

SHORT-PITCH AND LONG-PITCH MODES AS A KEY FOR THE UNDERSTANDING OF PHASE SEQUENCES AND TYPES OF ORDERING IN ANTIFERROELECTRIC SMECTIC LIQUID CRYSTALS

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A novel theoretical approach is suggested for the description of phase transitions and structures observed in antiferroelectric smectic liquid crystals. The allowance is made for the two types of ordering to be possible: short-pitch and long-pitch helical modes. The thermodynamic behavior of the material is treated as a result of the competition between these two modes. Formulated theory reproduces the main features of the experimentally observed phase sequences and structures thus explaining their physical nature.

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1. The main features of phase transitions and macroscopic properties of antiferroelectric smectic liquid crystals have been intensively studied during the last decade. The huge amount of experimental data was recently contributed by the information on the structural details obtained in the experiments on the scattering of the resonant X-rays [1, 2]. At the same time there was no theoretical model until now, which could describe both the phase sequences and structures observed. Thus, for instance, the so called "Ising-like" model [3] appears to explain the main features of phase diagrams, but the predicted structures of the phases are in a great discrepancy with the X-ray data [4,5]. Another well-developed model, which is usually referred to as "XY-model" [6], involves the short-pitch helical order, which is much more consistent with the X-ray data, but the theory seems to be unable to describe correspondent phase transitions. Therefore a great necessity of an appropriate theory still exists.

While creating such a theory one should hope to explain the main features of the antiferroelectric smectics behavior in the temperature interval between the high-temperature nontilted smectic-A* phase and the low-temperature antiferroelectric phase (AF, where the neighbor layers are tilted in opposite directions), which can be formulated as the following:

- In the racemic mixtures the phase sequence is quiet simple, and by decreasing the temperature the A-phase transits to the nontwisted synclinc C-phase (all the molecules there are tilted in the same direction), while the latter transits to the anticlinic phase (which is the nonchiral analog of the AF-phase) at some lower temperature.

- In the chiral materials more phases are observable. They arise in-between the phases mentioned above and, accordingly to the last experimental data, they all have the helical structures with an extremely short pitch [2].

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– The phase that arises between the A*- and C*-phases, called usually C_α*-phase, have the pitch that sufficiently changes with temperature being much less than that in the C*-phase.

The ferroelectric phases that are located between the C*- and AF-phases have the pitch very close to some integer number of smectic layers. By decreasing the temperature these phases change each other, so that the pitch decreases discretely (from 4 layers to 3 layers and finally to almost 2 layers in the twisted AF-phase in the case observed in [1,2]).

Below we present the new approach that seems to account for all of these main features, reproducing the observed phase sequences and structures. The main idea is to allow the substance to form two types of helical structures: the long-pitch helix with optical pitch and a short-pitch one with the pitch comparable to the smectic layer thickness. The idea of such approach was formulated firstly in semi-phenomenological way in Refs.[4,5,7]. Here we develop the idea in a different manner, taking into account that the physical background of these two modes can be connected, for instance, with the fact that interlayer interactions, which lead to the appearance of antiferroelectric order, are likely to be determined by the interaction between chiral tails of the molecules [8]. Then the molecules in neighboring layers, which are arranged tail-to-tail, should tend to form a short-pitch structure, while the others are likely to form the long-pitch helix.

2. In general the free energy density of the media, which is able to form both types of order, can be written with two order parameters

$$F(\theta_L, \theta_S) = F_L(\theta_L) + F_S(\theta_S) + F_{LS}(\theta_L, \theta_S), \quad (1)$$

where θ_L and θ_S are the amplitudes (tilt angles) of the long-pitch and short-pitch modes correspondingly, F_L and F_S are the free energies of the related individual modes, and F_{LS} is the contribution from the interaction of the modes. The phases of the system should possess the values θ_L and θ_S that minimize Eq.(1), and we can divide them into four classes: smectic-A phase, where both amplitudes are zero; L-phases, where only θ_L is nonzero; S-phases where θ_S is nonzero; and LS-phases, in which both types of ordering are presented simultaneously.

