisotropy, fluctuations with wave vectors either near the poles of the sphere, corresponding to $\alpha_\parallel<0$, or near the equator, with $\alpha_\parallel>0$, are important. In the first case, effects associated with the large phase volume over which the fluctuations are accumulated are absent, and the system undergoes a transition to a state with a one-dimensional density wave. This paper is devoted to a study of the second case, when the fluctuations are concentrated near the circle $|\mathbf{q}|=q_0$, $q_z=0$ in reciprocal space. A similar situation for another problem has been investigated by Swift.[5]

The three-point vertex μ in the expansion of the energy can be assumed to be a constant. The four-point vertex λ is, generally speaking, a certain function $\lambda(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)$ of the wave vectors of the field φ. Taking into account the conservation law $\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4=0$, and the fact that the wave vectors lie on the above-mentioned circle, we find that they form a rhombus. Thus, λ is a function only of the angle θ at a vertex of the rhombus. Using the symmetry properties of the four-point scattering vertex, we find

$$\lambda(\theta+2\pi)=\lambda(\theta),$$
$$\lambda(-\theta)=\lambda(\theta),$$
$$\lambda(\pi-\theta)=\lambda(\theta).$$

This function can be represented in the form of a Fourier series:

$$\lambda(\theta)=\lambda_0\left[1+\sum_{k=1}^{\infty}\lambda_k\cos(2k\theta)\right]. \tag{2}$$

In the following we shall confine ourselves to an analysis of the cases when only one term in the series (with $k=1$, 2, or 3) is nonzero. In order that the isotropic phase be absolutely stable, it is necessary to require $|\lambda_k|<1$. Otherwise, the model, when restricted to terms of up to fourth order in the expansion of the energy, is inapplicable.

The phase transition under investigation can be interpreted as a condensation of the field φ. In the initial smectic *A*, $\langle\varphi\rangle=0$, and therefore to calculate the bare correlation function $\langle\varphi\varphi\rangle$ we can confine ourselves to the quadratic part

 0038-5646/88/061144-04$04.00

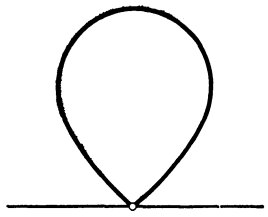

FIG. 1. Basic self-energy contribution to the correlator $\langle\varphi\varphi\rangle$.

of (1). As a result, we have

$$\langle\varphi(\mathbf{q})\varphi(-\mathbf{q})\rangle=T[\Delta+\alpha_{\parallel}q_z^2+\alpha(q-q_0)^2]^{-1}, \quad (3)$$

where $\Delta=\tau$. To obtain Eq. (3) we used the conditions for weakness of the transition described by the energy expansion (1), which take the following form:

$$\Delta\ll\alpha_{\parallel}q_0^2, \quad \Delta\ll\alpha q_0^2. \quad (4)$$

It is these inequalities which enable us to confine ourselves in (1) to a single anisotropic term, since higher terms of the expansion in $\nabla_{\parallel}$ lead to effects that are small in the parameter $\Delta/\alpha_{\parallel}q_0^2$.

The analysis performed by Brazovskiĭ[2] showed that satisfying the restrictions (4) allows us to neglect the λ-vertex renormalization that arises when fluctuations are taken into account. To calculate the energy of the crystalline phase we only need allow self-consistently for the self-energy contribution described by the diagram depicted in Fig. 1. It is easy to see that this contribution changes only the magnitude of the gap Δ in (3). Hence, for the gap in the smectic phase we obtain the equation

$$\Delta_A=\tau+\frac{\lambda_0 q_0 T}{8\pi(\alpha\alpha_{\parallel})^{1/2}}\ln\left(\frac{4\alpha_{\parallel}q_0^2}{\Delta_A}\right), \quad (5)$$

where λ_0 is the zeroth Fourier harmonic of the vertex $\lambda(\theta)$ in (2).

