7-1993

Field-Driven 1st-Order Structural Transition in the Restricted Geometry of a Smectic-A Cell

Oleg Lavrentovich
Kent State University, olavrent@kent.edu

M. Kléman
Université de Paris

RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 48, NUMBER 1 JULY 1993

Field-driven first-order structural transition in the restricted geometry of a smectic-A cell

O. D. Lavrentovich*
Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

M. Kléman
Laboratoire de Physique des Solides, Université de Paris–Sud, 91405 Orsay Cedex, France and Laboratoire de Minéralogie-Cristallographie, Universités Pierre et Marie Curie et Paris VII, 4 Place Jussieu, 75252 Paris Cedex 05, France

(Received 8 February 1993)

An external field gives rise to a first-order transition in a smectic-A cell; the transition occurs by nucleation of focal conic domains. The physical mechanisms that govern the behavior of the new domain phase are different for small ($\rho \ll 1$) and large ($\rho \gg 1$) values of the order parameters ρ [ρ=(domain radius)/(cell thickness)]. The nucleation ($\rho \ll 1$) is governed by the elastic and field energies and is facilitated by bulk or surface irregularities, while the expansion ($\rho \gg 1$) is determined by the balance of the field and anisotropic surface energy.

PACS number(s): 61.30.Gd, 61.30.Jf, 64.60.Qb, 64.70.Md

A field-induced instability in liquid crystals was first observed by Fréedericksz and Zolina for the nematic phase [1]. It is a second-order phase transition from a uniform state to a homogeneously deformed one, and it occurs when an external magnetic or electric field becomes greater than the threshold value. Direct application of the Fréedericksz idea to the instabilities in the smectic-A phase (Sm-A) has resulted in the prediction of a "ghost" transition [2]: the Sm-A phase is composed of nearly incompressible layers and their equidistance prohibits Fréedericksz-type distortions. A similar "ghost" problem appears in the layer undulation model [3,4]. As proposed by Parodi [5], well-developed distortions in the Sm-A phase could occur via the creation of dislocations. All models [2–5] thus deal with the layer dilation. We have proposed an opposite scenario of the field instability in the Sm-A phase that is based on the idea that the layers could be simply curved by the field: the energy of Sm-A curvatures is usually smaller than the energy of dilations.

A well-known type of curvature defect, which shows up in the Sm-A phase is the torical focal conic domain (TFCD) [6]. The geometry of the TFCD does not require layer dilation (Fig. 1) and thus the elastic energy cost of the domain appearance could be relatively small. On the other hand, the gain in the diamagnetic or dielectric energy could be significant, since the growth of the domain means maximal reorientation of layers (from horizontal packing outside the TFCD to vertical alignment inside the TFCD, Fig. 1). The TFCD instability will take place when the anisotropy in the magnetic or dielectric susceptibility is negative, i.e., $\chi_{\parallel}-\chi_{\perp}=\chi_a<0$ or $\epsilon_{\parallel}-\epsilon_{\perp}=\epsilon_a<0$, where the subscripts refer to the director $\mathbf{n}$ that coincides with the normal to the layer. In fact, the TFCD-mediated transition has already been observed in experiments with the new superparamagnetic Sm-A phase [7].

The study of focal conics has a long history. Observing these objects in the early 1920s, Friedel [8] proved that the Sm-A phase is composed of deformable but equidistant layers. However, up to now, there has been no answer to the basic questions, how does the focal conic domain arise from "nothing" and how does it grow?

There are more general aspects that make the study of the TFCD instability important. First, the appearance of the TFCD should be a first-order transition; the radius a of the stable domain was found to be larger than some macroscopic (a few micrometers) critical value [9]. It means that the appearance of the TFCD implies some kind of tunneling through the potential barrier. Second, the Sm-A cell is spatially restricted. Thus the physical mechanisms that govern the behavior of the domain phase may be different for domains smaller or larger than the cell thickness h. Consequently, an unusual problem arises: to describe the first-order transition adequately one must consider not only the case of small order parameter $\rho<1$ (which can be chosen as $\rho=a/h$) but also the case of large order parameter $\rho>1$. Here we study

