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ANTIFERROELECTRIC AND FERRIELECTRIC STRUCTURES INDUCED BY MULTILAYER ORDERING IN CHIRAL SMECTICS

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Abstract The systematic symmetry and thermodynamical analysis of the possible antiferroelectric and ferrielectric structures induced by the multilayer tilt ordering from parent SmA-phase is presented. It reduces greatly the choice of the models.

INTRODUCTION

Since the first antiferroelectric herringbone structured phase was discovered in liquid crystals [1-4] many other antiferroelectric and ferrielectric liquid crystals have been studied extensively. The antiferroelectric SmC_A^* phase has already been confirmed to exist in more than 300 compounds [5].

Most of these substances shows in addition to the standard ferroelectric SmC* phase and antiferroelectric SmC_A^* phase a number of subphases, designated as SmCα*, SmCγ* and some others [6-10]. A great set of experimental studies has been already performed on the preceding compounds, namely X-ray diffraction [11,12], differential scanning calorimetry (DSC) [6,13,14], dielectric measurements and the field induced apparent tilt angle studies [7,15,16], optical transmittance and electric current responses[7,14], the helicoidal structure studies [4,17], phason dispersion analysis[18] and the conoscopic observations of homeotropically aligned cells under an external electric field[8,9,19,20].

These experiments could establish unequivocally the dielectric natures of the reported phases (ferro-, antiferro- or ferrielectric ones) but no clear-cut conclusion can be done neither about the structures of the subphases nor about the steps of molecular reorganisation from one structure to another. This is due to the fact that X-ray analysis (neither powder spectra nor oriented plates) doesn't allow in this case to discriminate the different structures. The layer spacing d(T) in function of temperature [11,12,21] shows a very slow smooth dependence when crossing SmC*, SmCγ* and SmC_A^* phases. The X-ray studies on the oriented plates show the absence of any detectable modulation of electronic density along the z-axis[11], as if the tilt angle is identical from one layer to another. Actually, as the structure factor in X-ray diffraction is proportional to the square of $\mathrm{Sin}\,\Theta_i$, where Θ_i is the tilt angle in the i-th layer, the phases with identical tilts should

not be distinguishable in this experiment. So, only indirect way of structure determination is available for a moment. One should construct a model of the structure, deduce its physical properties and verify experimentally its consequences.

These facts make it very important to have a limited number of realistic structure models to analyse. In our previous work [22] we have shown that a set of experimental data concerning ferro-, antiferro- and ferrielectric phases can be understood in terms of an *azimutal reorientation of the molecular subunites*, assuming a *bilayer periodicity* for the smectic stacking. Bilayer model was first proposed by Orihara and Ishibashi [23] and developed by Zeks et al. [24,25]. We have given a detailed description of the inhomogeneous structures of the ferro-, antiferro- and ferrielectric phases and of the mechanisms of transitions between them, which were not considered in [23].

In the framework of the proposed model we have discussed the whole set of the dielectric and some of the optical properties of tolan C8 (C_nH_{2n+1} O-Ø-C-C-Ø-COO-C*H(CH_3)-C_6H_{13}) compound [26], especially the existence of the low-frequency soft mode through the SmC_A* - SmC_γ* phase transition, realised by the anti-phase azimutal rotations of the molecules in the adjacent layers. A simple generalisation of the model [27] permits also to describe the possibility of existence of two different isostructural helicoidal ferrielectric phases in the SmC_γ* region. The phases differ mainly by the sense and the length of the helicoidal pitch and have the same basic unwound structure. Phase transition between such kind of phases can have a critical end point. It can be also shown that these two phases appear in the substances with strongly first order phase transitions between ferro - ferri and ferri - antiferro phases. The existence of these phases has been confirmed experimentally in tolan C8 compound using DSC, optical rotatory power and Raman scattering measurements [27]. Let us also mention some other advantages of the bilayer model. As it is shown in [24,25] , taking into account of a coupling term in the Landau - de Gennes free energy of the model can explain the existence of even 12 subphases.