The calculation of the gap in the crystalline phase is performed analogously.[2,3] We now find a nonzero value for the condensate $\langle\varphi\rangle$, which has the form

$$\langle\varphi(\mathbf{r})\rangle=\sum_m a_m\cos(q_0\boldsymbol{\nu}_m\mathbf{r}), \quad (6)$$

where $\boldsymbol{\nu}_m$ are vectors specifying the lattice type and perpendicular to the z axis, and a_m are the amplitudes of the density waves that arise. The gap in the crystalline phase becomes, generally speaking, anisotropic. Its dependence on the angle θ, measured from one of the crystallization directions ($\boldsymbol{\nu}_1$), is given by the equation

$$\Delta(\theta)=\tau+\frac{1}{4}\sum_m\lambda(\theta-\theta_m)a_m^2 + \frac{q_0 T}{8\pi(\alpha\alpha_{\parallel})^{1/2}}\int_0^{2\pi}\frac{d\theta'}{2\pi}\lambda(\theta-\theta')\ln\left(\frac{4\alpha_{\parallel}q_0^2}{\Delta(\theta')}\right). \quad (7)$$

As indicated in Ref. 3, the solution of the analogous equation in a three-dimensional system can be found only numerically. In the present case, when two-dimensional crystallization occurs in a smectic layer, for the chosen dependence $\lambda(\theta)=\lambda_0[1+\lambda_k\cos(2k\theta)]$ it is possible to progress analytically practically to completion.

Before investigating the problem with allowance for fluctuations, we shall consider it in mean-field theory. For this it is sufficient to confine ourselves to the part of the energy (1) without gradient terms, taking into account that the condensate has the form (6). The solution of the resulting problem of two-dimensional crystallization in Landau theory for a constant vertex is well known. On the phase diagram there are three phases—the initial smectic-A phase (A), a hexagonal phase (H) with a condensate of the form

$$\langle\varphi(\mathbf{r})\rangle=a\left[\cos(q_0x)+\cos\left(q_0\frac{x+3^{1/2}y}{2}\right)+\cos\left(q_0\frac{x-3^{1/2}y}{2}\right)\right],$$

and a phase with one-dimensional density modulation in the smectic layer, which corresponds most closely to the so-called smectics $\tilde{A}$ (Ref. 6). In the $\tilde{A}$ phase the condensate has the form $\langle\varphi(\mathbf{r})\rangle=a\cos(q_0x)$. The constant a appearing in the expressions for $\langle\varphi(\mathbf{r})\rangle$ characterizes the depth of the density modulation in the smectic layer. The quantity a depends on the distance from the phase transition.

As the temperature is lowered there is a transition from the A phase to H at $\tau=4\mu^2/45\lambda$, and then a phase transition $H\to\tilde{A}$ at $\tau=-(7+3\sqrt{6})\mu^2/5\lambda$. In Ref. 3 it was shown that it is possible to solve the problem of two-dimensional crystallization for an anisotropic interaction vertex $\lambda(\theta)$. For the case under consideration

$$\lambda(\theta)=\lambda_0[1+\lambda_k\cos(2k\theta)]$$

it is found that for negative values of λ_k the phase diagram is not qualitatively changed in comparison with the diagram for $\lambda=$ const. For positive values of λ_k new phases appear. Thus, for $k=1$ with $\lambda_1>1/3$, instead of the smectic $\tilde{A}$ there appears on the diagonal a tetragonal phase T with condensate

$$\langle\varphi(\mathbf{r})\rangle=a[\cos(q_0x)+\cos(q_0y)].$$

As the temperature is lowered the sequence of transitions $T\leftarrow H\leftarrow A$ occurs.

For $k=2$ with $\lambda_2>1/3$ the one-dimensional phase $\tilde{A}$ is replaced by an orthorhombic crystal R, to which corresponds a condensate

$$\langle\varphi(\mathbf{r})\rangle=a\cos(q_0x)+a\cos\left(q_0\frac{x+y}{\sqrt{2}}\right).$$

Finally, for $k=3$ two transitions occur. First, analogously to the case $k=1$ with $\lambda_3>1/3$, the one-dimensional phase is replaced by a tetragonal phase T. Second, for $\lambda_3\geqslant 0.224$, between the regions of stability of $\tilde{A}$ and H on the phase diagram there appears a quasicrystal Q_6 with condensate of the form

$$\langle\varphi(\mathbf{r})\rangle=a\sum_{m=1}^{6}\cos(q_0\boldsymbol{\nu}_m\mathbf{r}),$$

where the six vectors $\boldsymbol{\nu}_m$ make angles $\pi/6$ with each other. Thus, a sucession of transitions $\tilde{A}(T)\leftarrow Q_6\leftarrow H\leftarrow A$ becomes possible. All the transitions in this chain are first-order phase transitions, even in mean-field theory.