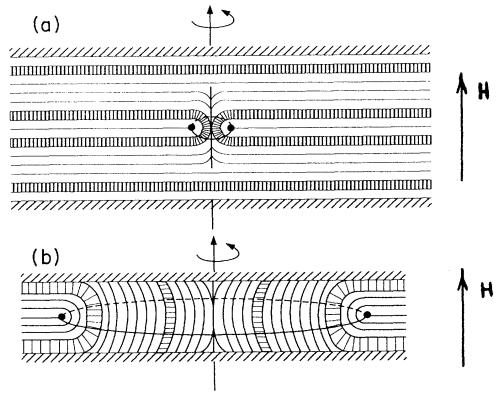

FIG. 1. The geometry of the torical focal conic domain nucleation (a) and expansion (b). The smectic layers are folded around the circle; this circle as well as the line of rotation symmetry are two linear defects in the director distribution. The nucleation does not change the orientation at boundaries and thus is defined by the elastic and field terms in Eqs. (6) and (7). In contrast, the expansion implies a significant reorientation at the boundaries and is governed by the balance of the field and anisotropic surface energies, Eqs. (6) and (12).

both the nucleation ($\rho<1$) and the expansion ($\rho>1$) of the TFCD.

In the initial state the smectic layers are parallel to the cell plates (homeotropic alignment of **n**). The magnetic (**H**) or electric (**E**) field is applied along **n**, i.e., along the vertical axis Z.

The layers are distorted inside the cylindrical volume with radius a and height h. The two principal radii of layer curvature, R_1 and R_2, are different in sign [10]:

$$R_1=r>0,\quad R_2=r-a/\sin\theta<0\ ; \tag{1}$$

here r is measured along **n** and varies in the range $[\xi, r_{\max}]$, ξ is the smectic coherence length and $r_{\max}$ is restricted by the finite cell thickness, and θ is an angle between the axis Z and **n**.

The elastic energy per unit volume reads as

$$f_{\rm el}=(K/2)[(1/R_1)+(1/R_2)]^2+\tfrac{1}{2}B\delta^2\ , \tag{2}$$

where the first term is associated with the mean curvature of the layers and splay constant K, while the second term with modulus B describes the dilation δ of layers and can be temporarily neglected because of the specific geometry of the TFCD. Elastic constants in Eq. (2) are related, $B\sim K/\lambda^2$, where λ is close to the layer thickness d ($d\sim 30$ Å) far from the Sm-A–nematic phase transition.

The diamagnetic energy density is

$$f_f=-\tfrac{1}{2}\chi_a(\mathbf{nH})^2\ , \tag{3}$$

where in the case of the electric field action, χ_a and **H** can be replaced by $\epsilon_a/4\pi$ (if $\epsilon_a\ll\epsilon_\parallel,\epsilon_\perp$) and **E**, respectively.

When the TFCD appears, the molecular orientation inclines at both surfaces [$0\le\theta\le\arctan(2a/h)$]. Thus the surface term in the form, for example,

$$f_s=W_a\sin^2\theta\ , \tag{4}$$

should be taken into account; W_a is the anisotropic part of the surface energy. In principle, W_a can be close to the anchoring coefficients measured for the nematic phase, 10^{-3}–10^{-1} erg/cm^2. However, if the surface tilt implies a melting of the smectic layers, W_a may be significantly higher.

The instability consists in the appearance and growth of the TFCD with variable radius a, when H becomes sufficiently strong. The free energy of the domain formation is expressed as the difference ΔF in the total energy of the defect state $F=(F_{\rm el}+F_f+F_s)$ and the uniform state $F_0=(F_{{\rm el},0}+F_{f,0}+F_{s,0})$. The latter is easy to calculate:

$$F_0=-\pi\chi_aH^2a^2h/2\ . \tag{5}$$

To obtain F, one should integrate Eqs. (2) and (3) over the domain volume and Eq. (4) over the corresponding surface area. One gets from Eqs. (1)–(5)

$$\Delta F=2\pi Kh\rho\left[\frac{\pi}{2}\ln 2+L(\operatorname{arccot}2\rho)+2\operatorname{arccot}2\rho\left[\ln\frac{h\rho}{\xi}-2\right]+\arctan 2\rho\ln\frac{\rho h}{\xi(4\rho^2+1)^{1/2}}-\frac{1}{\rho}\ln(1+4\rho^2)\right]$$
$$+\tfrac{1}{2}\pi h^2W_a[4\rho^2-4\rho\arctan 2\rho+\ln(1+4\rho^2)]+\frac{\pi}{24}\chi_aH^2h^3[8\rho^2-6\rho\arctan 2\rho+\ln(1+4\rho^2)+4\pi\rho^3-8\rho^3\arctan 2\rho]\ , \tag{6}$$

