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Dynamics of chiral antiferroelectric liquid crystal materials exhibiting the $S^*_{C_\alpha}$ phase§

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The dynamic properties of chiral smectic liquid crystals are studied theoretically by including competing interlayer interactions leading to the smectic C^*_α phase below the smectic A phase. In the smectic A phase only one doubly degenerate soft mode exists which becomes critical at the transition temperature for the critical wave vector corresponding to the helicoidal modulation extending over only a few smectic layers. In the tilted smectic C^*_α phase it splits into two modes, i.e. a phase and an amplitude mode.

1. Introduction

The first synthesized antiferroelectric liquid crystal MHPOBC has the following phase sequence: $S_A \leftrightarrow S^*_{C_\alpha} \leftrightarrow S^*_C \leftrightarrow S^*_{C_\gamma} \leftrightarrow S^*_{C_A}$ [1], where the smectic A phase corresponds to the paraelectric phase, S^*_C is the ferroelectric phase, $S^*_{C_A}$ is the antiferroelectric phase and $S^*_{C_\gamma}$ is the ferrielectric phase. Experimental observations have shown that the phase $S^*_{C_\alpha}$ with unknown structure is antiferroelectric close to the transition to the S_A phase and becomes ferrielectric on approaching the S^*_C phase. Soon after the discovery of this system, first theoretical attempts to explain the interactions leading to such phase sequences were made [2]. The continuous phenomenological theory was able to explain the phase sequence $S_A \leftrightarrow S^*_C \leftrightarrow S^*_{C_\gamma} \leftrightarrow S^*_{C_A}$ and the structure of the ferrielectric $S^*_{C_\gamma}$ phase [3, 4], but could not explain the appearance of the $S^*_{C_\alpha}$ phase and its structure. The idea of competing interactions was developed by Isozaki *et al.* [5], and different structures for the $S^*_{C_\alpha}$ phase have been proposed, but a consistent theoretical explanation of the phase sequence is still missing.

The experimental observation of two soft modes (the ferroelectric and the antiferroelectric mode) in the smectic A phase reported by Sun *et al.* [6] was a motivation to introduce a discrete phenomenological model, where next nearest neighbour interlayer interactions play an important role [6]. In the framework of this model, the authors explained the same phase sequence as with the corresponding continuous model, i.e. without the $S^*_{C_\alpha}$ phase, and also the dispersion relation of fluctuations in such systems over the whole Brillouin zone. In the smectic A phase, the dispersion relation consists of one doubly degenerate mode with two minima appearing close to the centre and close to the Brillouin zone boundary, respectively, that correspond to two soft modes. In the S^*_C phase and also in the $S^*_{C_A}$ phase, two modes appear in the dispersion relation with the minima close to the centre and close to the boundary of the Brillouin zone. Although the model contained the possibility of competing interlayer interactions, their consequences have not been analysed.

To study the possible structures appearing in the temperature region immediately below the transition temperature from the S_A phase to a tilted phase, a simple phenomenological model taking into account the competing interactions between nearest and next nearest layers bi-linear in their order parameters, has been proposed [7]. The structure, which minimizes the free energy at the temperature below the S_A phase, of this model has a constant magnitude of tilt, but its phase is helicoidally modulated with a pitch extending over only a few layers. The structure is in general not commensurate with the layer thickness. It is therefore of interest to study the dynamic properties of such a phase, while asking the question how the incommensurability affects the dispersion relation of tilt fluctuations.

In the second section, a short description of the model [7] is given and different stable structures corresponding to different model parameters are described. In the third section, the dynamical behaviour of possible low tem-

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perature phases appearing in this model is analysed. In conclusion, some suggestions for experimental observations, which could be a test of the model, are made.

2. The model

The tilt of the director from the normal to the smectic layers (z-axis) in the jth smectic layer can be expressed by a two component tilt vector ξ_j describing the magnitude and the direction of the tilt. We will study here the dynamics of the liquid crystals only in the vicinity of the transition temperature from the S_A phase to a tilted lower temperature phase, where the tilt of the molecules is still small. We also assume that mainly intralayer interactions cause the phase transition to the tilted phase and therefore are much stronger than the interlayer interactions which are taken into account up to the next nearest layers. The chiral interactions between layers are assumed to be weak in comparison with achiral interactions and to act only between nearest layers.