However, some recent experimental data, namely, conoscopic figures observations under an external electric field [19,20,28] can be also interpreted,when supposing the existence of the multilayer tilted ordered phases in the considered liquid crystals. In [17] the existence of the three-, four- and even more layered phases has been proposed as the steps of the possible Devil's staircase. However, neither symmetries of the structures, resulting from the phase transition from the usual SmA parent phase, nor symmetry restrictions on the parameters of the proposed structures has not been analysed.

This work presents *systematic symmetry and thermodynamical analysis of the possible antiferroelectric and ferrielectric structures* induced by the multilayer tilt ordering from SmA phase and reduced significantly the choice of the models.

The paper is organized as follows. In Sec.II a theoretical description is given of the possible molecular configurations that may arise in multilayer smectics. The structures with even and odd numbers of layers in the unit cell are considered separately. Special attention is paid to the difference between the basic unwound structures in chiral and nonchiral cases. It is shown that there can exist *five different unwound ordered phases for each integer number of layers in a substance with chiral molecules*, though there *seven phases when the molecules are nonchiral*. In the former case the existence of the *frustrated structures* with one (or several) smectic layers characterized by *zero value of the average tilt angle* is discussed. Homogeneous parts of the free energies together with the number of soft modes and Goldstone modes is given. Section III contains a discussion of the fluctuational mechanism of the phase transitions between multilayer tilted phases and its possible relation with a macroscopic fluctuational movement of defects in chiral smectics.

II. SYMMETRY ANALYSIS

A.General

The following symmetry analysis is based on the fact that all multilayer tilted phases are induced by the phase transitions from parent SmA phase , which has one-layer periodicity The analysis of all possible phase transitions from the SmA phase was first given by Indenbom et al. [29,30] and then resumed in the review work of J.C.Toledano and P.Toledano [31]. It is based on the classification of the irreducible representations of the space group of the SmA phase. In the present work we use the similar principles to enumerate all the multilayer tilted phases.

Let us introduce for the phenomenological description of the phases the axial vectors of the tilts η_i defined as follows:

$$\eta_i = (-n_{iy}\, n_{iz},\ n_{ix}\, n_{iz}) \qquad (1)$$

where n_{iu} (u= x,y,z) are the components of the director in the i-th layer and the space variables (x, y) and z are respectively the in-layer co-ordinates and the direction perpendicular to the smectic plane (Fig. 1).

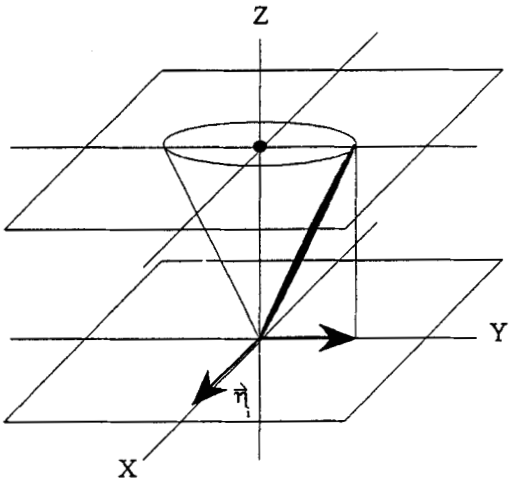


FIGURE 1 Polar vector η representing schematically axial vector of the tilt.

The components of the tilt axial vectors η_i span different representations of the space group G_0 of the parent SmA phase. For both cases of chiral and nonchiral molecules G_0 contains the subgroup of discrete one-dimensional translations along the z-axis T_z and continuous subgroup of all the in-plane rotations and displacements. But in the nonchiral case the point group of the smectic layer is $D_{\infty h}$, though in the chiral case the inversion of the media is lost and the point group of the layer is D_{∞}.