where $\rho=a/h$ and $L(x)$ is Lobachevskiy's function [11]:

$$L(x)=-\int_0^x\ln\cos t\,dt=x\ln 2-\tfrac{1}{2}\sum_{i=1}^{\infty}(-1)^{i-1}\frac{\sin 2ix}{i^2}\ .$$

The dimensionless radius ρ can be considered as an order parameter of the transition; for the initial state, $\rho=0$ and $\Delta F=0$. Despite the apparent complexity of Eq. (6), the equation is exact for domains of supramolecular size and allows us to describe the behavior of the system in the entire possible range of the order parameter ρ, i.e., from $\rho>\xi/h\cong 0$ to $\rho\to\infty$. The limit $\rho\ll 1$ corresponds to the nucleation of the TFCD's and the limit $\rho\gg 1$ describes the domain expansion.

For $\rho\ll 1$ the linear and quadratic in ρ terms are associated solely with the elastic energy, while the cubic term is defined by the field:

$$\Delta F(\rho\ll 1)=A_1\rho+A_2\rho^2+A_3\rho^3+A_4\rho^4+\cdots\ ,$$
$$A_1=2\pi^2Kh(\beta-2)\ ,\quad A_2=4\pi Kh(\ln\sqrt{2}-\beta-3)\ , \tag{7}$$
$$A_3=(\pi^2/6)\chi_aH^2h^3\ ,$$

where $\beta=\ln(2a/\xi)\approx$ const. The surface anchoring contribution begins only with ρ^4 and therefore can be neglected: the deformations caused by a small TFCD are restricted by the region of volume a^3 and practically do not change the orientation at the boundaries.

The behavior of the system is determined by the signs and values of the coefficients A_1, A_2, and A_3. A_1 should be positive. Otherwise, even in the absence of the field, the Sm-A phase will be unstable with respect to the formation of the TFCD's. A_2, in principle, is negative; however, since $\rho^2\ll\rho$, the corresponding contribution is small. A_3 is negative because $\chi_a<0$. The balance of the positive linear elastic term and negative cubic field term leads to a first-order character of the transition. Figure 2(a) shows $\Delta F(\rho,H)$ calculated from the exact expression, Eq. (6), for small ρ. Here and below we take estimations $h=100$ μm, $K=10^{-6}$ dyn, $\chi_a=-10^{-7}$ cgs, and $W_a=0.1$ erg/cm^2.

For $H=0$, ΔF has only one minimum at $\rho=0$. As H grows, the second local minimum appears for $\rho>0$. When H overcomes some critical field, this minimum is absolute and the uniform state becomes unstable versus the formation of the TFCD. However, $\Delta F(\rho)$ goes through a maximum ΔF^* at $\rho=\rho^*$ that defines the criti-

cal TFCD nucleus. Smaller TFCD's (embryos) are unstable, while the larger ones are stable growing nuclei. Equation (7), assuming that the field is strong enough, $A_2/\sqrt{A_1|A_3|}=\bar{\omega}\ll 1$, yields

$$\Delta F^* \cong \frac{A_1^{3/2}}{3\sqrt{3}|A_3|^{1/2}}(2-\sqrt{3}\bar{\omega}+\bar{\omega}^2)\approx\frac{8\pi^2K^{3/2}(\beta-2)^{3/2}}{3\sqrt{|\chi_a|}H} \quad (8)$$

and

$$\rho^* \cong (2/Hh)\{[K(\beta-2)]/|\chi_a|\}^{1/2} . \quad (9)$$

An analysis of Eq. (8) shows that the barrier ΔF^* is too high to be surmounted by thermal fluctuations for plausible H. Using estimations [12] for the characteristic rate of the microscopic processes for the Sm-A phase, one finds that the fluctuation-induced nucleation will be observable if $\Delta F^* \leq 80 k_B T$, or $\Delta F^* \leq 3\times 10^{-12}$ erg. In accordance with Eq. (8), the last inequality will be satisfied only if $H \geq 10^5$ kG for the thermotropic Sm-A phase or 200 G for the ferrosmectics described in [7]. It is worth noting that the barrier problem should also be intrinsic for the field-induced dislocation instability [5]; moreover, since the dislocations considered in [5] are straight lines rather than closed loops, the barrier is infinitely large.

