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A phenomenological model of antiferroelectric liquid crystals

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We present the analysis of static properties of a simple phenomenological model of antiferroelectric liquid crystals, capable of explaining some different sequences of phase transitions found experimentally. Stability analysis shows the existence of three simply modulated phases. Results are summed up in phase diagrams with dependence on the parameters of the model. The existence of doubly modulated incommensurate phases is predicted in parts of the phase diagrams.

1. Introduction

Antiferroelectric liquid crystals [1] are chiral smectic C (S_C^*) where the molecules in the neighbouring layers are tilted from the layer normal in almost opposite directions. Different sequences of tilted smectic phases have been observed in antiferroelectric liquid crystals by lowering the temperature. The most general is the one [2, 3] in the optically pure MHPOBC

$$S_A \leftrightarrow S_{C_\alpha}^* \leftrightarrow S_C^* \leftrightarrow S_{C_\gamma}^* \leftrightarrow S_{C_A}^*$$

Here S_C^* is the ferroelectric smectic C* phase, $S_{C_A}^*$ is the antiferroelectric phase and $S_{C_\gamma}^*$ is the ferrielectric phase. In the S_C^*, $S_{C_\gamma}^*$ and $S_{C_A}^*$ phases the ferroelectric, ferrielectric and antiferroelectric order changes in a helicoidal way in the direction perpendicular to the smectic layers. The $S_{C_\alpha}^*$ phase, which exists only in a narrow temperature interval, seems to be more complicated [4]. It is antiferroelectric at higher temperatures, while with decreasing temperature gradually the ferrielectric character develops. The nature of the ferrielectric order changes with temperature and it transforms eventually into the ferroelectric S_C^* phase.

For the mixture of *R*- and *S*-enantiomers of MHPOBC the $S_{C_\alpha}^*$ and $S_{C_\gamma}^*$ phases were not observed and only the sequence

$$S_A \leftrightarrow S_C^* \leftrightarrow S_{C_A}^*$$

has been found [1]. In some systems (for example in TFMHPOBC [5]) a direct transition from the S_A to the antiferroelectric $S_{C_A}^*$ phase has been observed.

A phenomenological theory of the antiferroelectric phase transition has been introduced by Orihara and Ishibashi [6]. The model consists of a Landau expansion in terms of ferroelectric and antiferroelectric order parameters. Because of the chirality of the molecules, expansion includes Lifshitz invariants with respect to both order parameters as well as a bilinear coupling between them. It is assumed that the changes

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of the order parameters from one smectic layer to another are small and therefore the continuum approximation can be used.

Orihara and Ishibashi [6] in their analysis did not take the chiral terms explicitly into account and obtained homogeneous ferroelectric, ferrielectric and antiferroelectric phases as three possible states of the system. Here the chiral terms will be taken into account and the structure of possible stable phases and their stability will be studied. With dependence on the parameters of the model, possible sequences of the phases will be determined.

2. Simply modulated phases and their stability

The tilt of molecules in the ith layer can be described by a two-component tilt vector

$$\xi_i=(n_{ix}n_{iz}, n_{iy}n_{iz}), \qquad i=1,2, \tag{1}$$

where $\mathbf{n}_i=(n_{ix}, n_{iy}, n_{iz})$ is the director of the even and odd layers, respectively, and the z axis is normal to the layers. In the $S^*_{C_A}$ phase the molecules in the neighbouring layers tilt in the opposite directions, in the S^*_C phase tilt from one layer to another does not change. We therefore introduce two new vectors instead of ξ_1 and ξ_2.

$$\xi_a=\tfrac{1}{2}(\xi_1-\xi_2), \qquad \xi_f=\tfrac{1}{2}(\xi_1+\xi_2), \tag{2}$$

where ξ_a represents the antiferroelectric and ξ_f the ferroelectric order.

