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What the Theory Says about the Six Layer Periodic Structures in Antiferroelectric Liquid Crystals?

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We discuss the prerequisites for the formation of the structure with a period of six layers in antiferroelectric liquid crystals. We find that such a structure can appear in the region where the incommensurate helical pitch in the SmC^*_α phase approaches six layers, if biquadratic coupling favoring uniplanar tilts in neighboring layers is already significant and if electrostatic dipolar interactions favor parallel ordering of dipoles in neighboring layers.

Keywords Antiferroelectric liquid crystal; lock-in; multilayer structure

1. Introduction

Antiferroelectric liquid crystals are materials, which posses a number of phases with various structures [1]. Some of them have complex periodic structures incommensurate to the layer thickness or commensurate structures where the period is being locked to two (SmC^*_A), three (SmC^*_{FI1}) or four layers (SmC^*_{FI2}) [2]. Structures with longer periodicities have been searched for a long time, and very recent polarized *x*-ray measurements have detected the existence of the structure having the six layer periodicity. The phase exists within the temperature window of the SmC^*_α phase and develops by a first order transition to the four layer structure of the SmC^*_{FI2} phase [3].

In this paper we analyse the conditions for lock-ins to multiple number of layers with special emphasis to the six layer periodicity. The analysis is done within the framework of the discrete phenomenological model [4]. We find conditions for the formation of structures having periods of six layers and we analyse also their possible structures. For the six layer structure surprisingly besides the helical structure, two additional structures locked to six layers exist. The non-helical six layer structure is described by one of the solutions in which the sequence of differences between neighbouring layers is α, α, β and from the symmetry point of view presents the same class of solutions as the three layer structure of the SmC^*_{FI1} phase.

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2. Theory

Antiferroelectric liquid crystalline systems are best described by the discrete phenomenological model which takes into account interlayer interactions explicitly and allows for large changes in tilt directions in neighboring layers. The free energy in its discrete form is

$$\sum_j \left[\frac{1}{2}\,a(T-T_0)\,\xi_j^2+\frac{1}{4}\,b_0\,\xi_j^4+\frac{1}{6}\,c_0\,\xi_j^6+C_p(\vec{\xi}_j\times\vec{P}_j)_z+\frac{1}{2\varepsilon}\,P_j^2+\frac{1}{2}a_1(\vec{\xi}_j\cdot\vec{\xi}_{j+1})\right.$$
$$\left.+\frac{1}{2\varepsilon_1}(\vec{P}_j\cdot\vec{P}_{j+1})+\frac{1}{2}f_1(\vec{\xi}_j\times\vec{\xi}_{j+1})_z+\frac{1}{2}\mu\,\vec{P}_j\cdot(\vec{\xi}_{j+1}-\vec{\xi}_{j-1})+\frac{1}{4}b_Q(\vec{\xi}_j\cdot\vec{\xi}_{j+1})^2\right] \tag{1}$$

where first three terms describe intralayer interactions expressed in tilt, the C_p term describes the fact that tilt induces polarization and vice versa and electrostatic intralayer term with ε positive appears because polarization P_j is an improper order parameter. Next two terms give interlayer couplings expressed in tilts (a_1) and in polarizations (ε_1). Both coefficients can be either positive, favoring antiparallel alignment of tilts or polarizations in neighboring layers, respectively, as negative favoring parallel orientations. Chiral interlayer interactions, Lifshitz term in its discrete form, are given by coefficient f_1 and μ gives flexoelectric coupling where variation of tilt induces polarization. The final term with the coefficient b_Q is a biquadratic coupling which is negative for the systems where the lock-in to well defined number of layers exists. Elimination of polarization leads to much simpler form of the free energy