It is clear from the physical point of view that the LS-phase is hardly probable in our case, at least when the pitches differ by few orders of magnitude. Actually, it can take place, for instance, if the helices unwind each other, thus forming a common helix. The corresponding elastic energy of this unwinding should make such coexistence thermodynamically unprofitable. In the other hypothetical case different areas of the substance can arrange structures with different pitch, but it would sufficiently disturb the orientation (nematic) order within the layers, thus being also strongly unprofitable.

Therefore the behavior of the system can be reduced to the competition between the L- and S-phases and the A-phase. Then at a given temperature the phase with the lowest free energy is stabilized. At temperatures when $F_L = F_S$ the first order transitions between L- and S-phases occur. The closeness of the free energies should lead to fluctuational appearance of the absent order parameter, what will be significant for our further consideration.

All of the intermolecular interactions in smectics can be divided in two parts: in-layer interactions between the molecules within the same layer and inter-layer interactions between the molecules from different layers. We suppose the first ones to be mainly responsible for the tilting amplitude of the molecules and appearance of the ferroelectric

polarization, while the interlayer interactions define the orientation of the tilting in different layers and the formation of the helices. It is established that the tilting amplitude is not affected by the transitions from one helical phase to another. Thus it is reasonable to assume that L- and S-modes differ only by interlayer contributions, and the in-layer part for both modes is the same.

Analyzing interlayer contribution we shall follow the general approach of the XY-model [6], accounting only for the nearest neighbor interactions. It is convenient to present the director of k -th layer in the form $\mathbf{n}_k = \mathbf{n}_z + \mathbf{c}_k$, where \mathbf{n}_z (the same for all layers) is parallel to crystalline axis z , and \mathbf{c}_k is the transversal part (C-director). Then the nonchiral quadratic in θ part of interaction between some n -th and $(n + 1)$ -th layers is proportional to

$$-n_z^2(\mathbf{c}_n \cdot \mathbf{c}_{n+1}) \approx -\theta^2 \cos \Psi, \quad (2)$$

where Ψ is the angle between C-director of the layers and the minus reflects that the synclinc ordering is preferable for this term. The chiral part should have the form

$$n_z^2((\mathbf{c}_n \times \mathbf{c}_{n+1}) \cdot \mathbf{e}) \approx -\theta^2 \sin \Psi, \quad (3)$$

the unit vector \mathbf{e} points along the z -axis in the direction of layer number increasing.

In addition to this the specific anticlinic interaction, responsible for the antiferroelectric ordering, should be added. Following the results for the dipole-dipole interactions between the chiral tails [8], we assume it to have the form $\theta^4 \cos \Psi$, with some positive factor for the anticlinic order to be preferable here. Some chiral interaction like $\theta^4 \sin \Psi$ also should exist. We omit the probable terms with $\cos 2\Psi$ and $\sin 2\Psi$, as accounting for them will complicate further calculations but bringing nothing qualitatively new. Then the free energy of the short-pitch mode can be written as

$$F_S = t\theta_S^2 + \frac{1}{2}b\theta_S^4 - (V \cos \Psi + \alpha \sin \Psi)\theta_S^2 + (U \cos \Psi - \beta \sin \Psi)\theta_S^4, \quad (4)$$

where we introduce phenomenological parameters of the interlayer interaction: V and U for the nonchiral interaction, and α and β for the chiral one. The in-layer part (the first pair of terms) is written in the ordinary form, the coefficient b being constant, and $t = A(T - T_0)$ is the only temperature dependent coefficient.

In the free energy of the long pitch mode, which can be constructed in the same way, anticlinic term should be absent. Unless the large value of the pitch means small values of the chiral parameters, we can neglect them and obtain

$$F_L = 1/2b\theta_L^4 + (t - V)\theta_L^2, \quad (5)$$

putting the same parameter of the synclinc interaction V .

