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Possible Stable Structures of Chiral Polar Smectics with Significant Interactions between Next Nearest Layers

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Possible Stable Structures of Chiral Polar Smectics with Significant Interactions between Next Nearest Layers

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We analyse stable structures in the model where interactions between the nearest and the next nearest layers are taken into acount. Interactions can be noncompeting or competing. We find five different stable structures stable at different values of model parameters. Three of them are already known: the ferroelectric SmC*, the antiferroelectric SmC^*_A phase and by recent experiments confirmed helicoidal short-pitch SmC^*_α structure. Aditionally we find two structures, the structure with a primitive cell which extends over 2 smectic layers SmC^*_2 and SmC^*_4 the primitive cell cosists of 4 smectic layers.

Keywords: chiral polar smectics; ferroelectric phase; antiferroelectric phase; nearest layers interactions; next nearest layers interactions

INTRODUCTION

Before a deccenium antiferroelectric liquid crystals have been discovered. They are chiral polar smectic liquid crystals, which exist in a narrow temperature region in many different phases. One of the phases behaves antiferroelectrically in an external electric field and it has given them their name [1, 2]. Soon after their discovery, various theoretical models were proposed [3-9], trying to describe them.

The aim of this article is to analyse the possible stable structures within the model [7, 8], which allow for experimentally observed phase

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sequences. The model takes into account interactions between nearest layers and between next nearest layers explicitely. Here we analyse the influence of the values and the signs of the model parameters on the structures of various phases as well as their stability, but we do not discuss their microscopic origin.

The paper is organised as follows: after Introduction, the model is presented, terms in the free energy expansion are explained and their influence on the tilted structures is discussed. The space of model parameters splits into two subspaces. In the first subspace interactions are noncompeting and in the second they compete. The next two sections are devoted to an analysis of structures and their stability in these two subspaces. In Conclusions the results are reviewed.

THE MODEL

In systems where smectic order is high [10], it is convenient to introduce the tilt order parameters $\vec{\xi}_j$, which are characteristic for j-th smectic layer. The free energy is expanded in terms of order parameters up to the fourth order and up to the next nearest layers interactions,

$$G = \sum_j \frac{1}{2} a_0 \vec{\xi}_j^2 + \frac{1}{4} b_0 \vec{\xi}_j^4 + \frac{1}{2} a_1 \left(\vec{\xi}_j \cdot \vec{\xi}_{j+1}\right) + \frac{1}{4} b_1 \left(\vec{\xi}_j \cdot \vec{\xi}_{j+1}\right)^2 + \\ + \frac{1}{8} a_2 \left(\vec{\xi}_j \cdot \vec{\xi}_{j+2}\right) + \frac{1}{2} f \left(\vec{\xi}_j \times \vec{\xi}_{j+1}\right)_z \qquad (1)$$

The first term $a_0 = a(T - T_0)$ is strongly temperature dependent and by lowering the temperature becomes negative at T_0, where molecules in an isolated layer would tilt. The sign of b_0, which is positive for a continuous transition, is irrelevant in work presented here, since we study structures and not the transitions between them. The a_1 term presents bilinear coupling between nearest layers and the b_1 term a biquadratic coupling between nearest layers. The a_2 term is a bilinear coupling between next nearest layers. Model parameters a_1, b_1 and a_2 vary with tilt, and since tilt depends on temperature, so do also the parameters. The consequence of this variation are different phases in relatively narrow temperature range. The last term f is present only in chiral systems and is assumed to be negligible in this analysis.

To make the influence of the model parameters a_1, a_2 and b_1 on the structure of the phases more transparent, in Table 1 the tilt orientations in the neighbouring layers, which minimize the term, are given.

$a_1 < 0$	$\uparrow\uparrow$	synclinic in nearest layers
$a_1 > 0$	$\uparrow\downarrow$	anticlinic in nearest layers
$b_1 < 0$	$\uparrow\uparrow$ or $\uparrow\downarrow$	synclinic or anticlinic in nearest layers
$b_1 > 0$	$\uparrow\rightarrow$ or $\uparrow\leftarrow$	perpendicular in nearest layers
$a_2 < 0$	$\uparrow \cdot \uparrow$	synclinic in next nearest layers
$a_2 > 0$	$\uparrow \cdot \downarrow$	anticlinic in next nearest layers

TABLE 1 Arrows present order parameters in neighbouring layers for three different model parameters and their signs.

