Pis'ma v ZhETF, vol. 87, iss. 5, pp. 301 – 305 © 2008 March 10

Ferrielectric smectic with layer-by-layer change of the two-component order parameter

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Submitted 28 January 2008

One of the most remarkable properties of smectics is the wide variety of possible equilibrium structures. In this paper, based on Landau theory of the phase transitions, the transitions between ferroelectric and antiferroelectric phases and structure formed by smectic layers with different azimuthal and polar orientation of molecules were calculated. This unique structure has been predicted (P.V. Dolganov et al., Pis'ma v ZhETF **76**, 579 (2002)) using the minimization of the free energy with respect to the phase and modulus of the two-component order parameter, but never detected before. Recently non-resonant Bragg reflection, consistent with the predictions of the model, was found (P. Fernandes et al., Eur. Phys. J. E **20**, 81 (2006)) in ferrielectric smectic C^*_{FI1} (SmC^*_{FI1}) phase. In the 3-layer ferrielectric structure with a macroscopic helical pitch the modulus of the order parameter is larger in anticlinic-like layers and smaller in layers with mixed ordering. The values of the interlayer interactions were determined for smectic liquid crystalline materials forming different polar structures.

PACS: 61.30.Eb, 64.70.Md, 68.10.Cr

Tilted smectic liquid crystals [1] form a layer structure in which the long molecular axis tilt with respect to the layer normal (Fig.1). Their orientational structure may be described by two-dimensional (2D) vectors $\boldsymbol{\xi}_i$, where index i stands for the ith layer. Modulus of $\boldsymbol{\xi}_i$ is the projection of the long molecular axis onto the layer plane and so characterizes the tilt angle θ. Direction of $\boldsymbol{\xi}_i$ characterizes the azimuthal molecular orientations (angle φ_i). Set of $\boldsymbol{\xi}_i$ may be considered as a two-component order parameter, whose modula $|\boldsymbol{\xi}_i|$ and phases φ_i describe the orientational order.

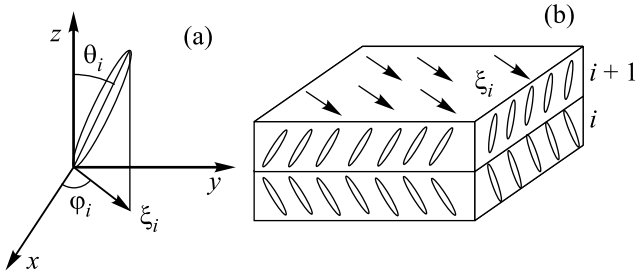

Fig.1. Orientation of molecules (a) and layer structure (b) in tilted smectics. θ_i and φ_i, are the polar and azimuthal angles. The two-component vector $\boldsymbol{\xi}_i$ is the order parameter. The helix axis is along the z direction

Up to 1975 only one tilted smectic was known, namely the smectic-C (SmC) phase (Fig.2a) in which both polar θ_i and azimuthal φ_i molecular orientations are constant in all smectic layers (synclinic phase). However since the order parameter of the tilted smectic is two-component it may be expected that other tilted structures exist in which phase (φ_i) and modulus (θ_i) of the order parameter change from layer to layer. The

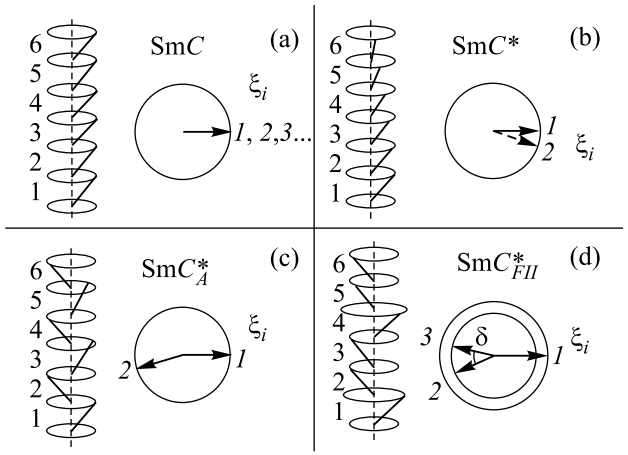

Fig.2. Schematic representation of nonchiral SmC and chiral SmC^*, SmC^*_A, SmC^*_{FI1} structures. Orientation of $\boldsymbol{\xi}_i$ is given in the right part of each Figure. Numbers (*1*, *2*, *3*, ...) denote subsequent layers. δ is the distortion angle between $\boldsymbol{\xi}_i$ in layers (*2*) and (*3*) in the three-layer cell of the SmC^*_{FI1} phase. In the SmC^*_{FI1} structure the modulus of the order parameter ξ_i is larger in layer (*1*) with nearly anticlinic ordering of molecules