Now that we know precisely which phases should be expected to appear, we shall investigate the problem with

allowance for fluctuations. We shall consider the calculation of the energy of the one-dimensional phase for

$$\lambda(\theta)=\lambda_0[1+\lambda_1\cos(2\theta)].$$

In this case Eq. (7) is written in the form

$$\tilde{\Delta}_{\tilde{A}}=\tilde{\tau}+\frac{a^2}{4}[1+\lambda_1\cos(2\theta)]+\frac{1}{8\pi}\int_0^{2\pi}\frac{d\theta'}{2\pi}\ln\left\{\frac{4}{\tilde{\Delta}_{\tilde{A}}(\theta')}\right\}[1+\lambda_1\cos\{2(\theta-\theta')\}].$$

Here, and down to Eq. (11), for convenience we have used dimensionless variables $\tilde{\Delta}$, $\tilde{\tau}$, and $\tilde{\mu}$, defined by the relations

$$\tilde{\Delta}=\frac{(\alpha\alpha_\parallel)^{1/2}}{\lambda_0 q_0 T}\Delta,\quad \tilde{\tau}=\frac{(\alpha\alpha_\parallel)^{1/2}}{\lambda_0 q_0 T}\tau,\quad \tilde{\mu}=\frac{(\alpha\alpha_\parallel)^{1/4}}{\lambda_0(q_0T)^{1/2}}\mu. \qquad (8)$$

This equation has the solution $\tilde{\Delta}_{\tilde{A}}=x+y\cos(2\theta)$, where the x and y satisfy the system

$$x=\tilde{\tau}+\frac{a^2}{4}+\frac{1}{8\pi}\ln\left\{\frac{8}{x+(x^2-y^2)^{1/2}}\right\},$$
$$y=\lambda_1\left[\frac{a^2}{4}-\frac{1}{8\pi}\frac{y}{x+(x^2-y^2)^{1/2}}\right]. \qquad (9)$$

The relation between the parameter a^2 and the magnitude of the gap in the crystalline phase is determined from the condition for the minimum of the energy with respect to a, and has the following form:

$$a^2=\frac{8}{1+\lambda_1}\tilde{\Delta}_{\tilde{A}}(\theta=0)=\frac{8}{1+\lambda_1}(x+y).$$

Hence, for the two harmonics of the gap of the one-dimensional phase we obtain the system

$$(1-\lambda_1)x+2y=-(1+\lambda_1)\left[\tilde{\tau}+\frac{1}{8\pi}\ln\left\{\frac{8}{x+(x^2-y^2)^{1/2}}\right\}\right],$$
$$2\lambda_1 x-(1-\lambda_1)y=\lambda_1(1+\lambda_1)\frac{1}{8\pi}\frac{y}{x+(x^2-y^2)^{1/2}},$$

which, after the change of variable $y=x\sin\psi$, where $0\leqslant\psi\,\mathrm{sign}(\lambda_1)\leqslant\pi/2$, reduces to the equation

$$\frac{1}{8\pi}\ln\left|\frac{64\pi[2\lambda_1-(1-\lambda_1)\sin\psi]}{\lambda_1(1+\lambda_1)\sin\psi}\right|+\tilde{\tau}+\frac{\lambda_1}{8\pi}\frac{\sin\psi}{1+\cos\psi}\frac{1-\lambda_1+2\sin\psi}{2\lambda_1-(1-\lambda_1)\sin\psi}=0. \qquad (10)$$

The quantity x is connected with the root of this equation by the relation

$$x=\frac{\lambda_1(1+\lambda_1)}{8\pi}\frac{\sin\psi}{1+\cos\psi}\frac{1}{2\lambda_1-(1-\lambda_1)\sin\psi}.$$

Analysis of Eq. (10) shows that, in the case $\lambda_1<1/3$, at a sufficiently low temperature there exist two solutions for ψ, of which we must choose the one that is largest in absolute value. For $\lambda_1<0$ this solution exists down to $\lambda_1=-1$. But for $\lambda_1>1/3$, the desired solution vanishes when the temperature is lowered. The vanishing of the solution is connected with the vanishing of the quantity $\Delta(\theta)$ in the direction perpendicular to the direction of crystallization, i.e., with the loss of stability of the one-dimensional phase.

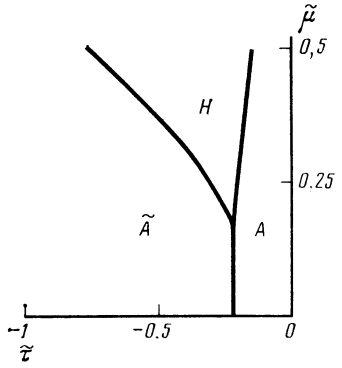

FIG. 2. Phase diagram of the system for $\lambda=$ const.