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We are looking only for stable structures, where the magnitude of the tilt is constant. Therefore we introduce polar coordinates θ and ϕ_j,

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

where θ is the magnitude and ϕ_j describes the direction of the tilt in the j-th layer. Due to the rotational symmetry of the sistem we are allowed to further reduction of the number of variables. Introducing a difference between tilt directions in the neighbouring layers α_j as

$$\alpha_j = \phi_{j+1} - \phi_j, \tag{3}$$

we can rewrite the free energy in terms of new parameters θ and α_j as a sum of two parts. The first one G_C depends only on the magnitude of the tilt θ,

$$G_C = \frac{1}{2} a_0 \theta^2 + \frac{1}{4} b_0 \theta^4. \tag{4}$$

The second part G_P depends also on differences between tilt directions i.e. phase differences in neighbouring layers G_P. It can be written as

$$G_P = \mid a_2 \mid \sum_j \frac{1}{2} a \cos\alpha_j + \frac{1}{4} b \cos^2\alpha_j \pm \frac{1}{8} \cos(\alpha_j + \alpha_{j+1}) \tag{5}$$

The phase part of the free energy G_P is expressed in the units of $|a_2|$ and consequently only two independent model parameters remain, a and b. As the temperature changes, also the tilt of the molecules changes and changing tilt influences the values of model parameters $a_1(\theta)$, $a_2(\theta)$ and $b_1(\theta)$, and consequently a and b, which are

$$\begin{aligned} a &= \frac{a_1(\theta)\ \theta^2}{\mid a_2(\theta) \mid \theta^2} \\ b &= \frac{b_1(\theta)\ \theta^4}{\mid a_2(\theta) \mid \theta^2} \end{aligned} \tag{6}$$

Due to the variation of the tilt θ with temperature, parameters a and b change and various structures can become stable.

NONCOMPETING INTERACTIONS

Interaction between next nearest layers are noncompeting when $a_2 < 0$. According to the Table 1, molecules in next nearest layers tend to tilt synclinic. For negative b synclinic tilts in nearest layers for negative a as well as anticlinic tilts in nearest layers for positive a minimize all the terms in G_P simultaneously. Therefore only synclinic and anticlinic tilts of nearest layers are stable for negative b.

For positive b, interactions described by the biquadratic term, compete with interactions described by bilinear term a. We are looking for the stable solution of the form where phase differences alternate as $\alpha_{2j} = \alpha$ and $\alpha_{2j+1} = \beta$. The average value of the phase dependent part of the free energy G_P per one layer expressed in units of $|a_2|$ is now given as

$$G_P = \frac{1}{2}\left(\frac{1}{2}\,a\,(\cos\alpha+\cos\beta)+\frac{1}{4}\,b\,\left(\cos^2\alpha+\cos^2\beta\right)-\right.$$
$$\left.-\;\frac{1}{8}\cos(\alpha+\beta)\right)\,. \qquad (7)$$

From the equation (7), we see that the last term is minimized when $\alpha = -\beta$. Looking for the solution of this type, the phase part of the free energy G_P adopts the form

$$G_P = \frac{1}{2}a\,\cos\alpha+\frac{1}{4}\,b\,\cos^2\alpha-\frac{1}{8}\,, \qquad (8)$$

with the minimal value for the following solutions:

a)	SmC^*	$\alpha = 0$	when	$-a > b > 0$
			or	$-a > 0 > b$
b)	SmC^*_A	$\alpha = \pi$	when	$a > b > 0$
			or	$a > 0 > b$
c)	SmC^*_2	$\cos\alpha = -\frac{a}{b}$	when	$b > \lvert a\rvert$

The solution (a) is the synclinic tilted phase - the ferroelectric SmC^* phase, Fig 1a. The solution (b) is the anticlinic tilted phase - the antiferroelectric SmC^*_A phase, Fig. 1b. The solution (c) represents a structure where the phase angle from layer to layer alternates, Fig. 1c. We call this

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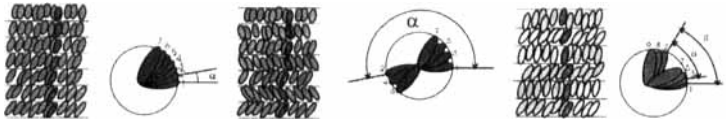

a) SmC* b) SmC^*_A c) SmC^*_2

FIGURE 1 Side view and a projection of the chosen set of molecules onto the smectic layer for three different structures stable in noncompeting region of model parameters.