The free energy of the system can be expressed as the sum over all smectic layers:

$$G = \sum_j \left[\frac{a_0}{2}\xi_j^2 + \frac{b_0}{4}\xi_j^4 + \frac{1}{2}a_1(\xi_j \cdot \xi_{j+1}) + \frac{1}{8}a_2(\xi_j \cdot \xi_{j+2}) + \frac{1}{2}f(\xi_{j+1} \times \xi_j)_z \right] \quad (1)$$

Here only the parameter $a_0 = a(T - T_0)$ is temperature dependent and T_0 is the transition temperature, at which the 'mean field' transition to the tilted phase should take place in each layer without interactions between layers. Parameter b_0 is positive reflecting the fact that a continuous transition from the S_A to the tilted phase is assumed. The third and the fourth terms describe the achiral bi-linear interactions between nearest and next nearest neighbours, respectively, and the fifth term describes the nearest neighbour chiral interactions. Here the subscript z denotes the z-component of the vector product.

For negative values of a_2, only the ferroelectric S_C^* phase ($a_1 < 0$) or the antiferroelectric $S_{C_A}^*$ phase ($a_1 > 0$) is possible below the phase transition. For positive values of a_2, when $|a_1| > a_2$, the S_C^* or the $S_{C_A}^*$ phase appears below the transition, but for $|a_1| < a_2$, the competition between nearest and next nearest interlayer interactions results in the helicoidally modulated structure, which is not originated by the chirality and has a pitch extending over only few smectic layers [7]. Minimization of the free energy gives the following expression for the structure of the low temperature phase:

$$\xi_j = \theta\{\cos(j\alpha + \alpha_0), \sin(j\alpha + \alpha_0)\} \quad (2)$$

where θ and α are the solution of the system of equations:

$$\theta(a_0 + a_1\cos\alpha + \tfrac{1}{4}\cos 2\alpha + f\sin\alpha) + b_0\theta^3 = 0 \quad (3a)$$

$$a_1 \sin\alpha + a_2 \sin\alpha\cos\alpha - f\cos\alpha = 0. \quad (3b)$$

Assuming that the chiral interactions are weak ($f \to 0$), the angle between the directions of the tilt in two neighbouring layers, i.e. the difference in the phases of the order parameters (α), is approximately given as $\alpha \approx \pm\arccos(-a_1/a_2)$ and the degeneracy of the arccos function is lifted only by the chiral term (f). The phase change from one layer to another for a constant angle α, resulting in the helicoidally modulated phase, is in general not commensurate with the layer thickness. Since chiral interactions are present, only one handedness of the modulation is possible. The value of α_0 which determines the direction of the tilt in the first layer is arbitrary, because the structure obtained is rotationally symmetric. The structure of the $S_{C_\alpha}^*$ phase is presented in figure 1.

As mentioned above (equation (3b)), for competing interactions ($a_2 > 0$), the phase difference between two neighbouring layers depends on the parameters a_1, a_2 and f (figure 2). In the absence of chiral interactions, the structure of the S_C^* phase appears when $a_1 \leqslant -a_2$. In the case of chiral interactions, the phase difference between nearest layers is not exactly zero, resulting in the S_C^* phase with modulation extending over many layers. Similar conclusions can be drawn for $a_1 \geqslant a_2$, where the unwound antiferroelectric structure is stable in the absence of chiral interactions, while a long pitch modulation of the antiferroelectric phase ($S_{C_A}^*$) is stable in the presence of chiral interactions. When chiral interactions exist, the structure of the S_C^* phase, as well as the structure of the $S_{C_A}^*$ phase, differ from the structure of $S_{C_\alpha}^*$ only in the magnitude of phase difference, and the structures of the S_C^* and $S_{C_A}^*$ phases are equal to the structures obtained when the interactions are non-com-

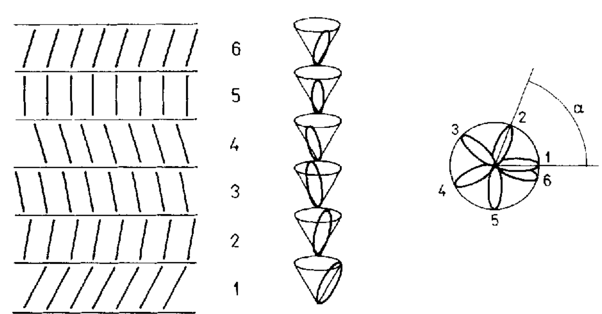

Figure 1. An example of the predicted structure of the $S_{C_\alpha}^*$ phase. The approximate length of the pitch is five interlayer distances and the helix is right handed. The structure is presented for values of the parameters $a_1 \approx -0{\cdot}3$, $a_2 \approx 1{\cdot}0$ and $f \approx -0{\cdot}01$, which gives $\alpha \approx 70°$.