It remains to calculate the energy of the one-dimensional phase. It is determined by the expression

$$\Delta E_{\tilde{A}}\equiv E_{\tilde{A}}-E_A=\int_0^{a^2}\frac{dE}{d(a'^2)}d(a'^2)=\int_0^{a^2}(x+y)\,d(a'^2)-\frac{(x+y)^2}{1+\lambda_1},$$

where x, y, and a'^2 are related by the system (9). As a result of the integration we obtain

$$\Delta E_{\tilde{A}}=\frac{x^2-\Delta_A{}^2}{2}+\frac{x-\Delta_A}{8\pi}+\frac{y^2}{2\lambda_1}-\frac{(x+y)^2}{1+\lambda_1}. \qquad (11)$$

The energies of the tetragonal and hexagonal phases are determined analogously. For these, in the case $k=1$ under consideration, the gap is found to be isotropic. To construct the phase diagram of the system it remains to solve an equation of the type (10) numerically and to calculate the energy using equations analogous to (11).

Figure 2 depicts the phase diagram of the system with allowance for fluctuations for $\lambda=$ const. In all the figures the dimensionless variables defined by the formulas (8) are used. In the region $\mu\gg\mu_0=0.17\lambda_0(q_0T)^{1/2}/(\alpha\alpha_\parallel)^{1/4}$, where μ_0 is the coordinate of the triple point, the phase-equilibrium lines are close to the curves obtained in mean-field theory. For small values of μ, i.e., in the region of strongly developed fluctuations, a direct first-order transition $A\to\tilde{A}$ occurs at $\tau\approx0.22\lambda_0 q_0 T/(\alpha\alpha_\parallel)^{1/2}$, a purely fluctuational effect. Figure 3 depicts the dependence of the gap

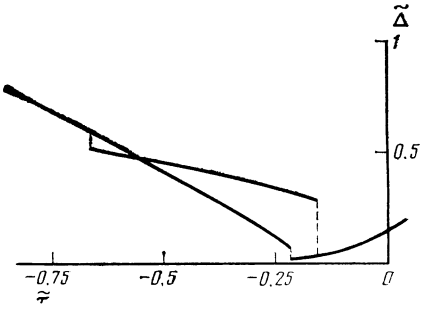

FIG. 3. Dependence of the gap $\tilde{\Delta}$ in the correlator on the temperature in the case $\lambda=$ const for $\tilde{\mu}=0$ and $\tilde{\mu}=0.45$.

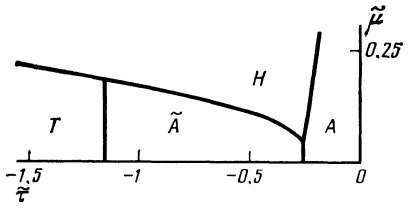

FIG. 4. Phase diagram for $\lambda_1 = 0.34$.

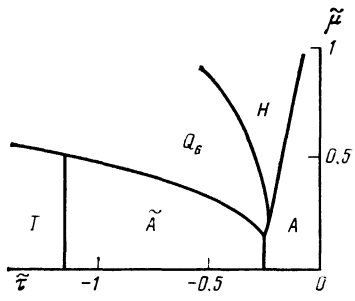

FIG. 5. Phase diagram for $\lambda_3 = 0.34$.

$\Delta(\theta = 0)$ in the correlator on the temperature for $\tilde{\mu} = 0$ and $\tilde{\mu} = 0.45$. It can be seen that at the phase transitions the magnitude of the gap increases discontinuously.

As in the mean-field theory, for negative values of the parameter λ_k the diagram is not qualitatively changed. For positive λ_k new phases arise. Figure 4 gives the phase diagram for $\lambda_1 = 0.34$. The fluctuations preserve the one-dimensional phase in a certain region for $\lambda_1 > 1/3$. This phase loses stability at the temperature

$$\tau = -\frac{\lambda_0 q_0 T}{8\pi(\alpha\alpha_\parallel)^{1/2}}\left[\ln\left\{\frac{64\pi(\alpha\alpha_\parallel^3)^{1/2}q_0(3\lambda_1-1)}{\lambda_0 T\lambda_1(1+\lambda_1)}\right\} + \frac{\lambda_1(3-\lambda_1)}{3\lambda_1-1}\right]. \quad (12)$$

The temperature of the transition $\tilde{A} \to T$ tends to $-\infty$ as $\lambda_1 \to 1/3 + 0$. The fluctuations make the $\tilde{A} \to T$ transition a first-order transition. Upon further increase of λ_1 the one-dimensional phase $\tilde{A}$ disappears.