The one-dimensional Brillouin zone of the SmA phase has only two points with particular symmetry $\mathbf{k}=0$ (the centre of the zone) and $\mathbf{k}=(1/2)c^*$ (its border) where $c^*=2\pi/d$ and is an interlayer distance (Fig. 2).

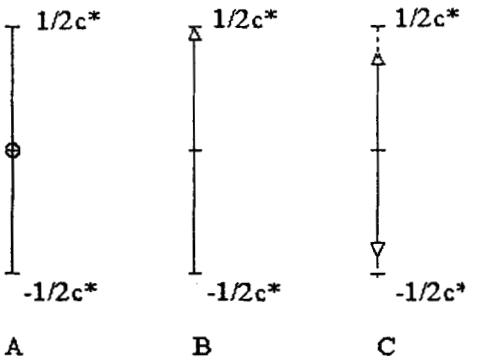


FIGURE 2 Different wave vectors in the Brillouin zone of the SmA phase A) $\mathbf{k}=0$ associated with one layer phases; B) $\mathbf{k}=(1/2)c^*$ associated with bilayer phases; C) $\mathbf{k}=(1/n)c^*$ associated with multilayer phases.

When the wave vector of the tilt ordering is associated with the centre of the zone (Fig. 2,A) corresponding phase transition leads to the phase in which one-layer periodicity is preserved. It is SmC phase in the non chiral substance and ferroelectric SmC* phase in chiral one. (Let us note that SmC phase could also be called ferro- phase, for example, *ferroclinic* phase, according to the classification of the ferroic phase transitions given by Aizu[32]). Analogously, when the wave vector $\mathbf{k}=(1/2)c^*$ (Fig. 2,B) is associated with the border of the zone, the corresponding ordered phase has bilayer periodicity. It is SmO phase in the nonchiral substances (one can call it bilayer *antiferroclinic* phase) or antiferroelectric SmC_A^* phase in the chiral smectics.

Let us now consider the case of the wave vector with the end lying inside the Brillouin zone, so that $\mathbf{k}=(1/n)c^*$, where $n > 2$ (Fig. 2,C). The symmetry of all the wave vectors lying between $\mathbf{k}=0$ and $\mathbf{k}=(1/2)c^*$ is exactly the same, consequently, the length of the wave vector of corresponding ordering can vary continuously with temperature. This is the simple reason of the possibility of so called Devil's staircase, which can result in existence of the succession of phases with different translational periodicity (different number of layers in the unit cell) connected by the regions of stability of the incommensurate phases [33,34]. The purpose of this work is to describe the *basic homogeneous unwound structures induced by the tilt ordering* associated with this third type of wave vectors. To obtain helicoidal or other inhomogeneous phases which correspond to the basic structures one should add the inhomogeneous term F_{inh} to the Landau- de Gennes free energy of the SmA phase :

$$\Phi = (S/V)\int(F_{hom} + F_{inhom})dz \qquad (2)$$

Where the sum runs over the thickness of the sample, S is its section area and V is its volume. F_{inhom} contains invariants depending on the gradients of the order parameter (OP), while F_{hom} depends usually only on invariants which are polynomials as functions of OP. Then classical Euler-Lagrange procedure should give the types of the inhomogeneous structures and their domains of stability (see, for example, [22] for the types and stability of the bilayer helicoidal structures).

To illustrate multilayer tilt ordering associated with $\mathbf{k}=(1/n)c^*$ ($n > 2$), let us take the case of $n=4$ as a representative of the orderings with even number of layers in the unit cell, and $n=3$ as a representative of the case with the odd number of layers. We will also distinguish the case of the chiral smectic and nonchiral one. As it will be shown hereafter, there is a *difference between the number and the types of the basic unwound structures*

in chiral and nonchiral cases. It is a new fact with respect to the cases of one-layer and bilayer tilted phases.