3. Minimizing Eq.(5) with respect to θ_L we obtain that the long-pitch phase can appear when $t < V$ and then

$$\theta_L^2 = -\frac{1}{b}(t - V), \quad F_L = -\frac{1}{2b}(t - V)^2. \quad (6)$$

Minimizing the free energy (4) with respect to Ψ we obtain the condition

$$\tan \Psi = \frac{\alpha + \beta\theta_S^2}{V - U\theta_S^2}, \quad (7)$$

and with such Ψ the free energy of the S-mode equals

$$F_S = 1/2b\theta_S^4 + t\theta_S^2 - \theta_S^2 \sqrt{(V - U\theta_S^2)^2 + (\alpha + \beta\theta_S^2)^2}. \quad (8)$$

In the vicinity of the phase transition from the A*-phase the tilt angle is small and can be neglected inside the square root. Then we obtain the temperature of the transition from A*-phase to S-phase, the short-pitch mode tilt angle and the free energy of the S-phase as

$$t_{A \rightarrow S} = \sqrt{V^2 + \alpha^2}, \quad \theta_S^2 = -\frac{1}{b}(t - \sqrt{V^2 + \alpha^2}), \quad F_S = -\frac{1}{2b}(t - \sqrt{V^2 + \alpha^2})^2. \quad (9)$$

Comparing Eqs.(6) and (9) gives that in this temperature range the S-phase has lower free energy and appears first. So far, as one decreases the temperature, the transition from A*-phase to the S-phase should be observed. We believe this to correspond to the so-called A*-C $_{\alpha}$ transition. It has the second order and its temperature $t_{A \rightarrow S}$ depends on chirality. Accordingly to Eq.(7), the pitch of the S-phase decrease with decreasing of temperature (with the increasing of θ_S^2), what is consistent with the results of the X-ray measurements [2].

Thus, in the closest vicinity of the transition point from the A*-phase the interlayer interactions change significantly the behavior of tilt angle of the modes, shifting the transition point. With further decreasing the temperature one reaches the temperature range $|t| \gg V$. Here this interlayer contribution to tilting becomes small. Then we can set $\theta_S^2 = -t/b$ in Eq.(8) and obtain the free energy of the S-phase as

$$F_S = -\frac{t^2}{2b} + \frac{t}{b} \sqrt{\left(V + U\frac{t}{b}\right)^2 + \left(\alpha - \beta\frac{t}{b}\right)^2}. \quad (10)$$

In the same approximation the free energy of the L-phase equals

$$F_L = -\frac{t^2}{2b} + V\frac{t}{b}. \quad (11)$$

To analyze the phase transitions between L- and S-phases one should find the temperatures when these free energies are equal. It happens at temperatures

$$t_{S \rightleftharpoons L} = -\frac{b}{U^2 + \beta^2} \left[UV - \alpha\beta \pm \sqrt{(UV - \alpha\beta)^2 - \alpha^2(U^2 + \beta^2)} \right] \quad (12)$$

the minus before the square root corresponding to S \rightarrow L transition and the plus corresponding to the L \rightarrow S transition as far as the temperature decreases. Therefore the L-phase appears in the interval between the temperatures (12). We believe this L-phase to describe the C*-phase in the observed phase sequences. The condition for the C*-phase appearance can be obtained as a requirement of the square root presence in Eq.(12), and it takes the form

$$V > \alpha \left[\sqrt{1 + (\beta/U)^2} + \beta/U \right]. \quad (13)$$

As a consequence of Eqs.(12), (13) we see so far that the C*-phase interval becomes narrower when the chirality is increasing and even disappears at large values of the chiral parameters.

As a result, we find that by starting from the A*-phase and decreasing the temperature, first the transition to the C $_{\alpha}$ -phase at point $t_{A \rightarrow S}$ takes place. Afterwards the transition to the C*-phase appears at temperature given by Eq.(12) with minus sign. Finally the transition back to some S-phase occurs at temperature (12) with plus sign.