The Landau free energy density expansion in ξ_a and ξ_f can be expressed as

$$\begin{aligned} g(z)=&\tfrac{1}{2}\alpha_a\xi_a^2+\tfrac{1}{2}\alpha_f\xi_f^2+\tfrac{1}{4}\beta_a\xi_a^4+\tfrac{1}{4}\beta_f\xi_f^4\\ &+\tfrac{1}{2}\gamma_1\xi_a^2\xi_f^2+\tfrac{1}{2}\gamma_2(\boldsymbol{\xi}_a\cdot\boldsymbol{\xi}_f)^2\\ &+\delta_a\left(\xi_{ax}\frac{\partial\xi_{ay}}{\partial z}-\xi_{ay}\frac{\partial\xi_{ax}}{\partial z}\right)+\delta_f\left(\xi_{fx}\frac{\partial\xi_{fy}}{\partial z}-\xi_{fy}\frac{\partial\xi_{fx}}{\partial z}\right)\\ &+\tfrac{1}{2}\kappa_a\left(\frac{\partial\xi_a}{\partial z}\right)^2+\tfrac{1}{2}\kappa_f\left(\frac{\partial\xi_f}{\partial z}\right)^2, \end{aligned} \tag{3}$$

where α and β terms represent the expansion up to the fourth order in magnitude of ξ_a and ξ_f. As usual, it is assumed that only the coefficients of the quadratic terms in the order parameters are temperature dependent:

$$\alpha_a=a(T-T_{a,0}), \qquad \alpha_f=a(T-T_{f,0}), \tag{4}$$

where $T_{a,0}$ and $T_{f,0}$ are the temperatures where the coefficients change their signs. The δ terms are the Lifshitz terms, which appear due to the chirality of the molecules, and the elastic energy is described by κ terms. The γ terms represent the coupling between the two order parameters. The above free energy density is obtained from the one introduced by Orihara and Ishibashi [6] after minimization of the free energy with respect to the antiferroelectric and to the ferroelectric polarization. Chirality of the molecules introduces into the system the optical activity, leading to a helicoidal structure.

If there was no coupling between the two order parameters, each of them would form its own helicoidal structure. Because of the coupling between the two order parameters, the general solution of the minimization problem of the above Landau free energy is a soliton-lattice on a helix, representing the incommensurate structure where the two order parameters change with a constant phase difference in some intervals along the z axis and between these regions domain walls exist, corresponding to the

changes of the phase difference between ξ_a and ξ_f. Only when the lock-in term γ_2 is strong enough, the two order parameters keep a fixed phase difference in the whole sample and therefore form one single helicoidal structure. Here we shall study in more detail only such simply modulated phases.

Positive γ_2 prefers perpendicular orientation of ξ_a and ξ_f,

$$\xi_a=(\theta_a\cos qz,\theta_a\sin qz),\qquad \xi_f=(-\theta_f\sin qz,\theta_f\cos qz), \tag{5}$$

while for negative γ_2 the parallel orientation minimizes the free energy density:

$$\xi_a=(\theta_a\cos qz,\theta_a\sin qz),\qquad \xi_f=(\theta_f\cos qz,\theta_f\sin qz). \tag{6}$$

For directionally decoupled systems $\gamma_2=0$, ferro and antiferro order parameters follow its own helices with different helix parameters q. Dynamical properties of such systems are presented in [7].

We must minimize the free energy with respect to three parameters θ_a, θ_f and q. Solutions are of four types

$$\begin{array}{lll}\theta_a=0, & \theta_f=0 & S_A\\ \theta_a=0, & \theta_f\neq 0 & S_C^*\\ \theta_a\neq 0, & \theta_f=0 & S_{C_A}^*\\ \theta_a\neq 0, & \theta_f\neq 0 & S_{C_\gamma}^*.\end{array}$$

The first solution with both parameters equal to zero represents the S_A phase and is trivial.

Both ferroelectric and antiferroelectric solutions are qualitatively equivalent. The ferroelectric solution is

$$\theta_a=0,\quad \theta_f^2=-\frac{\alpha_f-\kappa_f q_f^2}{\beta_f},\quad q_f=-\frac{\delta_f}{\kappa_f} \tag{7}$$

and the antiferroelectric solution is given by

$$\theta_a^2=-\frac{\alpha_a-\kappa_a q_a^2}{\beta_a},\quad \theta_f=0,\quad q_a=-\frac{\delta_a}{\kappa_a}. \tag{8}$$

By lowering the temperature, the S_A phase becomes unstable and transforms for $T_{a,0}>T_{f,0}$ to the antiferroelectric phase and for $T_{f,0}>T_{a,0}$, to the ferroelectric phase. Here only the second case will be studied with the aim to reproduce the observed sequence of phases: $S_A\leftrightarrow S_C^*\leftrightarrow S_{C_A}^*$. The results for $T_{a,0}>T_{f,0}$ can be easily obtained by exchanging the indices a and f.