B. Case of n = 4

In this case four successive layers involved in the ordering are characterized by four axial vectors of the tilt η_1, η_2, η_3, η_4 defined as in Eq. (1). They form four symmetric vector combinations which can be considered as different vector order parameters:

$$\begin{aligned} \eta_P &= \eta_1 + \eta_2 + \eta_3 + \eta_4 \\ \eta_{A1} &= \eta_1 + \eta_2 - \eta_3 - \eta_4 \\ \eta_{A2} &= \eta_1 - \eta_2 - \eta_3 + \eta_4 \\ \eta_{A3} &= \eta_1 - \eta_2 + \eta_3 - \eta_4 \end{aligned} \tag{3}$$

Note that all the vectors in Eq. (3) are planar and have zero z-component. The first vector η_P transforms in the same way as the macroscopic polarization and is associated with **k**=0. Such OP can lead only to SmC (or SmC* in the chiral case) phase. The last vector η_{A3} transforms as a vector of the bilayer antipolarization $\mathbf{A} = \mathbf{P}_1 - \mathbf{P}_2$ and is associated with **k**=(1/2)c*. Such OP can lead only to the SmO phase (or SmC_A* phase in the chiral case). The vectors η_{A1} and η_{A2} in their turn are associated with **k**=(1/4)c*. They transform as two different vectors of antipolarization of the four-layer structure. They represent essential characteristics of the four-layer antiferroelectric ordering (or antiferroclinic in the nonchiral case).

C. Nonchiral case

Let us start with the case of nonchiral molecules. Then the components of η_1 and η_2 span one irreducible four-dimensional representation of the space group of the SmA phase and form consequently one OP of the four-layer tilt ordering. If we are interested only in pure four-layer ordering we can put that OP η_P associated with k=0 is equal to zero, together with OP η_{A3} associated with bilayer periodicity : η_{A3}=0. These two conditions give immediately $\eta_1 = -\ \eta_3$ and $\eta_2 = -\ \eta_4$. This means that in all the four-layer antiferro- phases the tilt of the first layer is always opposite to the tilt of the third one, and the tilt of the second layer is always opposite to the tilt of the fourth layer. Thus, in all the four-layer antiferroclinic phases there will be common symmetry element which is the two-fold screw axis along the z-direction.

The homogeneous part of the Landau- de Gennes free energy, describing basic unwound structures of the four-layer ordering depends only on three basis invariants:

$$F_{hom} = F (I_1, I_2, I_3) \qquad (4)$$

where $I_1 = (\eta_{A1})^2 + (\eta_{A2})^2$; $I_2 = (\eta_{A1})^2 \cdot (\eta_{A2})^2$; $I_3 = (\eta_{A1} \cdot \eta_{A2})^2 = (\eta_{A1})^2 \cdot (\eta_{A2})^2 \, Cos \, \alpha$. Here α is the angle between η_{A1} and η_{A2} vectors.All other invariants can be expressed as polynomials of these ones. This result allows to predict the number of soft modes and Goldstone modes and to enumerate all the possible phases. Actually, the homogeneous part of the free energy depends only on three variables, modules of the η_{A1} and η_{A2} vectors and on the angle α between them., although the representation is four-dimensional. These three "normal co-ordinates" will generate three soft modes in dynamics. By contrast, the fourth variable, responsible of the rotation of the four-layer unit cell as a whole doesn't give its contribution to the homogeneous free energy and corresponds to only one Goldstone mode which can arise in dynamics of the considered structures.