$$G=\frac{1}{2}\sum_j\left[\sum_{k=1}^{3}a_k(\vec{\xi}_j\cdot\vec{\xi}_{j+k})+\sum_{k=1}^{2}f_k(\vec{\xi}_j\times\vec{\xi}_{j+k})_z\right]+\frac{1}{4}\,b_Q\,(\vec{\xi}_j\cdot\vec{\xi}_{j+1})^2$$
$$\tilde{a}_1=a_1+\frac{\varepsilon^2}{\varepsilon_1}(C_p^2+\mu^2);\quad \tilde{f}_1=f_1-\varepsilon\,C_p\,\mu;$$
$$\tilde{a}_2=2\varepsilon\,\mu^2;\qquad\qquad \tilde{f}_2=\frac{\varepsilon^2}{\varepsilon_1}C_p\,\mu; \tag{2}$$
$$\tilde{a}_3=-\frac{1}{2}\frac{\varepsilon^2}{\varepsilon_1}\mu^2;$$

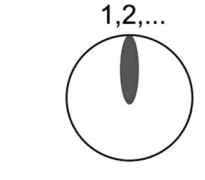
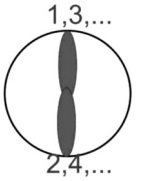
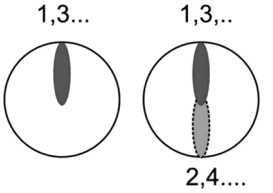
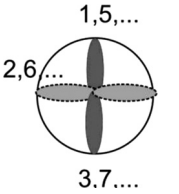
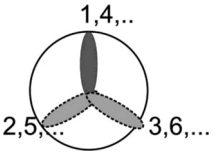
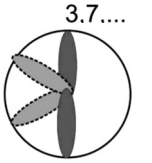
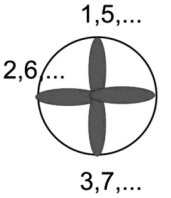
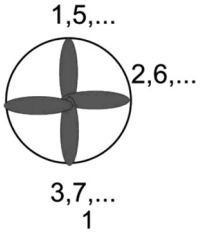
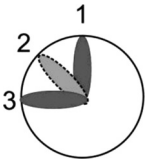
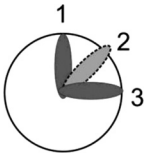
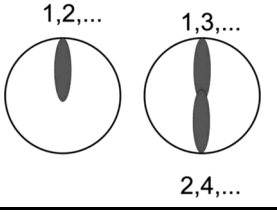
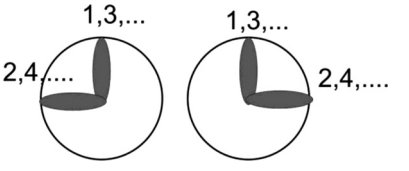
where indirect interactions expressed in tilts extend to more distant layers. Achiral effective interactions $\tilde{a}_k$ and competition between them define the basic multilayer structure, the effective chiral interactions $\tilde{f}_k$ give the sense of the helical modulation that is imposed on the basic structure.

3. Structures

Various interlayer interactions favor different structures. Usually they compete and when one of the interactions is much stronger than the others, the structure which reflects the most important interaction is formed. For example, the synclinic ferroelectric structure is formed, when coefficient $\tilde{a}_1$ is negative and very large by its magnitude with respect to the magnitudes of other coefficients.

The closer look to Table 1 shows the following: for negative achiral coefficients, considered isolated, the most favorable structure is the structure having the basic period extending over the number of layers equal to the length of the interaction. So, the single layer period is favored by negative $\tilde{a}_1$, the double layer period for negative $\tilde{a}_2$ and the three layer period for negative $\tilde{a}_3$. We have to bear in mind the orientations of non-interacting layers is arbitrary. For example, for negative $\tilde{a}_2$ all structures given in Figure 1 are equivalent, providing other interlayer interactions

Table 1. Tilt orientations, which are favored by specific coefficients. Ellipses represent the projection of "average" molecule onto the layer marked by number 1,2 etc. Dark grey ellipses mark interacting layers with respect to the considered coefficient; the light grey ellipses mark non-interacting layers