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structure SmC^*_2 phase to stress, that a structure is essentially a bilayer one since tilts in next nearest layers are synclinic and the primitive cell consists of two layers.

To analyse the stability of these three structures, we expand the free energy in fluctuations of phase changes, $\alpha_{2j} = \alpha + \delta\alpha_{2j}$ and $\beta_{2j+1} = \beta + \delta\alpha_{2j+1}$ up to the second order. The fluctuation part of the free energy is now

$$\begin{aligned} G_{2,P} &= \frac{1}{8}\sum_j -a\left(\delta\alpha_{2j}^2\cos\alpha + \delta\alpha_{2j+1}^2\cos\beta\right) - \\ &\quad - b\left(\delta\alpha_{2j}^2\cos 2\alpha + \delta\alpha_{2j+1}^2\cos 2\beta\right) + \\ &\quad + \frac{1}{2}\delta\alpha_{2j}^2\cos(\alpha+\beta) + \\ &\quad + \frac{1}{4}(\delta\alpha_{2j}\,\delta\alpha_{2j+1} + \delta\alpha_{2j}\,\delta\alpha_{2j-1})\cos(\alpha+\beta) \end{aligned} \tag{9}$$

or written in a matrix form

$$G_{2,P} = \frac{1}{8}\vec{\chi}\,\underline{G}_2\,\vec{\chi}. \tag{10}$$

For a system with N layers the tridiagonal $(N-1)$ dimensional matrix $\underline{G}_2$ has on the diagonal elements

$$\begin{aligned} G_{2,P}(i,i) = A &= -a\cos\alpha - b\cos 2\alpha + \frac{1}{2} \\ G_{2,P}(i+1,i+1) = B &= -a\cos\beta - b\cos 2\beta + \frac{1}{2}, \end{aligned} \tag{11}$$

while all the off-diagonal elements C are equal

$$G_{2,P}(i,i\pm 1) = C = +\frac{1}{4}. \tag{12}$$

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Vector $\vec{\chi} = \{\delta\alpha_1, \delta\alpha_2, ..., \delta\alpha_{2j}, \delta\alpha_{2j+1}, ...\delta\alpha_{N-1}\}$ is a vector of phase fluctuations. For the structure to be stable, all the eigenvalues of the fluctuation matrix $\underline{G}_2$ have to be nonnegative. Transforming the matrix to the eigensystem, where the eigenfluctuations are of the form $\vec{\chi} = \{\cos\varphi, \cos 2\varphi, ..., \cos 2j\varphi, \cos(2j+1)\varphi, ... \cos(N-1)\varphi\}$, with φ as parameter, we find that eigenvalues λ_ϕ are:

$$\lambda_\varphi = \frac{1}{2}\left((A+B) \pm \sqrt{(A-B)^2 + 16\,C^2\cos^2\varphi}\right) \tag{13}$$

In general, the lowest eigenvalue becomes negative only for two types of fluctuations, for a ferroic one, where $\varphi = 0$, and for the antiferroic one, where $\varphi = \pi$. In ferroic fluctuation all phase differences enlarge or diminish for the same amount, $\delta\alpha_j = \delta\alpha_i$ for any i, j. In antiferroic fluctuation phase differences alternatingly enlarge and diminish for the same amount, $\delta\alpha_j = -\delta\alpha_{j+1}$.

For the special case, where $\beta = -\alpha$, diagonal terms are all equal and the eigenvalues have a simple form:

$$\lambda_\varphi = 2\,C\cos\varphi + A. \tag{14}$$

Searching for the conditions for the lowest eigenvalue of (14) to become negative, we find the following stability conditions for the three solutions

structure	stable for $b > 0$	stable for $b < 0$	metastable for $b < 0$
SmC^*	$-a > b$	$a < 0$	$0 > a > b$
SmC^*_A	$a > b$	$a > 0$	$0 < a < b$
SmC^*_2	$\|a\| < b$	nonexisting	nonexisting

For positive b, the system destabilizes at the same ratio of model parameters as the nontrivial solution vanishes. Therefore the transition is continuous. For negative b, biquadratic term aditionally stabilize the synclinic or anticlinic structures, and they can also be metastable. The transition between the synclinic and the anticlinic structure is of the first order. The results of the analysis are presented in Fig.2.