Possible phases correspond to the minima of the homogeneous part of the Landau-de Gennes free energy :

$$(d F_{hom} / d \eta_i) = (d F_{hom} / dI_m) (d I_m / d \eta_i) = 0 \qquad (5)$$

where $\{ \eta_i \} = \{ \eta_{A1}^x, \eta_{A1}^y, \eta_{A2}^x, \eta_{A2}^y \}$, m = 1, 2, 3. As it is easy to show [35,36] the most low-symmetry phase corresponds to the maximal rank of the matrix($d I_m / d \eta_i$) and consequently to ($d F_{hom} / dI_m$) = 0 . Other ordered phases correspond to the different degenerations of the matrix : ($d I_m / d \eta_i$) = 0 . In the parent SmA phase all the components of the OP are equal to zero together with the rank of ($d I_m / d \eta_i$). Using this method we obtain seven different four-layer antiferroclinic phases, characterized by the following relations between η_{A1} and η_{A2} vectors (and consequently between the axial vectors η_1, η_2, η_3, η_4 of the tilts of four successive layers) :

I.	$(\eta_{A1})^2 = (\eta_{A2})^2$ and $\eta_{A1} \perp \eta_{A2}$	or $(\eta_i)^2 = (\eta_m)^2$ and $\eta_i \perp \eta_{i+1}$	
II.	$\eta_{A1} = 0$; $\eta_{A2} \neq 0$	or $(\eta_i)^2 = (\eta_m)^2$ and $\eta_1 = - \eta_2$	
III.	$(\eta_{A1})^2 = (\eta_{A2})^2$ and $\eta_{A1} // \eta_{A2}$	or $\eta_2 = \eta_4 = 0$	
IV.	$(\eta_{A1})^2 = (\eta_{A2})^2$	or $(\eta_i)^2 \neq (\eta_m)^2$ and $\eta_i \perp \eta_{i+1}$	(6)
V.	$\eta_{A1} // \eta_{A2}$	or $(\eta_i)^2 \neq (\eta_m)^2$ and $\eta_i // \eta_m$	
VI.	$\eta_{A1} \perp \eta_{A2}$	or $(\eta_i)^2 = (\eta_m)^2$	
VII.	no relation between η_{A1} and η_{A2}.		

Corresponding structures are shown in Fig. 3.