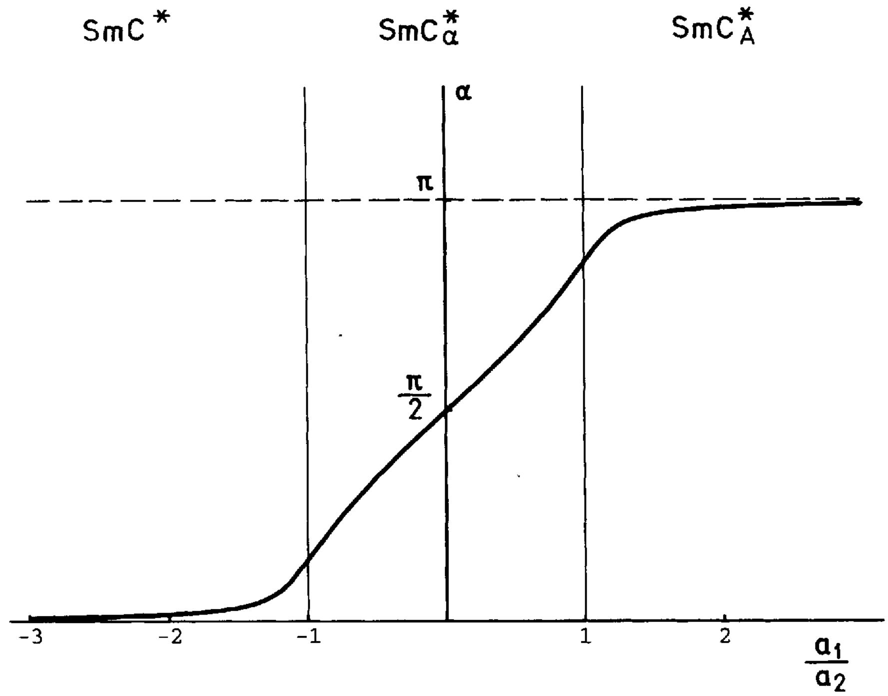

Figure 2. Dependence of the phase difference between two neighbouring layers on the ratio a_1/a_2; $a_2 = 0{\cdot}2$ and $f = -0{\cdot}01$.

petitive. However, the dispersion relations in systems with competitive interactions are expected to differ from the dispersion relations in systems with non-competitive interactions.

3. The order parameter fluctuations

3.1. *The smectic A phase*

We are interested here only in small deviations from the equilibrium state and therefore we consider in the expansion of the free energy (equation (1)) around the equilibrium structure only quadratic terms in the deviations. The equilibrium structure above the transition temperature is the structure of the S_A phase, where all order parameters ξ_j are equal to zero. The order parameter in the jth layer can be therefore expressed by the deviations from the equilibrium state:

$$\xi_j = \{\delta\xi_{j,x}, \delta\xi_{j,y}\}. \quad (3)$$

Here x and y are two axes lying in the plane of the smectic layer. The deviations can be expressed as a linear combination of helicoidal fluctuations with wave vector q:

$$\begin{aligned}\delta\xi_{j,x} &= \sum_q \delta\xi_{q,x}\exp(iqjd)\\ \delta\xi_{j,y} &= \sum_q \delta\xi_{q,y}\exp(iqjd),\end{aligned} \quad (4)$$

where the discreteness of the smectic structure has been taken into account. The thickness of the smectic layer is d. The part of the free energy G (equation (1)), harmonic in the deviations is:

$$G_2 = \tfrac{1}{2}\sum_q \delta\xi_{-q} \boldsymbol{G}_2(q)\, \delta\xi_q \quad (5)$$

where

$$\delta\xi_q = \{\delta\xi_{q,x}, \delta\xi_{q,y}\} \quad (6)$$

and the matrix $\boldsymbol{G}_2(q)$ is

$$\boldsymbol{G}_2(q) = \begin{bmatrix} A & -iC \\ iC & A \end{bmatrix} \quad (7)$$

with the elements

$$\begin{aligned} A &= a_0 + a_1\cos(qd) + \tfrac{1}{4}a_2\cos(2qd)\\ C &= f\sin(qd). \end{aligned} \quad (8)$$