The problem is thus to find the real path of the macroscopic TFCD tunneling. An apparent solution is that the nucleation starts from a nonuniform state with nonzero elastic energy rather than from the ideal uniform structure. This assumption was used in Refs. [13–15] to explain the experimentally observed TFCD formation at the particular sites of a cell that are probably connected with local inhomogeneities. The nucleation was observed also at instabilities of the Sm-A – isotropic interface [16]. Moreover, observations [17,18] directly support the scenario of heterogeneous nucleation: it has been revealed that the focal conic domains appear along the sets of dislocations rather than in dislocation-free regions.

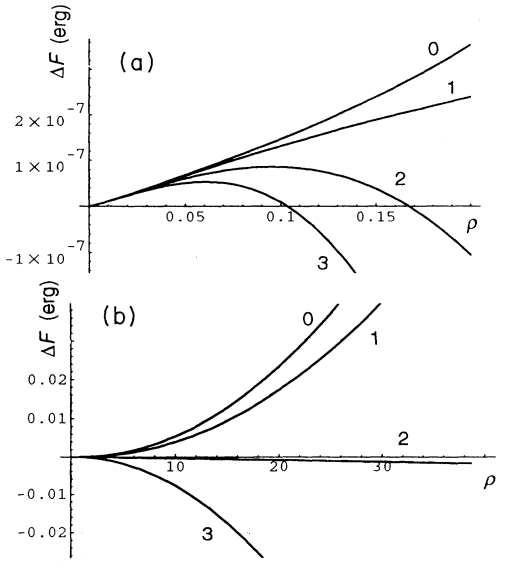

FIG. 2. The free energy of the domain formation calculated from the exact expression (6) for different values of the external field: (0) $H=0$, (1) $H=10$ kG, (2) $H=20$ kG, and (3) $H=30$ kG. The results of the calculations are represented for two different scales: (a) $\rho \ll 1$ (nucleation) and (b) $\rho \gg 1$ (expansion).

The main idea is simple: the bulk dust particle or surface irregularity dilates (or compresses) the smectic layers and thus the initial state is characterized by some nonzero energy due to the B term in Eq. (2). The nucleation of the TFCD means the substitution of the dilation by curvature deformations [the K term in Eq. (2)], which generally have less energy. The last circumstance should decrease the barrier ΔF^*.

Let us consider, as an example, a dust particle whose shape is close to a circular bicone of height $2l$ and base radius R. It creates deformations that are relaxed by a set of dislocation loops. The energy of a dislocation loop with radius r_d is [12,19] $f_0=\pi\lambda B d^2 r_d/\xi$, where ξ is a core radius and d is the Burgers vector taken equal to one layer thickness. The energy of all $n=2l/d$ circular dislocations is

$$F_{\text{disl}}=\pi B d l R(\lambda/\xi)=\pi K(ld/\lambda\xi)R . \quad (10)$$

Equation (10) assumes that the dislocations are independent (which is close to reality when $l \ll R$) and does not take into account the contribution of strains that are not relaxed by the loops. Estimations similar to Eq. (10) are valid also for surface irregularity with conical shape.

The nonzero elastic energy F_{disl} of the initial state drastically changes the ΔF behavior in the initially distorted region, because it leads to a new negative contribution $(-A_1')$ to the ΔF expansion:

$$\Delta F(\rho \ll 1)=(A_1-A_1')\rho+\cdots$$

$$=2\pi^2 Kh[\beta-2-(ld/2\pi\lambda\xi)]\rho+\cdots . \quad (11)$$

In principle, the last equation can also contain an additional field term because of the tilt of layers ($\sim l/R$) in the vicinity of the inhomogeneity; however, this term is negligibly small ($\sim\rho^4$) for $R \ll \sqrt{\lambda h}$. We also omit the possible anchoring term describing the reorientation of molecules at the boundary of the irregularity, since it is proportional to ρ^2.