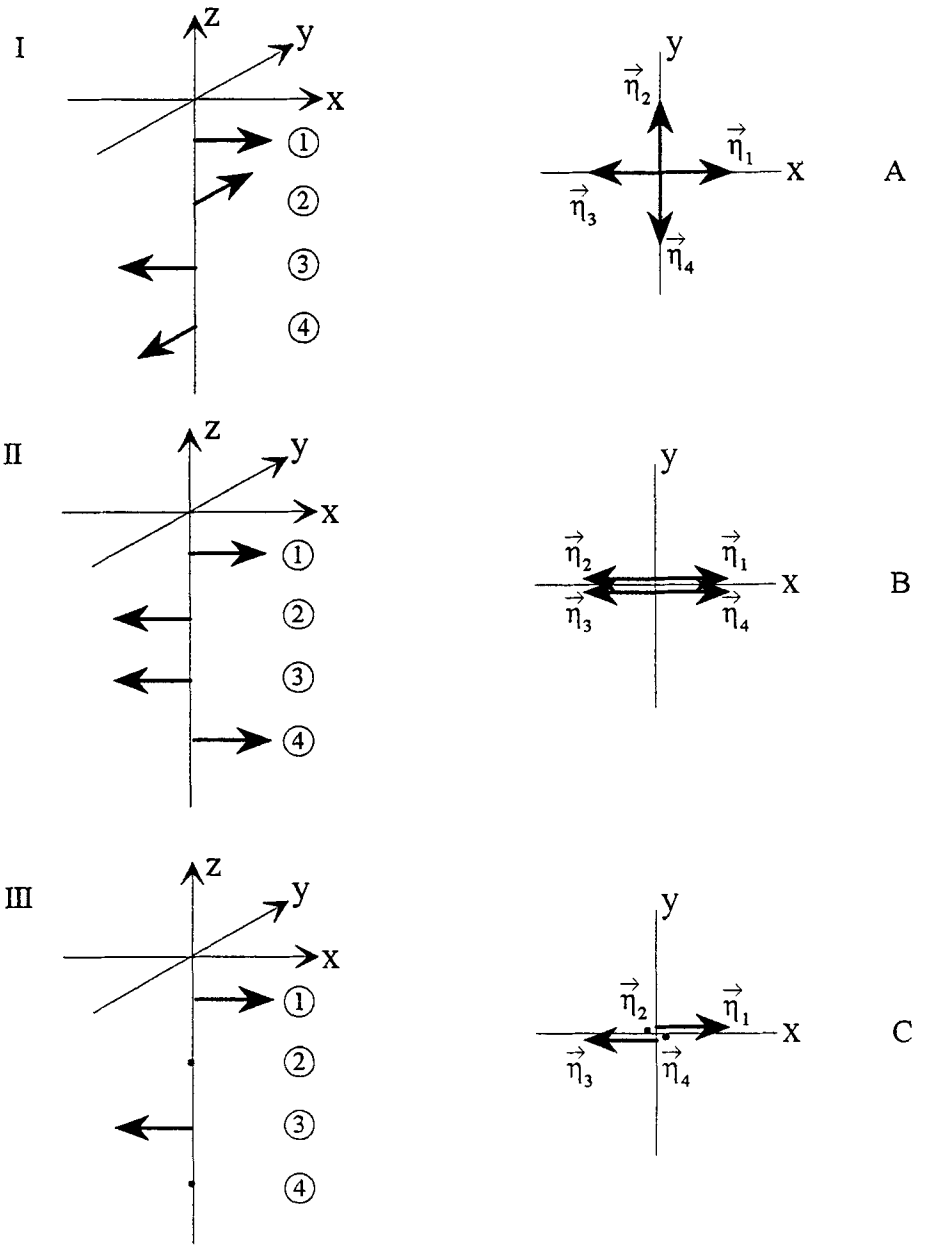
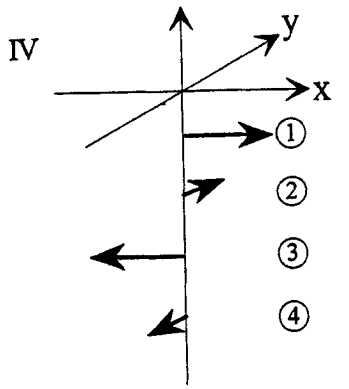
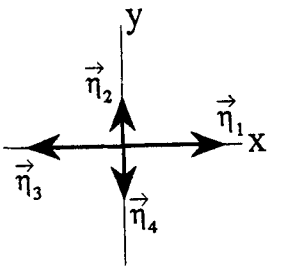


FIGURE 3 Structures of the different tilted four-layer smectic phases. The vectors of the tilts in four successive layers are presented and their projection on the smectic plane. Relations between modules and directions of corresponding vectors are given by Eq. (6).
A) Phase **I** ; B) Phase **II** ; C) Phase **III** ; D) Phase **IV** ; E) Phase **V** ;
F) Phase **VI** ; G) Phase **VII**





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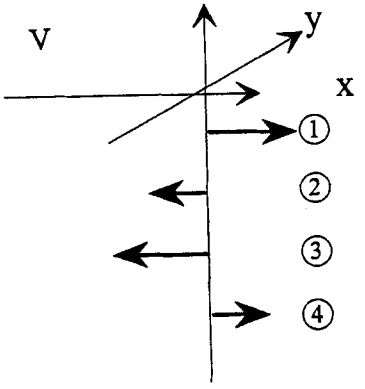

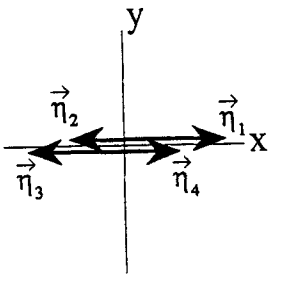

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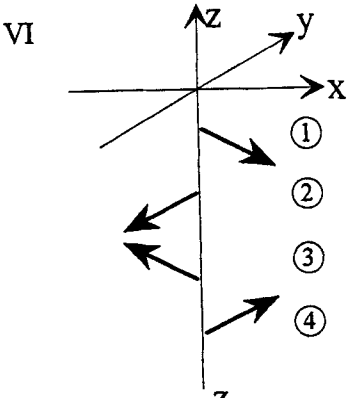

