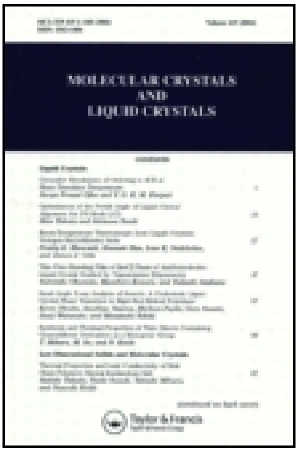

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INFLUENCE OF COMPETING INTERLAYER INTERACTIONS ON THE STRUCTURE OF THE Sm C_α^* PHASE

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Abstract In a discrete phenomenological description of tilted smectic phases, the order parameter, which describes the magnitude and the direction of the tilt of the molecules, is defined for each smectic layer. The free energy expansion in terms of order parameter takes into account interactions between nearest and next nearest smectic layers, and allows for competing interactions. By minimizing the free energy of the system the structure of the frustrated Sm C_α^* phase is obtained.

INTRODUCTION

Since the existence of the two subphases Sm C_α^* and Sm C_γ^* has been discovered in optically pure MHPOBC[1], similar subphases have been reported in some other compounds[2]. The structure of the two phases has not been clarified yet. Sun et al.[3] concluded from the existence of ferroelectric and antiferroelectric modes in the Sm A phase that an interlayer interaction between the nearest neighbouring layers and the next-nearest neighbouring layers are very important and introduced the discrete phenomenological model which led to the explanation of the structure of Sm C^*, Sm C_γ^* and Sm C_A^* phase. The obtained structures are equivalent to those proposed by the continuous phenomenological theory[4] and the discrete model represents only a microscopic visualization of the continuous description.

The discreteness of the model becomes relevant and unavoidable when the interlayer interactions between nearest and next nearest neighbouring layers are competing. We shall therefore analyze here the influence of the competing nearest and next nearest neighbouring layers interactions.

THE MODEL

The tilt of the molecules in the j-th smectic layer can be expressed by two component tilt vector $\vec{\xi}_j$ describing the magnitude and the direction of the tilt of the director from the normal to smectic layers (z-axis). Free energy can be expressed as the sum over all layers:

$$\begin{aligned} \mathcal{G} &= \sum_j \Big(\frac{a_0}{2}\vec{\xi}_j^2 + \frac{b_0}{4}\vec{\xi}_j^4 + \frac{1}{4}a_1 \left[(\vec{\xi}_j \cdot \vec{\xi}_{j-1}) + (\vec{\xi}_j \cdot \vec{\xi}_{j+1}) \right] + \\ &+ \frac{1}{16}a_2 \left[(\vec{\xi}_j \cdot \vec{\xi}_{j-2}) + (\vec{\xi}_j \cdot \vec{\xi}_{j+2}) \right] + \frac{1}{4}f \left[(\vec{\xi}_j \times \vec{\xi}_{j-1}) + (\vec{\xi}_{j+1} \times \vec{\xi}_j) \right] \Big). \end{aligned} \qquad (1)$$

Here only the parameter $a_0 = a(T - T_0)$ is temperature dependent and T_0 is the transition temperature , where the transition to the tilted phase should take place in each layer even without interactions with neighbouring layers. Parameter b_0 is positive reflecting the fact that continuous phase transition is assumed. The third and the fourth terms describe achiral interactions up to the second nearest neighbours and the fifth term describes nearest neighbour chiral interactions.

Chiral interactions are ussualy small in comparison with achiral interactions. Also, the Sm C_α^* phases were found as subphases in racemic antiferroelectric liquid crystals[5], where the chiral interactions disappear. In our analysis of the model the chiral terms will be assumed to be infinitesimally small and therefore will not be taken explicitly into account. Only their qualitative effect on the structure of the phases will be discussed.

Since the first two terms in expansion (1) depend only on the magnitude of the order parameter i.e. the magnitude of the tilt, the direction of the tilt is determined by the competing interactions described by the third and fourth term in Eq.(1). For different signs of parameters a_1 and a_2 the following configurations minimize the energy of the corresponding term:

$a_1 > 0$	↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓	antiparallell orientation of nearest layers
$a_1 < 0$	↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑	parallel orientation of nearest layers
$a_2 > 0$	↑ · ↓ · ↑ · ↓	antiparallel orientation of next nearest layers
$a_2 < 0$	↑ · ↑ · ↑ · ↑	parallel orientation of next nearest layers

In the upper scheme arrows denote the direction of the order parameters. There are eight layers schematically drawn. Dots denote intermediate layers because the fourth term (a_2) describes only interactions between next nearest layers, so the direction of the order parameters in the intermediate layers is not important.