To investigate the dynamics of these systems we use the Landau–Khalatnikov kinetic equations:

$$\gamma\frac{\partial\delta\xi_q}{\partial t} = -\frac{\partial G_2}{\partial\delta\xi_{-q}} \quad (9)$$

where γ is the rotational viscosity coefficient and G_2 is the free energy given by equation (5). The solution of equation (9) is of the form:

$$\delta\xi_q = \delta\xi_{q,0}\exp[-t/\tau(q)], \quad (10)$$

and equation (9) is transformed into the eigenvalue problem of the matrix $\boldsymbol{G}_2(q)$. The corresponding eigenvalues of the matrix are doubly degenerate and the

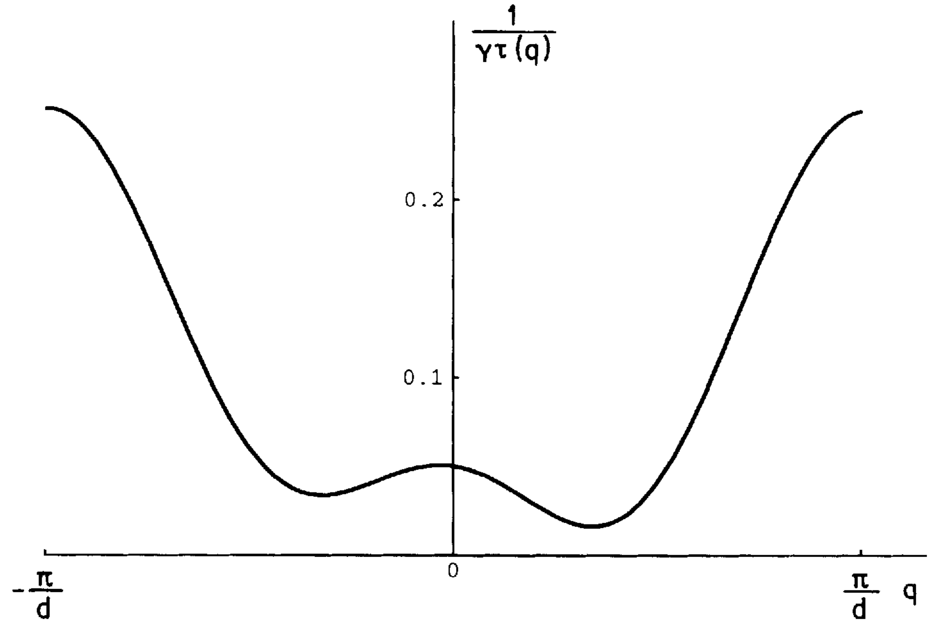

Figure 3. The dispersion relation in the S_A phase. The mode is doubly degenerate and becomes critical at the transition temperature at wave vector $q=\alpha/d$, resulting in freezing out of the helicoidal fluctuations with the wave vector $q=\alpha/d$. ($a_0=0{\cdot}1$, $a_1=-0{\cdot}1$, $a_2=0{\cdot}2$ and $f=-0{\cdot}01$.)

inverse relaxation times are:

$$\frac{1}{\tau(q)}=\gamma(a_0+a_1\cos(qd)+\tfrac{1}{4}a_2\cos(2qd)+f\sin(qd)) \tag{11}$$

In the S_A phase, only one doubly degenerate mode exists, which becomes critical at the transition temperature T_c for the critical wave vector $q=\alpha/d$. The $1/\tau$ dependence on the wave vector q is presented in figure 3. This dispersion relation has a maximum near the wave vector $q\approx 0$, which appears to be due to the favourable antiparallel orientation in next nearest layers.

3.2. *The low temperature phase*

Looking for the dispersion relation in the low temperature phase, we express the order parameter in the jth layer as a sum of the equilibrium value of the order parameter ($\xi_{j,0}$), a small change in the magnitude of the order parameter ($\delta\xi_{j,\parallel}$) and a small change in the direction of the order parameter, i.e. in the phase of the order parameter ($\delta\xi_{j,\perp}$).