COMPETING NEXT NEAREST LAYERS INTERACTIONS

Competing next nearest layers interactions are present when $a_2 > 0$. In this case the last term in G_P is minimal when tilts in the next

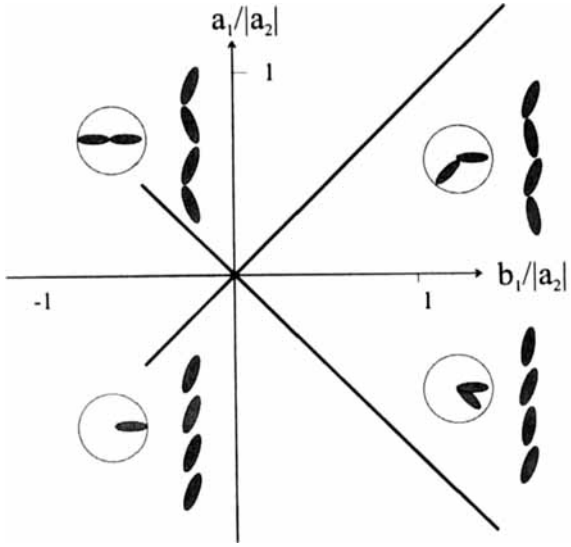

FIGURE 2 Phase diagram of the noncompeting region of model parameters. Stable structures are schematically shown.

nearest layers are anticlinic. It is impossible to simultaneously minimize all three terms in the free energy. We shall analyse the solution where phase differences are equal between all neighbouring layers, $\alpha = \beta$. Inserting this Ansatz to the free energy expression (7), we obtain

$$G_P = \frac{1}{2} a \cos\alpha + \frac{1}{4} b \cos^2\alpha + \frac{1}{8} \cos 2\alpha \qquad (15)$$

Minimizing the free energy (Eq.15) with respect to, we obtain three different solutions:

a)	SmC^*	$\alpha = 0$	when	$-a > b + 1 > 0$
b)	SmC^*_A	$\alpha = \pi$	when	$a > b + 1 > 0$
c)	SmC^*_α	$\cos\alpha = -\frac{a}{b+1}$	when	$b + 1 > \|a\|$

A solution (a) is again the synclinic tilted phase - the ferroelectric Sm C^* phase. The solution (b) is again the anticlinic tilted phase - the antiferroelectric Sm C^*_A phase. The solution (c) represents a

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helicoidally modulated structure, where the pitch of modulation is in general incomensurate with the layer thickness and can be anything between 2 and infinite number of layers, Fig. 3a. The first ($\alpha = 0$) and the second ($\alpha = \pi$) solution are the two extrema of the third, general solution, with phase difference α anywhere inbetween.

To analyse the stability of these phases, we put $\alpha = \beta$ in the stability matrix. Its elements are now

$$\begin{aligned} A &= -a\cos\alpha - b\cos 2\alpha - \frac{1}{2}\cos 2\alpha \\ B &= A, \end{aligned} \tag{16}$$

while all the off-diagonal terms C are equal,

$$C = -\frac{1}{4}\cos 2\alpha. \tag{17}$$

We find the following stability conditions for these three phases.

structure	stable for $b > 0$	stable or metastable for $b < 0$
SmC^*	$-a > b + 1$	$-a > b + 1$
SmC^*_A	$a > b + 1$	$a > b + 1$
SmC^*_α	$\|a\| < b + 1$	$a^2 > \frac{b(b+1)^2}{1-b}$

The phase diagram for positive a_2 is more complicated and is presented in Fig.4. Solid lines are the stability limits of the simple phases like SmC^* and Sm C^*_A and dashed line presents the stability limit of the helicoidally modulated SmC^*_α phase. The collective fluctuation, which destabilizes the SmC^*_α phase, is an antiferroic one since at the limiting ratio of the model parameters, phase diferrences alternatingly enlarge and diminish. The structure, which is stable in the region of parameters inside the dashed line, has two alternating phase differences, $\alpha = 0$ and $\beta = \pi$. We name this structure the SmC^*_4 in order to stress that its period extends over four layers. It is worth while to mention, that the four-layers period of the SmC^*_4 structure is not a consequence of interactions, which extend more than up to the next nearest layers, Fig. 3b.