first smectic with a non-constant over the layers phase of the order parameter was found in 1975 [2]. It was the ferroelectric smectic-C^* (SmC^*) structure (Fig.2b). Later in 1989 antiferroelectric smectic-C_A^* (SmC_A^*) phase and a number of subphases (SmC_α^*, SmC_{FI1}^*, SmC_{FI2}^*) were found [3, 4]. These phases are characterized by variation of φ_i from layer to layer. In the SmC^* structure $\boldsymbol{\xi}_i$ rotate slightly between nearest layers thus forming a helix along the layer normal. In the SmC_A^* phase (Fig.2c), $\boldsymbol{\xi}_i$ alternate between almost opposite directions in neighboring layers ($\varphi_{i+1} - \varphi_i \approx \pi$, anticlinic phase). In addition, SmC_A^* phase forms a helical structure. In SmC_{FI1}^* and SmC_{FI2}^* the variations of φ_i are richer with three and four layer periodicity [5–8].

It was believed for a long time that all smectic structures are formed by the change only of the phase of the order parameter. However the discrete phenomenological Landau theory predicted [9] the existence of a smectic structure with a variable modulus of the order parameter. This structure with periodicity of three smectic layers must appear above the temperature range of the antiferroelectric phase. A reliable candidate for this structure is the SmC_{FI1}^* phase. Theory [9] pointed the way of detecting this new structure. If the structure is formed only by change of the azimuthal angle φ_i, the electron density is constant in different layers. In such a structure the satellite Fourier harmonics at the wave vectors $Q = Q_1\,(1 \pm n/3)$, with integer n, may be observed only in resonant X-ray scattering ($Q_1 = 2\pi/d$, d is the layer thickness) [5–8]. However the difference in the modulus of the order parameter θ_i leads to the modulation of the layer thickness $d_i = d_0 \cos\theta_i$. This modulation of d_i should result in one-third satellites to the main diffraction peaks for conventional (non-resonant) diffraction. It was a challenge to experiment since this unique structure was predicted by the model that has already explained the structure of a number of liquid crystals but with change of only the phase of the order parameter. Recently [10] one-third non-resonant Bragg reflections were indeed found in the SmC_{FI1}^* phase which confirmed that SmC_{FI1}^* phase is the structure with modulation of electron density from layer to layer in the three-layer cell.

In this paper, the structure of the SmC_{FI1}^* phase was calculated in agreement with experimental observations [10]. Values of the interlayer interactions were determined in materials with various sequences of the polar phases. In the three-layer structure the modulus of the order parameter (tilt angle θ_i) is larger in the layer with nearly anticlinic ordering and smaller in two layers with nearly synclinic ordering between them and anticlinic ordering between another nearest layer.

The discrete phenomenological Landau model of the phase transitions [11–18] was used to describe the many possible structures observed experimentally. The basic expression for the free energy with interactions between nearest smectic layers reads [11–18]:

$$F_0 = \sum_i \left[\frac{1}{2}\alpha(T - T^*)\xi_i^2 + \frac{1}{4}b_0\xi_i^4 + \right.$$
$$\left. + \frac{1}{2}a_1\boldsymbol{\xi}_i\boldsymbol{\xi}_{i+1} + b_1\xi_i^2(\boldsymbol{\xi}_{i-1}\boldsymbol{\xi}_i + \boldsymbol{\xi}_i\boldsymbol{\xi}_{i+1})\right], \qquad (1)$$

where the first two terms describe the transition between nontilted SmA and tilted SmC phases in noninteracting layers. Next two terms describe the coupling between the nearest-neighbor (NN) layers. Interlayer interactions stabilize the synclinic structure (SmC) for negative coefficients a_1 and b_1 and anticlinic structure (SmC_A) for positive a_1 and b_1. The fourth term due to biquadratic interaction becomes more essential at low temperature, when the tilt angle is larger. The free energy in the form (1) may describe nonchiral SmC and SmC_A structures and the transition between them.