Comparison of Eqs. (7), (8), and (11) shows that the barrier $\Delta F^* \cong 2(A_1-A_1')^{3/2}/3\sqrt{3}|A_3|^{1/2}$ is significantly reduced by the contribution A_1' from the dislocation energy. The barrier even completely disappears, if $A_1 < A_1'$ or $\beta-2 < ld/2\pi\lambda\xi$. With $d\sim\xi\sim\lambda$, $\beta\sim 4$–9 this is satisfied for irregularities as small as $l\sim(10$–$30)d$, i.e., a few hundred angstroms. It simply means that irregularity can nucleate the TFCD even when the external field is absent.

The inhomogeneity-induced TFCD will expand up to the point when $a=R$. For $a>R$, one should return to the case of Eqs. (6) and (7), because the layers outside the domain are uniform. If the field is sufficiently strong to satisfy the condition $\rho^*(H)h<R$, the TFCD can grow further; if $\rho^*(H)h>R$, it stops at $a=R$. Equation (9) shows that the irregularities with lateral size as small as $R\approx 1$ μm can satisfy condition $\rho^*(H)h<R$ starting with fields ≈ 130 kG; this field is smaller than the threshold of the undulation instability (≈ 200 kG for the 100-μm cell [6]). In fact, in real cells one can find irregularities that are even larger than 1 μm; e.g., the spacers fixing the separation of the cell plates and the oily streaks composed of dislocations [18]. The remaining problem is to fill the whole cell with the new phase, i.e., to consider the TFCD

expansion when $\rho \gg 1$.

The behavior of the free energy ΔF differs principally for $\rho \gg 1$ [Fig. 2(b)] and $\rho \ll 1$ [Fig. 2(a)], because of the confined nature of the system (finite h). First of all, the volume of the completely reoriented layers for $\rho \gg 1$ scales as $a^2 h$ [Fig. 1(b)] rather than as a^3 [Fig. 1(a)]; thus the driving term $\pi a^2 h \chi_a H^2/2$ is now proportional to ρ^2 rather than to ρ^3. Furthermore, the layers in the TFCD region are practically completely reoriented along the field [Fig. 1(b)] and the anchoring term $2\pi a^2 W_a \propto \rho^2$ should be considered. The elastic term, in contrast, retains its behavior $\propto Ka \propto \rho$ and thus can be neglected in comparison with the field and surface contributions. More precisely, Eq. (6) asymptotically transforms into

$$\Delta F(\rho \gg 1) = (\chi_a H^2 h^3/2 + 2W_a h^2)\rho^2 + \pi^2 K h \rho \ln(h/\xi) + \cdots , \tag{12}$$

where only the leading terms in ρ are retained for each type of contribution. Equation (11) describes a completely different situation in comparison with Eq. (7): domain expansion is defined mainly by the competition between the surface and the field energies. The balance of these energies defines a "saturation" field H_{sat}, above which the first term in Eq. (12) is negative and which provides the expansion of the TFCD:

$$H_{sat} = 2(W_a/|\chi_a|h)^{1/2} . \tag{13}$$

The thickness dependency $H_{sat} \sim 1/\sqrt{h}$ coincides with that found experimentally [7]. The saturation field does not depend on the bulk elastic constants K and B; however, the anchoring strength W_a might be related to these constants. Equation (13) can be used for the quantitative determination of W_a. However, one should keep in mind that H_{sat} is not necessarily the field that provides the nucleation of the TFCD: in cells without irregularities the metastable uniform state can remain supercooled for $H > H_{sat}$.

It is worth noting that H_{sat} for modest W_a is significantly smaller than the thresholds of the Helfrich-Hurault undulation instability [2,3] and Parodi's dislocation instability [5]. These two instabilities are defined by the balance of the field energy and the dilation energy, $H_{HH} = \sqrt{2\pi\lambda B/h|\chi_a|} \approx H_P$. Thus the ratios

$$H_{sat}/H_{HH} \sim H_{sat}/H_P \sim (W_a/\lambda B)^{1/2} \tag{14}$$

can be small, ~ 0.06, with $W_a \sim 0.1$ erg/cm^2, $\lambda = 30$ Å, and $B \sim 10^8$ dyn/cm^2. For the strongly anchored Sm-A phase, however, one can expect surface layer melting, $W_a \sim Bd$, and thus the ratios (14) will be close to unity. It is interesting to note that the low-threshold transition is predicted also for specific cycloid textures with virtual defects when the Sm-A cell is located in between two isotropic media [20].