For negative values of a_2 it is clearly seen that for both parallel and antiparallel alignment of the nearest layers, the energy is minimal. Next nearest neighbours are parallel in both configurations. But for positive values of a_2, the parallel or antiparallel orientation in nearest layers is obtained only when the interactions between nearest layers are stronger in comparison with interactions between next nearest layers ($|\frac{a_1}{a_2}| > 1$). As soon as nearest neighbour interactions and next nearest neighbour interactions are comparable, the order parameters in the neighbouring layers cannot be neither parallel nor antiparallel.

The X-ray measurements have shown[6], that Sm C$_\alpha^*$ phase is tilted and the layer thickness is constant. Therefore looking for the solution, where the magnitude of the order parameters is constant seems reasonable.

$$\vec{\xi}_j = \theta\{\cos\phi_j, \sin\phi_j\} \tag{2}$$

Using the above expression, the free energy of the system (1) is:

$$\begin{aligned} \mathcal{G} \; = \; \sum_j \Bigg(& \frac{a_0}{2}\theta^2 + \frac{b_0}{4}\theta^4 + \frac{1}{4}a_1\theta^2\Big[\cos(\phi_j - \phi_{j-1}) + \cos(\phi_{j+1} - \phi_j)\Big] + \\ & + \frac{1}{16}a_2\theta^2\Big[\cos(\phi_j - \phi_{j-2}) + \cos(\phi_{j+2} - \phi_j)\Big]\Bigg) \end{aligned} \tag{3}$$

Introducing a new variable

$$\alpha_j = \phi_{j+1} - \phi_j, \tag{4}$$

which express the difference between phase of the order parameters in nearest layers, the structure of the system with N-layers is generally given by the vector

$$\{\alpha_1, \alpha_2, ..., \alpha_{N-1}\} \tag{5}$$

and the magnitude of the order parameter θ. As the simplest solution of the free energy minimization problem we expect the one where α_j is constant. The free energy (1) is than expressed as:

$$\mathcal{G} = \frac{1}{2}\, a_0\, \theta^2 + \frac{1}{4}\, b_0\, \theta^4 + \frac{1}{2}\, a_1\, \theta^2\, \cos\alpha + \frac{1}{8}\, a_2\, \theta^2\, \cos 2\alpha. \tag{6}$$

Minimizing this expression with respect to the magnitude of the tilt θ and the phase difference between two neighbouring layers α we get the following solutions:

a)		$\theta^2 = 0$	Sm A phase
b)	$\alpha = 0$	$\theta^2 = -\frac{a_0+a_1+a_2}{b_0}$	Sm C* phase
c)	$\alpha = \pi$	$\theta^2 = -\frac{a_0-a_1+a_2}{b_0}$	Sm C_A^* phase
d)	$\alpha = \arccos(-\frac{a_1}{a_2})$	$\theta^2 = -\frac{a_0a_2+a_1^2-a_2^2}{b_0a_2}$	Sm C_α^* phase

Structures given by solutions a,b and c are already known paraelectric SmA phase above the transition temperature from isotropic to tilted phase, homogeneous ferroelectric SmC phase bellow the transition temperature when $a_1 < 0$ and $a_2 < 0$ or $|a_1| > a_2 > 0$ and homogeneous antiferroelectric phase when $a_1 > 0$ and $a_2 < 0$ or $a_1 > a_2 > 0$. Weak chiral interactions introduce into the ferroelectric or antiferroelectric structures helicoidal modulation over few hundred smectic layers.

The frustrated SmC$_\alpha$ phase appears bellow the transition temperature when $a_2 > 0$ and $-a_2 < a_1 < a_2$. The solution minimizes the free energy when the next nearest interactions favour antiparallel orientation of order parameters, otherwise it represents the maximum of the free energy. Such a solution is doubly degenerate and two energetically equivalent short pitch helical structures differing only in handedness are possible. For optically active systems where chiral interactions are small but not negligible, the degeneracy is lifted. The tilt of the molecules is constant through all the layers, the phase difference between the two nearest layers is also constant and the helicoidal modulation extends only over few layers. Analogous phase is known to exist also in one dimensional magnetic systems with two-component order parameter[7]. The structure of racemic and chiral antiferroelectric liquid crystal in Sm C_α^* phase is presented on Fig.1.