In our calculations, we also used three additional terms in the free energy [11–18]:

$$F_1 = \sum_i a_2\left[\boldsymbol{\xi}_i \times \boldsymbol{\xi}_{i+1}\right]^2, \qquad (2)$$

$$F_2 = \sum_i f\left[\boldsymbol{\xi}_i \times \boldsymbol{\xi}_{i+1}\right]_z, \qquad (3)$$

and

$$F_3 = \sum_i a_3\boldsymbol{\xi}_i\boldsymbol{\xi}_{i+2}. \qquad (4)$$

The first term describes the energetic barrier between synclinic and anticlinic structures. The polar phases are observed in compounds with chiral molecules [19]. We introduced in the free energy the so-called Lifshits term (3) providing the chiral interaction. The third term F_3 favors anticlinic orientation in the next-nearest neighbor (NNN) layers for positive a_3. This orientation is incompatible with both synclinic and anticlinic structures. Competition between NN and NNN interactions may lead to frustration and formation of nontrivial compromise structures. One of the ways for releasing the frustration is the formation of the structure with change of both the phase and the modulus of the order parameter.

In the calculations we set b_0 equal to 1, thus α was measured in 1/K and the other coefficients were dimensionless. The calculations of the structures were performed by means of numerical minimization of the free

energy (1)–(4) over θ_i and φ_i in all layers. The method of numerical minimization was described earlier [17]. The number of layers was taken from 50 to 500 in order that the surface effects do not influence the most part of the sample.

We first consider a simple transition between synclinic SmC^* and anticlinic SmC^*_A phases. This transition may be described by the free energy $F_0 + F_1 + F_2$. In both phases the tilt angle θ is constant in all smectic layers. For comparison with experiments the results of measurements of the SmC^*-SmC^*_A transition [20] were chosen with a large change of the tilt angle θ at the transition between synclinic and anticlinic structures. Results of the calculation are shown in Fig.3. Arrows

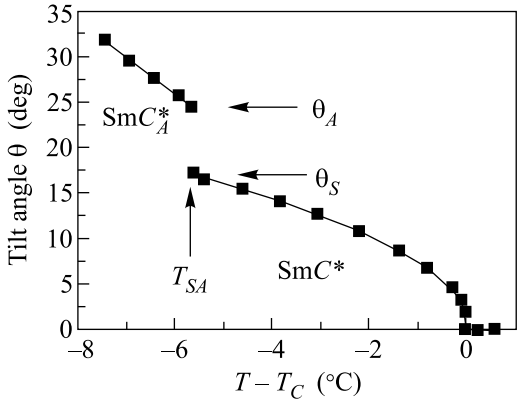

Fig.3. The tilt angle versus temperature in the phases with synclinic (SmC^*) and anticlinic (SmC^*_A) structures. The results of calculations correspond to the jump of the tilt angle in MHPB(F)PBC [20]. The set of model parameters is $\alpha = 0.024$ K^{-1}, $a_1 = -3.32 \cdot 10^{-2}$, $b_1 = 7.3 \cdot 10^{-2}$, $a_2 = 5 \cdot 10^{-2}$, $f = 10^{-4}$

point the temperature of the phase transition and tilt angles just before and after the transition. The main features of the phase transitions [20] may be well described by the theory. Different terms of the free energy are responsible for the specific features of the temperature dependence of the tilt angle. α is responsible for the temperature dependence of θ without interlayer interaction. The ratio between F_2 and interlayer interactions (two last terms in (1) and the barrier term F_1) determines the helical pitch p. Notice that for $p > 100$ layers the tilt angle and the characteristics of the phase transition are scarcely affected by the chiral term. The main peculiarities of the transition are determined by quadratic and biquadratic interlayer interaction in the free energy F_0. Relative values of a_1 and b_1 determine the temperature of the synclinic-anticlinic transition. The absolute values (with respect to $b_0 = 1$) determine the change of θ at the transition. Jump of θ at the phase transition points differs essentially in different compounds. The transition may occur even without noticeable change in θ [21, 22]. So the value of the interlayer interaction may vary in a wide range (for the case of the transition in Fig.3 the value a_1 equals $-3.32 \cdot 10^{-2}$).