	<0	>0
$\tilde{a}_1$		
$\tilde{a}_2$		
$\tilde{a}_3$		
$\tilde{f}_1$		
$\tilde{f}_2$		
b_Q		

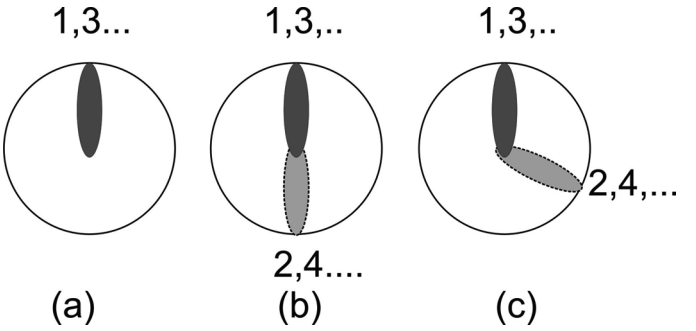


Figure 1. Parallely oriented next nearest layers are possible in number of configurations (a) parallel tilts in neighboring layers, (b) antiparallel tilts in neighboring layer and (c) general angle between tilts in neighboring layers flipping back and forth.

are absent. However, for positive achiral coefficients, the basic favorable repeating unit is double of the interaction range. For positive $\tilde{a}_1$ the favorable structure is the anticlinic antiferroelectric structure of the SmC^*_A phase. For positive $\tilde{a}_2$ the favorable structure is the four layer structure and is in reality quite stable in the form of the SmC^*_{FI2} phase. Therefore, the positive sign of achiral coefficient $\tilde{a}_3$ would give rise for the stabilization of the structure having the six layer periodicity. Equation (2) shows that such situation is possible only in systems where ε_1 is negative. The favorable parallel orientation of polarization in neighboring layers is counterintuitive, but it was shown several years ago, that for systems where the length to width rations of molecules is not large, such behaviour might take place. Let us also check the possibility for the stable six layer structure by comparison of the free energy for a helical structure of the SmC^*_α phase, for the four layer SmC^*_{FI2} phase and for the six layer SmC^*_{6d} phase. In the continuation we shall consider chiral terms as negligible which is legitimate for systems where $\mu \gg C_p$.

The SmC^*_α phase is described by the fixed phase difference α between neighboring layers. The SmC^*_{FI2} phase is described by alternating phase differences α and β, where $\alpha + \beta = \pi$. The six layer SmC^*_{6d} phase is described by the sequence of phase differences α, α, β and $2\alpha + \beta = \pi$. The conditions for the sum are imposed by positive achiral a_2 and a_3 coefficients. Figure 2 shows the free energy in dependence of the angle α for three types of the free energy (3, a–c).

$$G_{SmC^*_\alpha} = \frac{1}{2}a_1\,\theta^2\,\cos\alpha + \frac{1}{2}a_2\,\theta^2\,\cos(2\alpha) + \frac{1}{2}a_3\,\theta^2\,\cos(3\alpha) + \frac{1}{4}\,b_Q\,\theta^4\cos^2\alpha; \tag{3a}$$

$$\begin{aligned} G_{SmC^*_{FI2}*} = {} & \frac{1}{4}a_1\,\theta^2\,(\cos\alpha + \cos\beta) + \frac{1}{4}a_2\,\theta^2\,\cos(\alpha+\beta) + \\ & \frac{1}{4}a_3\,\theta^2\,(\cos(2\alpha+\beta) + \cos(\alpha+2\beta)) + \frac{1}{8}\,b_Q\,\theta^4(\cos^2\alpha + \cos^2\beta); \end{aligned} \tag{3b}$$

$$\begin{aligned} G_{SmC^*_{6d}} = {} & \frac{1}{6}a_1\,\theta^2\,(2\cos\alpha + \cos\beta) + \frac{1}{6}a_2\,\theta^2\,(\cos(2\alpha) + 2\cos(\alpha+\beta) + \\ & \frac{1}{6}a_3\,\theta^2\,\cos(2\alpha+\beta) + \frac{1}{12}\,b_Q\,\theta^4(2\cos^2\alpha + \cos^2\beta). \end{aligned} \tag{3c}$$