The cases $k = 2$ and $k = 3$ can be treated analogously. Here the magnitude of the gap for the tetragonal phase depends on the angle θ for $k = 2$ only, while for the hexagonal phase it depends on θ for $k = 3$ only. For the crystal $R(k = 2)$ and for Q_6 $(k = 3)$ the magnitude of the gap is also independent of the angle.

The phase diagram for $k = 2$ with $\lambda_2 = 0.34$ coincides exactly with that depicted in Fig. 4, except that the crystal R appears in it in place of the tetragonal phase. All the remarks made above can be applied to this case as well. The phase diagram for $k = 3$ with $\lambda = 0.34$ is given in Fig. 5. As λ_3 increases the phase $\tilde{A}$ disappears. It is curious to note that in the approximation used for $k = 3$ the energies of the tetragonal phase and of the crystal R' with condensate of the form $\langle\varphi(r)\rangle = a\{\cos(q_0 x) + \cos[q_0(x\cdot 3^{1/2} + y)/2]\}$ coincide exactly, both in the Landau theory and with allowance for fluctuations.

The investigation carried out above makes it possible to draw the following conclusions about the character of the phase diagram in the variables $\tilde{\tau}, \tilde{\mu}$. In the Landau theory all the phase-equilibrium curves have the form of parabolas $\tilde{\tau} \sim \tilde{\mu}^2$. Allowance for fluctuations leads to the result that in the region of strongly developed fluctuations, which is situated near the coordinate origin, all the intermediate phases disappear, and a direct first-order phase transition occurs from the initial phase to the phase that is stable at low temperatures.

For the case of an isotropic scattering vertex the phase diagram is given in Fig. 2, in which three phases are present—smectic A, hexagonal crystal, and smectic $\tilde{A}$. The presence of anisotropy of the scattering vertex substantially changes the form of the diagram of states. As before, it is arranged in the form of three sectors, but now the low-temperature phase can be either a tetragonal phase or another orthorhombic phase, and between this phase and the hexagonal phase a quasicrystal can be wedged in. In the Landau theory, transitions of this type occur independently of τ and μ when the anisotropy parameters λ_k are changed. Allowance for fluctuations leads to the appearance of a dependence of the transition point with respect to λ_k on τ and μ. The above pertains to the dependence $\lambda(\theta)$, which has minima (absolute) at certain angles to the direction of crystallization. If there are no such minima, the phases remain the same, although the transition lines are, of course, displaced.

The phase transitions described above lead to discontinuities of observable quantities—compression moduli of the smectic layers, Franck constants, specific heats, sound velocities, viscosities, etc. In addition, in these quantities fluctuation contributions appear. These changes are considered in Ref. 7.

In conclusion, the author expresses his deep gratitude to I. E. Dzyaloshinskiĭ for suggesting the topic of the work, and also to E. I. Kats and V. V. Lebedev for useful discussions.

[1]L. D. Landau, Zh. Eksp. Teor. Fiz. **7**, 19 (1937) [English translation: Collected Papers of L. D. Landau (ed. D. ter Haar), Pergamon Press, Oxford (1965)].
[2]S. A Brazovskiĭ, Zh. Eksp. Teor. Fiz. **68**, 175 (1975) [Sov. Phys. JETP **41**, 85 (1975)].
[3]S. A. Brazovskiĭ, I. E. Dzyaloshinskiĭ, and A. R. Muratov, Zh. Eksp. Teor. Fiz. **93**, 1110 (1987) [Sov. Phys. JETP **66**, 625 (1987)].
[4]E. I. Kats and A. R. Muratov, Zh. Eksp. Teor. Fiz. **94**, No. 4, 159 (1988) [Sov. Phys. JETP **67**, 736 (1988)].
[5]J. Swift, Phys. Rev. A **14**, 2274 (1976).
[6]A. M. Levelut, J. Phys. Lett. (Paris) **45**, 603 (1984).
[7]E. I. Kats, V. V. Lebedev, and A. R. Muratov, Fiz. Tverd. Tela **30**, 1338 (1988) [Sov. Phys. Solid State **30**, 775 (1988)].

Translated by P. J. Shepherd