To analyse the stability of this phase, we use the equation (13), since matrix elements are now

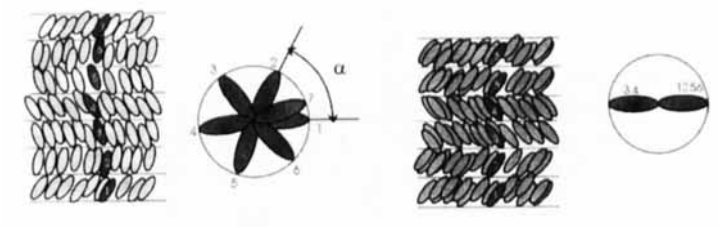

FIGURE 3 Side view and a projection of the chosen set of molecules onto the smectic layer for two additional structures stable in competing region of model parameters.

$$\begin{aligned} A &= -a - b + \frac{1}{2}, \\ B &= +a - b + \frac{1}{2}, \end{aligned} \tag{18}$$

while all the off-diagonal terms C are equal,

$$C = +\frac{1}{4}. \tag{19}$$

We find that it is stable or metastable in the parameter region where $a^2 < b(b-1)$. The stability limit is presented in Fig. 4 as a dotted line.

CONCLUSIONS

In this paper we analyse the model which takes into account interactions up to the next nearest layers. The origin of various model parameters is discussed elsewhere [11, 8]. Here we analyse only the stable structures, which may appear in such a model for various model parameters, without analysis of their microscopic origin, neither we study the phase transitions between different structures.

The space of model parameters splits into two subspaces. In the first one ($a_2 < 0$) interactions do not compete and only structures where the primitive cell extends over one or two smectic layers are

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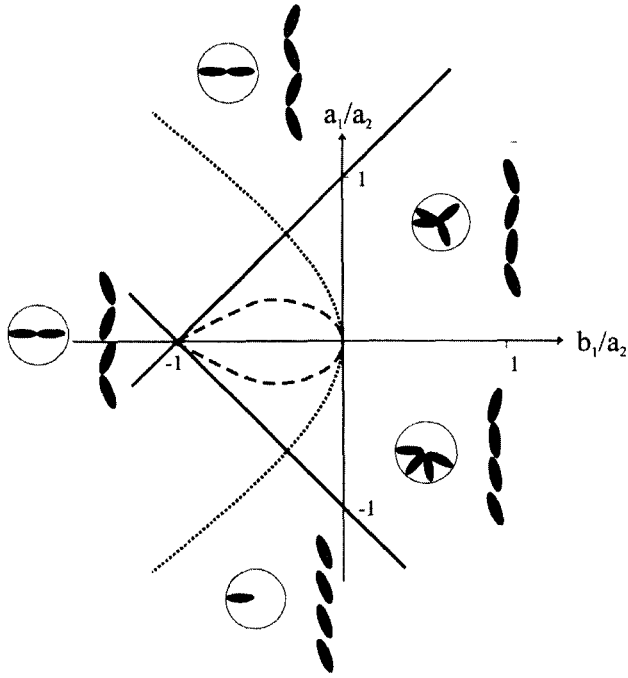

FIGURE 4 Phase diagram of the competing region of model parameters. Stable structures are schematically shown.

possible. Three different structures can be stable: SmC*, SmC^*_A and SmC^*_2. Here the SmC* and SmC^*_A present already known structures of the ferroelectric and the antiferroelectric phase, respectively. In the last structure SmC^*_2 two ferroelectric lattices gear into each other shifted with respect to each other for a general angle, defined by the ratio b/a.

In the subspace where $a_2 > 0$, we found two additional stable structures: SmC^*_α and SmC^*_4. The SmC^*_α is a helicoidally modulated phase where pitch is not commensurate with the layer thickness and varies with a ratio of model parameters. It can have any value from 2 to infinite number of smectic layers and was already experimentally confirmed as a structure of the SmC^*_α phase [12]. Therefore we use the SmC^*_α notation for this structure. For a special ratio of model

parameters, the period of modulation extends over 3 or 4 layers, which correspond to the structures seen by resonant X-ray scattering in the region of the SmC^*_γ phase[12]. It is therefore possible, that the SmC^*_γ phase is the reentrant SmC^*_α phase. The last stable structure is the SmC^*_4, which is stable in a region of small a and negative b. Its primitive cell consists of four layers, tilts in neighbouring layers are sequentially and regularly synclinic and anticlinic, and in all the layers bound to one plane. Although the primitive cell is larger than the range of interactions it is nevertheless a consequence of the interactions which extend over next nearest layers only. We did not find any aditional structures, which become stable due to the freezing of collective fluctuations.

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