$$\xi_j=\xi_{j,0}+\delta\xi_{j,\parallel}+\delta\xi_{j,\perp} \tag{12}$$

Expressing phase and magnitude fluctuations as a linear combination of helicoidal fluctuations with the wave vector k in the helicoidal coordinate system, which follows the direction of the tilt from layer to layer,

$$\begin{aligned}\delta\xi_{j,\parallel}&=\sum_k\delta\xi_{k,\parallel}\exp(ikjd)\\ \delta\xi_{j,\perp}&=\sum_k\delta\xi_{k,\perp}\exp(ikjd),\end{aligned} \tag{13}$$

the contribution of the fluctuations to the free energy (equation (1)) can be written as in equation (5), only the matrix has the following form:

$$\boldsymbol{G}_2(k)=\begin{bmatrix}A & -iC\\ iC & B\end{bmatrix} \tag{14}$$

with the elements

$$\begin{aligned}A&=a_0+3b_0\theta^2+a_1\cos(\alpha)\cos(kd)\\ &\quad+\tfrac{1}{4}a_2\cos(2\alpha)\cos(2kd)+f\sin(\alpha)\cos(kd)\\ B&=a_0+b_0\theta^2+a_1\cos(\alpha)\cos(kd)\\ &\quad+\tfrac{1}{4}a_2\cos(2\alpha)\cos(2kd)+f\sin(\alpha)\cos(kd)\\ C&=a_1\sin(\alpha)\sin(kd)\\ &\quad+\tfrac{1}{4}a_2\sin(2\alpha)\sin(2kd)+f\cos(\alpha)\sin(kd)\end{aligned} \tag{15}$$

and the fluctuation vector is now expressed as the two component vector consisting of the changes of the magnitude of the tilt and the changes of the phase of the tilt:

$$\delta\xi_k=\{\delta\xi_{k,\parallel},\delta\xi_{k,\perp}\} \tag{16}$$

Following the same procedure as in equation (9), we found two modes in the tilted phase (figure 4). The one with the lower frequency is due to the phase fluctuations and can be recognized as the Goldstone mode in its lowest value corresponding to the critical wave vector α/d. For this wave vector, the frequency is zero and it represents the rotation of the liquid crystal sample as a whole. The dispersion relations change with lowering temperature, i.e. with increasing magitude of the tilt (figure 5).

The mode with the higher frequency is due to the fluctuations of the magnitude of the tilt. Therefore its

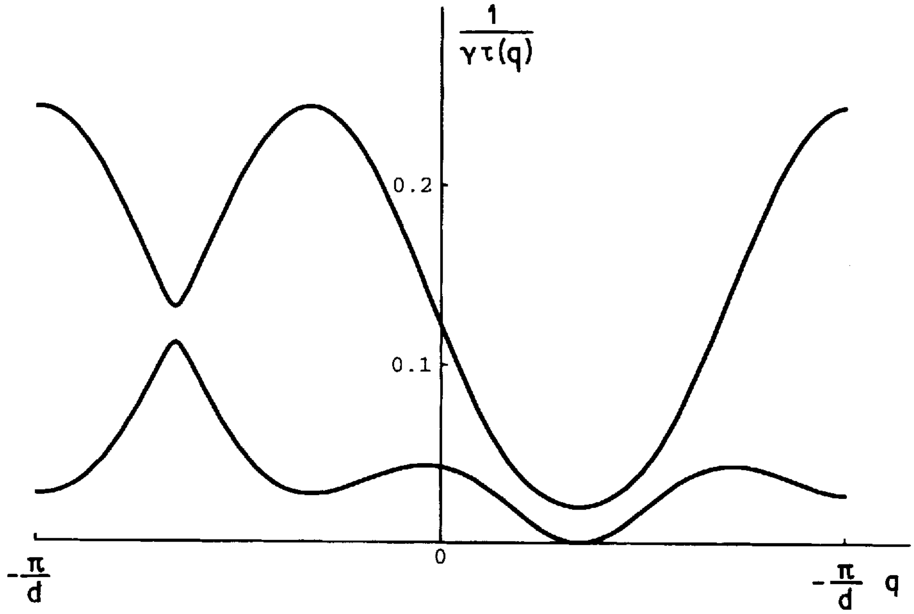

Figure 4. The Goldstone mode and the soft mode dispersion relation in the $S^*_{C_\alpha}$ phase directly below the transition temperature ($a_0 = 0{\cdot}074$). Other parameters are the same as in figure 3 and $b_0 = 100$. The splitting of the degenerate mode in S_A phase at $q = \alpha/d$ is clearly seen. The modes are presented in the laboratory system: $q = k - \alpha/d$.