We have described the first-order field-induced transition in the smectic-A cell, which takes place due to the nucleation of the TFCD. Because of the restricted geometry of the system, the behavior of the domain phase is different for the cases when the order parameter ρ is smaller and larger than unity.

The nucleation ($\rho \ll 1$) is defined by the balance of the elastic and field energies. It is a heterogeneous process controlled by irregularities such as dust particles, surface roughness, and dislocation sets. The TFCD nucleation from the uniform state is hindered by the high-energy barrier. Similar situations with high potential barriers are known for bubble nucleation in the electroweak theory [21], vortex nucleation in superconductors [22], defect transitions in nematic droplets [23], etc. Among the listed fields, a detailed experimental study of the tunneling through the barrier is especially convenient for the Sm-A phase, since the transition from the homeotropic to the TFCD state can be easily detected by polarizing microscopy [7].

The expansion ($\rho \gg 1$) of the new phase is governed by the balance of the field and the surface anchoring energies. The last circumstance allows the quantitative study of the anchoring phenomena in the Sm-A phase and, more generally, the effect of the intrinsic surface anisotropy on the growth pattern during the first-order transition.

We benefited from valuable discussions with P. Fabre, M. Veyssié, C. Quilliet, A. Jákli, V. Pergamenshchik, and A. Saupe. The support provided to O.D.L. by the National Science Foundation under Grant No. DMR89-20147 (ALCOM), by DARPA under Contract No. MDA972-90-C-0037 (NCIPT) and Laboratoire de Physique des Solides is gratefully acknowledged.

*Also with Institute of Physics, Ukrainian Academy of Science, pr. Nauki, 46, Kyyiv, Ukraine.

[1] V. Fréedericksz and V. Zolina, Z. Krist. **79**, 255 (1931).
[2] W. Helfrich, Appl. Phys. Lett. **17**, 531 (1970).
[3] J. P. Hurault, J. Chem. Phys. **59**, 2068 (1973).
[4] A. Rapini, J. Phys. (Paris) **33**, 237 (1972).
[5] O. Parodi, Solid State Commun. **11**, 1503 (1972).
[6] P. G. De Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
[7] P. Fabre *et al.*, Phys. Rev. Lett. **64**, 539 (1990); J. C. Dabadie *et al.*, J. Phys. Condens. Matter **2**, SA291 (1990).
[8] G. Friedel, Ann. Phys. **18**, 273 (1922).
[9] O. D. Lavrentovich, Zh. Eksp. Teor. Fiz. **91**, 1666 (1986) [Sov. Phys. JETP **64**, 984 (1986)]; Mol. Cryst. Liq. Cryst. **151**, 417 (1987).
[10] M. Kléman, J. Phys. (Paris) **38**, 1511 (1977).
[11] I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series, and Products* (Academic, New York, 1980).
[12] P. S. Pershan and J. Prost, J. Appl. Phys. **46**, 2343 (1974).
[13] N. J. Chou *et al.*, J. Appl. Phys. **54**, 1827 (1983).
[14] H. P. Hinov, Liq. Cryst. **3**, 1481 (1988).
[15] A. Jákli and A. Saupe, Mol. Cryst. Liq. Cryst. **222**, 101 (1992).
[16] J. B. Fournier *et al.*, Phys. Rev. E **47**, 1144 (1993).
[17] J. Rault, Philos. Mag. **34**, 1511 (1976).
[18] P. Boltenhagen *et al.*, J. Phys. II France **1**, 1233 (1991).
[19] M. Kléman, J. Phys. (Paris) **36**, 595 (1974).
[20] J. B. Fournier, Phys. Rev. Lett. **70**, 1445 (1993).
[21] A. D. Linde, *Particle Physics and Inflationary Cosmology* (Harwood Academic, Chur, Switzerland, 1990).
[22] A. Buzdin and D. Fainberg, Phys. Lett. **A167**, 89 (1992).
[23] V. G. Bodnar *et al.*, Zh. Eksp. Teor. Fiz. **101**, 111 (1992) [Sov. Phys. JETP **74**, 60 (1992)].