The ferrielectric solution ($S_{C_\gamma}^*$) is different for positive and for negative γ_2. For $\gamma_2>0$ we obtain:

$$\left.\begin{aligned}\theta_a^2&=\frac{(\alpha_f+2\delta_f q+\kappa_f q^2)\gamma_1+(\alpha_a+2\delta_a q+\kappa_a q^2)\beta_f}{\beta_a\beta_f-\gamma_1^2},\\ \theta_f^2&=\frac{(\alpha_a+2\delta_a q+\kappa_a q^2)\gamma_1+(\alpha_f+2\delta_f q+\kappa_f q^2)\beta_f}{\beta_a\beta_f-\gamma_1^2},\end{aligned}\right\} \tag{9}$$

while for $\gamma_2 < 0$ the two order parameters are related to the wave vector of the helix (q) as

$$\left.\begin{aligned}\theta_a^2 &= \frac{(\alpha_f + 2\delta_f q + \kappa_f q^2)(\gamma_1 + \gamma_2) + (\alpha_a + 2\delta_a q + \kappa_a q^2)\beta_f}{\beta_a\beta_f - (\gamma_1 + \gamma_2)^2},\\ \theta_f^2 &= \frac{(\alpha_a + 2\delta_a q + \kappa_a q^2)(\gamma_1 + \gamma_2) + (\alpha_f + 2\delta_f q + \kappa_f q^2)\beta_f}{\beta_a\beta_f - (\gamma_1 + \gamma_2)^2}.\end{aligned}\right\} \tag{10}$$

The solution is then obtained by minimizing the free energy with respect to q. As we are interested only in real solutions, q must be real and θ_a^2, θ_f^2 positive. The necessary condition for the existence of the $S^*_{C_\gamma}$ phase is $\beta_a\beta_f > \gamma_1^2$ for positive γ_2 and $\beta_a\beta_f > (\gamma_1 + \gamma_2)^2$ for negative γ_2. It turns out that the obtained wave vector of the ferrielectric helix is between q_f and q_a. The calculated $S^*_{C_\gamma}$ phase exists at temperatures between the S^*_C and $S^*_{C_A}$ phases and parameters θ_a, θ_f and q change continuously with temperature (see figures 1 and 2). The phase transition between the S^*_C and $S^*_{C_A}$ phases is

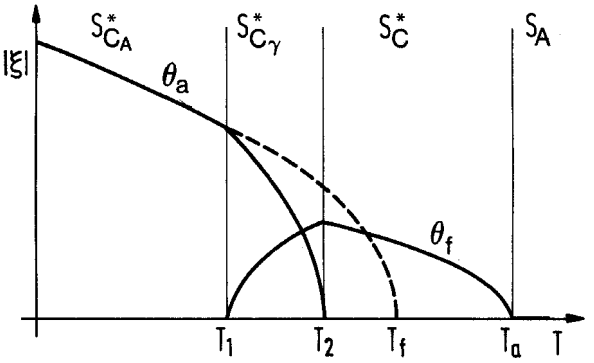

Figure 1. Temperature dependence of the magnitudes of the order parameters, θ_a and θ_f for the case of second order transitions $S^*_C \leftrightarrow S^*_{C_\gamma}$ and $S^*_{C_\gamma} \leftrightarrow S^*_{C_A}$.

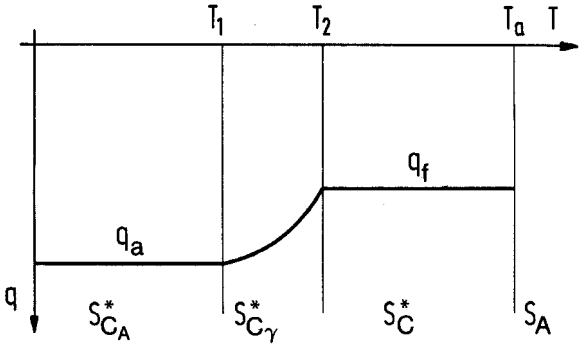

Figure 2. Temperature dependence of the wave vector of the helix q for the same parameters as in figure 1.

of first order, while the transitions between the $S^*_{C_\gamma}$ and S^*_C or $S^*_{C_\gamma}$ and $S^*_{C_A}$ phases could be either of first or second order. If the difference between the wave vectors in the S^*_C and $S^*_{C_A}$ phases is small, a second order transition is more favoured, otherwise the first order transition appears.