4. To analyze the S-phase, which occurs below the C*-phase, one should account for the fact, that the free energies of the both types of order are very close, being different only by the contributions from the interlayer interactions. Then the L-order can appear fluctuationally in the S-phase. If the characteristic times of such fluctuations are larger than the short-pitch helix relaxation times, then this phenomena is similar locally to the action of some external vector-like field on the short-pitch helix perpendicular to the helical axis.

The free energy of the short-pitch mode (4) under the action of the external vector field L should include the field dependent terms. The interaction of some n -th layer with the field can be presented as a sum of terms proportional to the powers of the product $(L \cdot c_n)$. The correspondent contribution from all layers to the free energy density can be reduced to

$$\Delta F_S = \frac{1}{N} \sum_{k=1}^{\infty} \sum_{n=1}^N u_k \cos[k(\Psi n + \varepsilon - \varphi)], \quad (14)$$

where φ is the azimuth angle of the field, ε is the phase of the short-pitch helix, and N is a macroscopic number of smectic layers. The coefficients $u_k \propto L^k \theta_S^k$ characterize phenomenologically the interaction energy.

After the summation over n , the Eq.(14) appears to have a singular dependence on Ψ , being nonzero only if $\Psi = 2\pi s/k$ with integer s and k . After minimization over the phase ε we obtain it to be equal to φ or $\varphi + \pi/k$, depending on the sign of the correspondent constant u_k and therefore providing the negative sign of the contribution to the free energy. Then the free energy contains the "locking" terms that make the commensurate structure profitable. The correspondent full energies of such commensurate states are for instance

$$F_{\pi/2} = -\frac{t^2}{2b} - \frac{t}{b} \left(\beta \frac{t}{b} - \alpha \right) - |u_4| \quad (15)$$

for the 4-layered structure and

$$F_{2\pi/3} = -\frac{t^2}{2b} - \frac{t}{2b} \left[\frac{t}{b} (U + \beta\sqrt{3}) + (V - \alpha\sqrt{3}) \right] - |u_3| \quad (16)$$

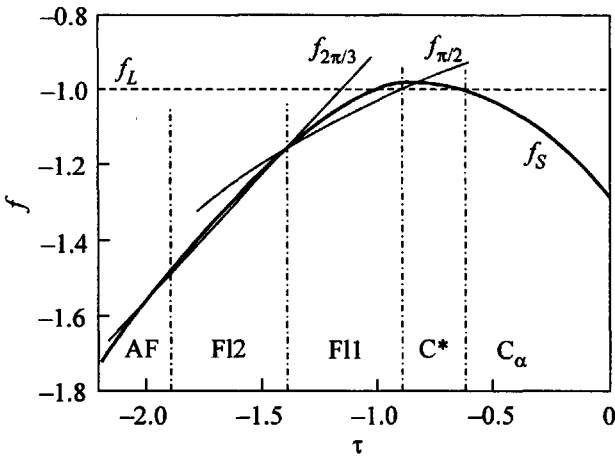
for the 3-layered one. The interaction parameters of the lowest order are presented here since u_k should decrease with k increasing. It is also clear that these parameters have sufficient temperature dependence since the amplitude of L-fluctuations decreases vastly with the difference $(F_L - F_S)$ increasing. These locking terms make the commensurate structure profitable compared to the incommensurate one, as free energies (15) and (16) are less than incommensurate energy (10) in certain temperature intervals near the points, at which Ψ defined by Eq.(7) is close to the values $\pi/2$ and $2\pi/3$, respectively.

We can suggest that the ferrielectric-like electrooptic behavior occurs as a result of the L-order induction by the electric field. Thus, following the notations confirmed in literature, we denote our 4-layered phase as FI1 and the 3-layered one as FI2. Obviously, in general such locking occurs every time when the ratio $\Psi/2\pi$ equals any rational number

s/k . The value of the correspondent locking energy then equals $|u_k|$, which is comparably small at large k , so that the phases with small k have much wider temperature range.