The predicted difference of θ in the three-layer smectic stucture [9] depends on the interlayer interaction. In the investigated compounds with ferrielectric phase the change of θ at the phase transitions was not observed (or it is too small). It is likely that this was the reason that the structures with change of both phase and modulus of the order parameter were not discovered for a long time.

Now we consider smectics with polar subphases. The non-resonant peak with wave vector $Q = 4/3Q_1$ in the three-layer SmC^*_{FI1} structure was detected in experiment [10]. We remind that previously only resonant peaks were observed [5–8] that appear since the structure factor becomes a tensor near the absorption edge of atoms and depends on molecular orientation in smectic layers [23]. According to model [9] the non-resonant scattering in the three-layer SmC^*_{FI1} structure is related to the difference in θ_i and hence layer thickness $d_i = d_0 \cos\theta_i$ in smectic layers. In the three-layer cell of the ferrielectric structure (Fig.2d) the molecules in layer (1) form nearly anticlinic structures with molecules in nearest layers. The molecules in layer (2) form nearly anticlinic structures with molecules in layers (1) and nearly synclinic structure with molecules in layer (3). Similar molecular environment exists for molecules in layer (3). So tilt angle θ_i and layer thickness must differ in layer (1) and (2), (3). Modulation in layer thickness leads to non-resonant scattering. In the model with a sinusoidal electron density within each smectic layer, the ratio of the satellite Fourier harmonics to the main harmonic with Q_1 can be easily calculated. For the harmonics with wave vectors in the vicinity of Q_1 they read:

$$\frac{A_{4/3}}{A_1} = \frac{72\sqrt{3}}{49\pi}\frac{\Delta d}{d} \tag{5}$$

for $Q = 4/3Q_1$ and

$$\frac{A_{5/3}}{A_1} = \frac{45\sqrt{3}}{128\pi}\frac{\Delta d}{d} \tag{6}$$

for $Q = 5/3Q_1$, where Δd is the difference in layer thickness $\Delta d = d_{2(3)} - d_1$. Eqs. (5), (6) were obtained in a linear over $\Delta d/d$ approximation. At $\Delta d/d \approx 2.8 \cdot 10^{-3}$ and $\Delta\theta = \theta_1 - \theta_2 \approx 0.7°$ the ratio of the main Bragg to satellite peak corresponds to the measured value [10]. To determine $\Delta\theta$ the mean value of the tilt angle in the SmC^*_{FI1} phase was taken to be 13° [24]. Additional test of our model is as follows. According to Eqs. (5), (6)

the ratio between the intensities of two satellite peaks $I_{4/3}/I_{5/3} \approx 17.5$. Approximately the same ratio was observed in experiment [10].

Non-resonant scattering in the four-layer SmC^*_{FI2} phase can appear due to distortion of the orientational order when the layers in the unit cell have different electronic density [25]. However, up to now nonresonant scattering in the SmC^*_{FI2} phase was not observed.

The non-resonant X-ray diffraction was found in the three-layer SmC^*_{FI1} structure [10] in chiral liquid crystal MHPOBC with sequence of phases: SmC^*_A, SmC^*_{FI1}, SmC^*_{FI2}, SmC^*_α, SmA. For their description the frustration interaction F_3 must be also introduced in the free energy expansion. Chiral interaction F_2 leads to formation of macroscopic helix and nonzero distortion angle δ (Fig.2d) in SmC^*_{FI1} and SmC^*_{FI2} phases [26–29]. The experimentally observed phase sequence was obtained in calculations (Fig.4) by choosing appropriate