In order for the phase to exist it is necessary that the corresponding solution is stable with respect to small fluctuations of the order parameters. The stable solution is the one with lowest energy and non-negative eigenvalues of the matrix of second derivatives with respect to the deviation from the solution.

For any given set of model parameters, we have analysed at each temperature the existence and stability of possible simply modulated phases (S^*_C, $S^*_{C_\gamma}$ and $S^*_{C_A}$). Usually the lowest free energy solution is stable, while others are not. Sometimes it happens that also some solutions with higher free energies are (meta)stable, for example close to first order phase transitions. But there exist also cases, where the lowest free energy solution is not stable. This means, that the equilibrium solution in this case is not simply modulated but should be of the soliton $\simeq$ lattice type. We have not analysed the detailed structure of these solutions, but we expect that they represent an incommensurate structure on a helix, where also the magnitudes of the two order parameters change with z. It has been shown, that for some values of parameters and some temperatures a single soliton solution has lower energy than the ferrielectric phase, meaning that in this regime a multi-soliton solution represents a stable state.

3. Possible sequences of phases

By such an analysis we can determine for a given set of model parameters the sequence of phases which is obtained by lowering the temperature and the order of the phase transitions between the phases. If we limit ourselves to the case $T_{f,0} > T_{a,0}$ and if we choose the parameters so that the low temperature phase is antiferroelectric ($\beta_f > \beta_a$), we get 11 different phase sequences, which are shown below. As the twelfth possibility the case is listed, where the low temperature phase is antiferroelectric and we have only $S_A \leftrightarrow S^*_{C_A}$ transition.

1	S^*_C	$\overset{I}{\leftrightarrow}$	$S^*_{C_A}$							
2	S^*_C	$\leftrightarrow$	IC	$\leftrightarrow$	$S^*_{C_A}$					
3	S^*_C	$\overset{II}{\leftrightarrow}$	$S^*_{C_\gamma}$	$\overset{II}{\leftrightarrow}$	$S^*_{C_A}$					
4	S^*_C	$\overset{I}{\leftrightarrow}$	$S^*_{C_\gamma}$	$\overset{II}{\leftrightarrow}$	$S^*_{C_A}$					
5	S^*_C	$\overset{II}{\leftrightarrow}$	$S^*_{C_\gamma}$	$\overset{I}{\leftrightarrow}$	$S^*_{C_A}$					
6	S^*_C	$\overset{I}{\leftrightarrow}$	$S^*_{C_\gamma}$	$\overset{I}{\leftrightarrow}$	$S^*_{C_A}$					
7	S^*_C	$\leftrightarrow$	IC	$\leftrightarrow$	$S^*_{C_\gamma}$	$\overset{II}{\leftrightarrow}$	$S^*_{C_A}$			
8	S^*_C	$\leftrightarrow$	IC	$\leftrightarrow$	$S^*_{C_\gamma}$	$\overset{I}{\leftrightarrow}$	$S^*_{C_A}$			
9	S^*_C	$\overset{II}{\leftrightarrow}$	$S^*_{C_\gamma}$	$\leftrightarrow$	IC	$\leftrightarrow$	$S^*_{C_A}$			
10	S^*_C	$\overset{I}{\leftrightarrow}$	$S^*_{C_\gamma}$	$\leftrightarrow$	IC	$\leftrightarrow$	$S^*_{C_A}$			
11	S^*_C	$\leftrightarrow$	IC	$\leftrightarrow$	$S^*_{C_\gamma}$	$\leftrightarrow$	IC	$\leftrightarrow$	$S^*_{C_A}$	
12	$S^*_{C_A}$									

The order of each transition is denoted by I or II. The direct transition between the ferroelectric and the antiferroelectric phase is always of the first order by symmetry reasons (1), but the indirect transition through the ferrielectric phase can be continuous or discontinuous (3–6). The transitions $S^*_C \leftrightarrow S^*_{C_\gamma}$ and $S^*_{C_A} \leftrightarrow S^*_{C_\gamma}$ can also go through incommensurate phases (7–11) and also an indirect transition between S^*_C and $S^*_{C_A}$ through an incommensurate phase is possible (2). The other set of twelve sequences for the case $T_{a,0} > T_{f,0}$ can be obtained by changing $S^*_{C_A}$ and S^*_C.