When the interactions between nearest layers and next nearest layers change with temperature, it is possible that interactions between nearest layers become weak in comparison with interactions between next nearest layers. The structure which minimizes free energy (Eq.6) for $a_2 > 0$ and $|a_1| << a_2$ has a phase difference between nearest layers near $\frac{\pi}{2}$. Such structure has four layer period approximately and is in racemic systems doubly degenerate as the difference between nearest layer can be $\pm\frac{\pi}{2}$. Antiferroelectric character of such a structure is due to the nearly an-

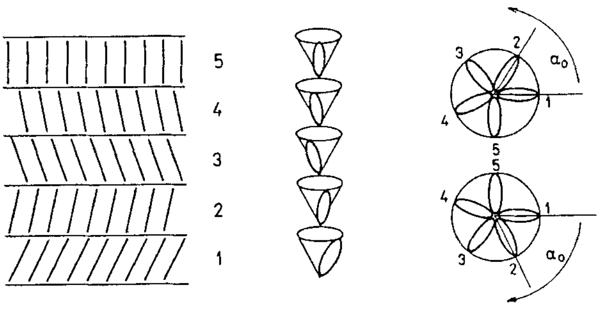

Figure 1a: In the achiral Sm C$^*_\alpha$ phase the phase of the order parameters in two nearest layers differ for the angle α_0. The structure is helicoidal (left or right handed) with the pitch over only few layers.

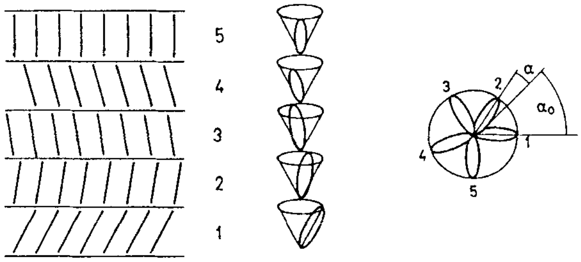

Figure 1b: In the chiral Sm C$^*_\alpha$ phase the angle between nearest layers is little larger and the helix has only one handedness.

tiparallel orientation in next nearest layers. It is a candidate for the structure of AF phase[5]. The structure of racemic and chiral antiferroelectric liquid crystal in AF phase is presented on Fig.2.

CONCLUSIONS

In this paper we have studied a discrete model of antiferroelectric liquid crystal ex-

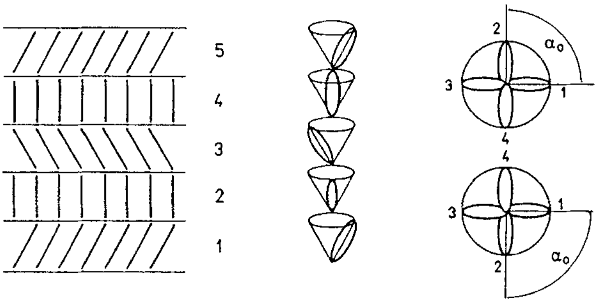

Figure 2a: In the racemic AF phase the phase of the order parameters in two nearest layers differ for the angle $\pi/2$. The structure is helicoidal (left or right handed) with the pitch over four layers.

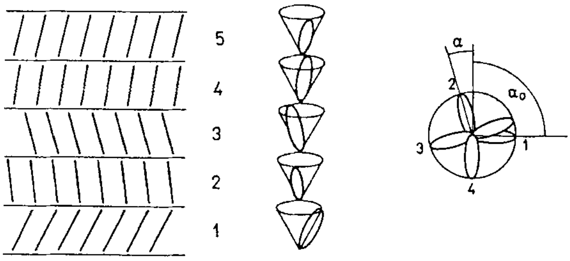

Figure 2b: In the chiral AF phase the helix has only one handedness.

hibiting Sm C^*_α phase. The competing interactions between nearest layers and next nearest layers have been taken into account. By minimizing the free energy we obtain the two-fold double degenerate helicoidal structure of Sm C^*_α phase where the pitch extends only over few layers and is in general incommensurate with the layer thickness. When chiral interactions between layers are not negligible, the degeneracy does not occur. This structure is different from the one proposed by Isozaki et al.[6], where the order parameters in nearest layers always form ferroelectric (parallel orientation) or antiferroelectric (antiparallel orientation) pairs and the structure of the phase is given by a certain repetitive pattern of such pairs.

At certain values of parameters the phase with antiferroelectric character and different structure than Sm C_A^* phase is obtained as possible structure for AF phase.

Since in this simple model only bilinear interaction terms between nearest and next nearest layers have been taken into account, different experimentally observed phase sequences cannot be obtained. But taking into account higher order terms, where the interaction constants of our model effectively depend on the tilt and therefore on temperature, could lead to experimentally observed sequences.

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