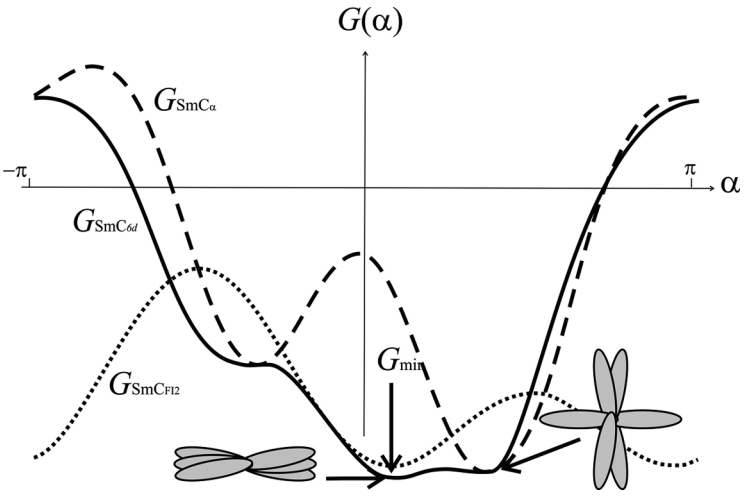


Figure 2. Free energies for three different structures. It is clearly seen that the structure locked to 6 layers has a global minimum showed by an arrow and the corresponding structure. Coefficients used were: $\frac{a_0}{a_2} = -7.8$; $\frac{a_1}{a_2} = -0.2$; $\frac{a_3}{a_2} = 0.1$; $\frac{f_1}{a_2} = -0.11$; $\frac{b_Q}{a_2} = -17$.

Equations (3b) and (3c) can be significantly simplified by using relations $\alpha + \beta = \pi$ for (3b) and $2\alpha + \beta = \pi$ for (3c).

$$G_{\mathrm{SmC}^*_{\mathrm{FI2}}} = -\frac{1}{4} a_2 \theta^2 + \frac{1}{4} b_Q \theta^4 \cos^2 \alpha \tag{4a}$$

$$G_{\mathrm{SmC}^*_{6\mathrm{d}}} = \frac{1}{6}(a_1 - a_2)\theta^2 (2\cos\alpha - \cos(2\alpha)) - \frac{1}{6} a_3 \theta^2 + \frac{1}{12} b_Q \theta^4 \left(2\cos^2\alpha + \cos^2(2\alpha)\right) \tag{4b}$$

Figure 2 shows the free energy for three structures which develop one to another. It is clearly seen that the structure of the six layer exhibit the global minimum. One can see also another minimum, which presents the metastable structure having the six layer period but optically almost uniaxial properties.

4. Conclusions

The structure locked to six layers in antiferroelectric was recently found after a long detailed search in various materials [3]. Here we present the theoretical analysis of the discrete phenomenological model for model coefficients which allow for such structure. We found that three conditions have to be fulfilled: the interactions between neighboring have to be weak in comparison with interactions to next nearest neighboring layers and have to favor parallel tilt ordering in neighboring layers $\left(\frac{a_1}{a_2} < 0\right)$; the interactions to the third neighboring layers have to favor antiparallel tilt ordering $\left(\frac{a_3}{a_2} > 0\right)$; and finally, the biquadratic coupling has to favor parallel and antiparallel ordering in neighboring layers at the same time $(\frac{b_Q}{a_2} < 0)$. For some special values the competition between these interactions results in the structure

locked six layers similar to the one proposed by the results of experimental observations.

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