The phase diagrams in dependence of κ_a/κ_f and q_a/q_f are presented in figures 3 and 4.

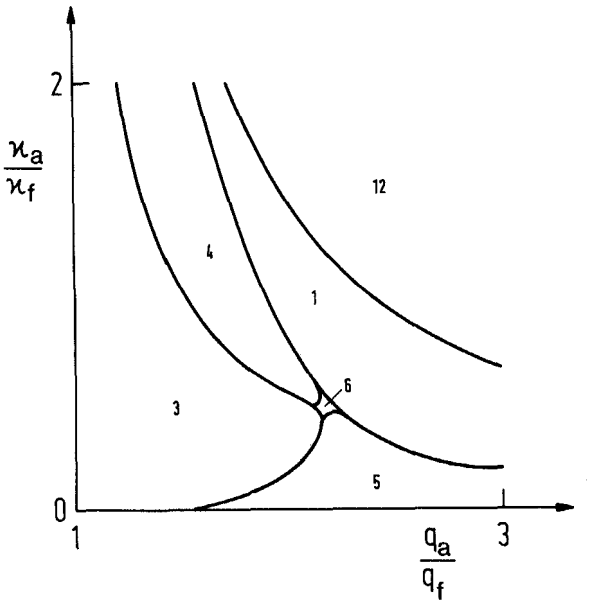

Figure 3. Phase diagram for $\gamma_2 = 0{\cdot}4$.

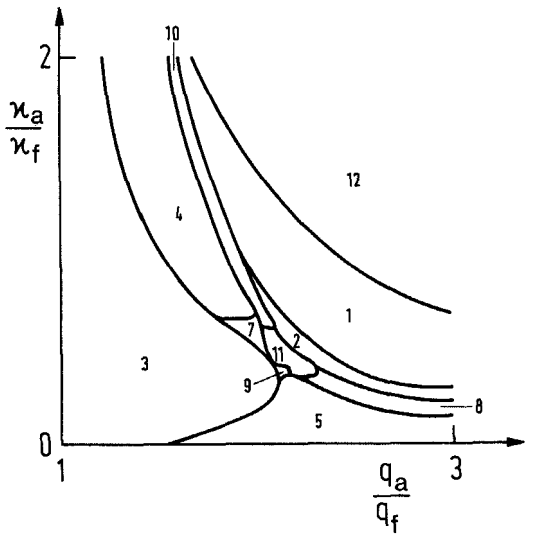

Figure 4. Phase diagram for $\gamma_2 = 0{\cdot}27$.

4. Conclusions

We have shown that the model can predict 24 different sequences of phases. How do these sequences compare to the measured ones? The most often observed sequence $S_A \leftrightarrow S_C^* \leftrightarrow S_{C_\gamma}^* \leftrightarrow S_{C_A}^*$ is one of the possibilities predicted by the model, where the $S_{C_\gamma}^* \leftrightarrow S_C^*$ and $S_{C_\gamma}^* \leftrightarrow S_{C_A}^*$ transitions can be of first or second order. The experiments, on the other hand, do not give any indication of the existence of intermediate incommensurate phases predicted by the model.

The sequence $S_A \leftrightarrow S^*_{C_\alpha} \leftrightarrow S^*_C \leftrightarrow S^*_{C_\gamma} \leftrightarrow S^*_{C_A}$ cannot be reproduced by the model. It should be mentioned that, considering that the $S^*_{C_\alpha}$ phase is believed to be first antiferroelectric and then ferroelectric with a strongly temperature dependent structure, it is possible to interpret the first part of the above sequence as $S_A \leftrightarrow S^*_{C_A} \leftrightarrow IC \leftrightarrow S^*_C \leftrightarrow \ldots$ which would correspond to sequence (2) for the case $T_{a,0} > T_{f,0}$.

The model can therefore describe some parts of the observed behaviour. As the antiferroelectric phase seems to appear twice in the measured sequence, two types of molecular interactions leading to the antiferroelectric phase should exist in the system. It has been recently proposed [4] that for the appearance of the $S^*_{C_\alpha}$ phase the interactions between electric polarization in neighbouring layers are important, while for the $S^*_{C_A}$ phase pairing of molecules is relevant. The generalization of the above model by taking into account two types of interactions can be expected to reproduce the whole measured sequence, but the model in its present form can nevertheless be used to analyse most parts of the transition scheme.

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