At temperatures below the regions of the commensurate phases the incommensurate pitch of the S-structure is slightly larger than 2-layers, what means that it corresponds to the twisted antiferroelectric phase. With further temperature decreasing the short pitch also decreases approaching asymptotically 2-layers. This means that effectively the pitch of the AF-phase twisting increases as the temperature goes down, what was clearly seen experimentally by means of optical selective reflections [9,10]. The twisting sign of the antiferroelectric helix is opposite compared to the ferroelectric one.

To analyze the phase sequence it is convenient to compare the reduced dimensionless free energies $f = (F + t^2/2b)/V\theta^2$. Thus, for the L-phase this reduced energy equals $f_L = -1$, the reduced energies of the commensurate states $f_{\pi/2}$ and $f_{2\pi/3}$ accordingly to Eqs.(15), (16) possess almost linear temperature dependence as only the locking terms give small nonlinear contributions. The correspondent analysis of the phase sequence is



Reduced free energies of the long-pitch state (f_L), incommensurate short-pitch state (f_s), and commensurate states ($f_{\pi/2}$ and $f_{2\pi/3}$) as functions of dimensionless temperature τ . Phase transitions occur at the intersections of the lowest curves. Correspondent phases are indicated underneath

illustrated on Figure, where the typical reduced free energies of the states are presented as functions of the dimensionless temperature $\tau = tU/bV$. The system follows the lowest possible curve and the transitions occur at intersection points. The arising phases are indicated underneath.

The small incommensurability of the FI-phases that was observed in the X-ray experiments can arise due to the twisting of the L-field. The finite size of the fluctuating areas should wide the δ -function-like dependence of the Eq.(14) making it Lorentzian-like. This can also give rise to the incommensurability, which will be temperature dependent in this case.

5. Our approach reproduces the main features of phase sequences and structures observed in antiferroelectric smectics. It can be used also for the description of the nonchiral (racemic) mixtures. As we put α and β to have the zero values, the S-state describes the synclinic order above the temperature $t = -bV/U$ and anticlinic order below it. From the Eqs.(9), (12) it follows that in a racemate the temperature range of the C_α -phase vanishes completely and the A-phase transits directly to the C-phase. The transition to the S-phase given by Eq.(12) then happens at the point $t = -2bV/U$, i.e., at

the point where the S-mode already forms anticlinic structure. So far the last transition corresponds to the C-AF one in the racemate.

As a conclusion we can make some estimations of the involved parameters for the substance 10OTBBB1M7, that was thoroughly studied both by the X-ray [2] and optical [11] techniques. As it was found, the S-pitch in the C_α -phase in this compound varies monotonously from about 8-layers close to the A^* -phase up to 5-layers near the C^* -phase. The 8-layers periodicity means the value $\Psi \approx \pi/4$ when $\theta_S \rightarrow 0$, and accordingly to Eq.(7) it yields $V \approx \alpha$. So far for the S-mode the chiral interlayer interactions in this case are of the same order as the nonchiral ones. Certainly it does not necessary mean that the substance possesses anomalous high chirality. It is more likely to be the consequence of the low value of the parameter V , what can be treated as a result of some anticlinic contribution to the correspondent quadratic in θ term in Eq.(4).

For $V \approx \alpha$ our approach predicts the narrow temperature range of the C^* -phase, what is consistent with the observed phase sequence [2,11], where this range is only about 1 °C. From its low temperature side the C^* -phase bounds the 4-layered FI1-phase. Unless the latter appears near the temperature, for which the incommensurate S-pitch equals 4-layers, above the upper edge of the C^* -phase this pitch should be slightly larger, i.e., about 5-layers. This is consistent with the observed 5-layers structure of the C_α -phase before the transition to C^* .

Obviously, to fit the whole phase sequence one must know the temperature behavior of the locking parameters u_k . These parameters must decrease strongly as the difference ($F_L - F_S$) grows, being larger near the L-S-transition point. It means that the locking in the FI1-phase, which neighbors the L-phase, is stronger than that in the FI2-phase. That is why the temperature interval of the FI2-phase is smaller. This can explain also why the structure of the FI1-phase is rather well stabilized compared to the FI2 structure, which is quiet unstable, giving the low-accuracy experimental data.

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