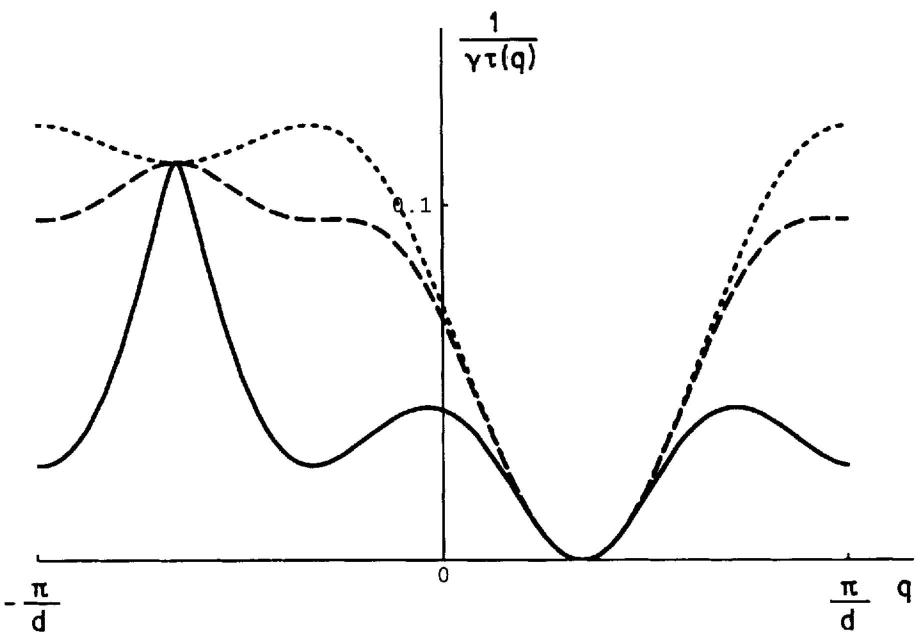

Figure 5. Phase modes corresponding to three different temperatures in the $S^*_{C_\alpha}$ phase; $a_0 = 0{\cdot}074$ (solid line), $a_0 = -0{\cdot}1$ (dashed line) and $a_0 = -2$ (dotted line). The modes are also presented in the laboratory system and the parameters are the same as in figure 4.

frequency is higher and rises with growing tilt, i.e. with decreasing temperature. The mode is a typical amplitude mode, well known in ferroelectric liquid crystals [8]. It is also critical at the transition temperature for the critical value of the wave vector α/d (figure 4).

4. Conclusions

The theoretical analysis of the fluctuations of the tilt order parameter in systems where the competing interlayer interactions lead to a helicoidally modulated structure with short pitch, proposed as the structure of $S^*_{C_\alpha}$ phase [7], is presented. In these systems, in the S_A phase, only one doubly degenerate mode with two minima in the middle of the Brillouin zone and a maximum near wave vector $q \approx 0$ appears when the low temperature phase is the $S^*_{C_\alpha}$ phase. The mode becomes critical at the transition temperature for the wave vector α/d and splits into two modes—a phase and an amplitude mode—in the $S^*_{C_\alpha}$ phase. The phase mode has an infinite relaxation time at the wave vector α/d, which appears somewhere in the middle of the Brillouin zone and corresponds to the helicoidal modulation extending over only a few smectic layers.

Previous studies of the dynamical properties of the

S_C^* and $S_{C_A}^*$ phase in the framework of the continuous phenomenological model [9] implicitly assumed the commensurate system with the pitch extending over two layers in the absence of chirality. In these systems the phenomenological description considering the primitive cell extending over two layers and therefore introducing two two-dimensional order parameters—ferroelectric and antiferroelectric—is appropriate. The dynamical analysis of the system with two two-dimensional order parameters showed the existence of the four modes, but the Brillouin zone is only one half of the Brillouin zone corresponding to the S_A phase.

All the commensurate structures appearing in the framework of the phenomenological model, taking into account the competing interactions between nearest and next nearest layers bi-linear in the order parameters [7], with the pitch extending over N layers, can be treated similarly by introducing N two-dimensional order parameters; the analysis of the dynamical properties of such systems shows the existence of $2N$ modes [10] in the Brillouin zone which is $1/N$ smaller.

As a possible experimental test of the model, experimental observations of the dispersion relations in the S_A phase for systems where the $S_{C_\alpha}^*$ phase appears as the low temperature phase can be suggested. The dispersion relation should show a maximum near the wave vector zero as a consequence of the competing nearest and next nearest interlayer interactions, in contrast to the systems where interactions are non-competitive and therefore the minimum of the dispersion relation near wave vector zero is expected. Additionally, in the S_A phase, the dispersion relation should have a maximum near $q=0$ for competing nearest and next nearest interactions and a minimum for $q=0$ for non-competing interactions.

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