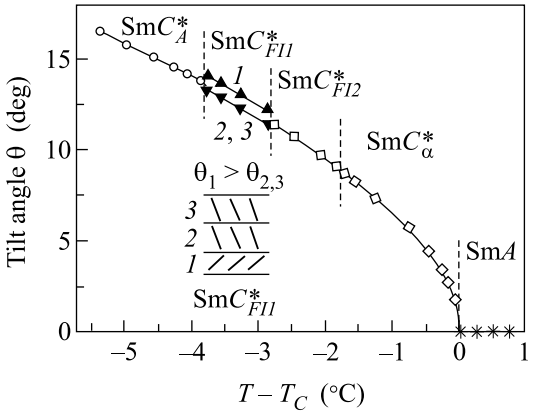

Fig.4. The temperature dependence of the tilt angle in SmC^*_A (circles), SmC^*_{FI1} (triangles), SmC^*_{FI2} (squares), SmC^*_α (diamonds), SmA (stars) phases. Up and down triangles (SmC^*_{FI1} phase) correspond to layers denoted *1* and *2*(*3*) in Fig.2d. Schematic representation of the three-layer cell of the SmC^*_{FI1} structure is shown in the lower part of the Figure. The set of model parameters is α=0.015 K^{-1}, $a_1 = 2.45 \cdot 10^{-3}$, $b_1 = 4.8 \cdot 10^{-3}$, $a_2 = 5.05 \cdot 10^{-2}$, $f = 9.8 \cdot 10^{-4}$, $a_3 = 7 \cdot 10^{-3}$

values of model parameters. The temperature range of the SmC^*_{FI1} phase correlates with the experimental observations [10, 24]. In the ferrielectric SmC^*_{FI1} phase the tilt angle θ splits into two branches. The difference in the tilt angles $\Delta\theta \approx 0.7°$ (Fig.4), i.e., corresponding to the value given above. The tilt angle is larger in layer (1) forming anticlinic ordering both with nearest and next-nearest neighbor layers (two layers on each side). Interactions with *NN* layers for positive a_1, b_1 and frustration interaction (*NNN* layers) favor anticlinic ordering and increase the tilt angle θ_1. In antiferroelectric SmC^*_A only *NN* interaction favors the structure of this phase. This is the reason why at SmC^*_A–SmC^*_{FI1} transition the tilt angle θ_1 is even higher than in the lower temperature SmC^*_A phase (Fig.4). Layers (2) and (3) form favorable anticlinic orientation only with two layers. Synclinic orientation with other two layers decreases the tilt angles in layers (2) and (3).

It is important to note that non-resonant satellite peaks were found only in the three-layer (SmC^*_{FI1}) structure [10]. In other phases (SmC^*_A, SmC^*_{FI2}) the satellite peaks were observed only in resonant scattering. This means that SmC^*_{FI1} phase is formed by layers with different electronic density whereas other phases are formed by layers with constant thickness and tilt angle. It is just such structures and X-ray scattering that were predicted by theory [9]. In summary one may state that smectic liquid crystal with the change of the phase and the modulus of the order parameter exists in the nature.

The authors thank V.E. Dmitrienko for fruitful discussions. This work was supported in part by RFFI grants # 08-02-00827 and # 08-02-00441, grant of the President of Russian Federation # MK-2382.2007.2, and by the Russian Science Support Foundation.

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19. A possible mechanism for the coupling between the tilt and the polarization $\mathbf{p}$ is the following. In an environment with mirror symmetry (SmA phase) at any particular moment, the molecules have with equal probability left- or right handed conformations, i.e., on average the molecules are nonchiral. The collective molecular tilt breaks the mirror symmetry, so that left- and right-handed conformations are no longer equally probable. From the macroscopic symmetry point of view to describe chiral, tilted, and polar smectics, one has to introduce three order parameters χ, $\boldsymbol{\xi}$, and $\boldsymbol{p}$ respectively. Note that these order parameters are not independent ones, and condensation of any pair amid them, inevitably induces the non-zero value for the third one. This fact leads to the presence of the specific third order term (the product of these order parameters). In principle one can include the dipole smectic layer polarization as a secondary order parameter in our model, and polar orientational order parameter configurations also imply electrical polarity. The non-uniform orientational deformations in such a case should produce space charges and long range Coulomb interaction. In practice, however, the molecules involved may have large steric anisotropy, without a large electric dipole moment. Besides, ionic impurities can screen the Coulomb interaction. Thus in this paper we disregard electrostatics.
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