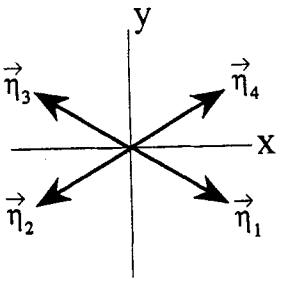

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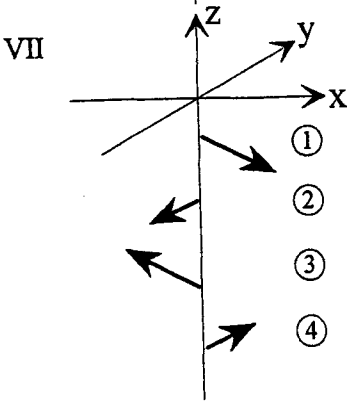

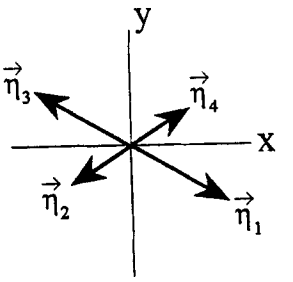

G

The vectors of the tilts in four layers are presented and their projection on the (x, y)-plane. Let us remind that the direction of the η_i vector is perpendicular to the molecular tilt plane and its module is proportional to the sinus of the tilt angle. The first three phases are the most probable from the thermodynamical point of view. In these phases only one component of the OP is varying with temperature. They can be described by the simplest Landau-de Gennes free energy expansion of the fourth degree. The observation of the phases IV-VII needs some additional condition, namely, some high degree terms in the free energy. Free energy expansion up to the eighth degree will give the regions of stability of all the phases.

The structure of the phase I represents 4-layer spiral. The molecules are tilted to the same angles Θ, but there is 90° difference in azimuthal angle from one layer to another, so that 4-fold screw axis is preserved.

The phase II is a planar one with two layers tilted in the same direction and two following layers tilted in opposite direction to the same angle Θ. Such kind of phase was proposed by [17] as a possible basic structure of the new antiferroelectric phase SmAF supposed to exist in 4-(1-methylheptyloxycarbonyl)phenyl 4'-octylbiphenyl-4-carboxylate (MHPBC) according to the conoscopic figure measurements in external electric filed. However such kind of structure can exist only in the case of nonchiral molecules. As it will be shown hereafter, there is no such kind of phase among the stable antiferroelectric phases in the chiral case.

The phase III´presents the most interesting structure. Actually, the layers number one and three are tilted to the same angle in the opposite directions, while the layers number two and four have average tilt angle equal to zero. One can imagine two different mechanisms of formation of such kind of structure. The first mechanism which seems to be very improbable : the molecules in the layers 2 and 4 are really not tilted. Such structure has a strong modulation of the electronic density along z-axis and should be clearly seen in the X- ray experiment. Another mechanism is statistical one : molecules in the layer 2 (or in the layer 4) are tilted, but they have two equivalent positions on the cone with the same tilt angle Θ : $+\Theta$ and $-\Theta$, and they spend equal time in these two positions, so that the average tilt angle is zero. It is a typical example of frustration and we can call the phase III the structure with frustrated layers 2 and 4.

Phases IV-VI are characterized either by different tilt angles in even and odd layers or by the azimuthal angles between the layers which are different from 0° or 90°. In the most low-symmetry phase VII both tilt angles and azimuthal angles of even and odd layers are different.

D. Chiral case.

In the case of chiral molecules, the symmetry of the SmA parent phase looses spatial inversion. Correspondingly, the point group which preserves the wave vector $\mathbf{k}=(1/n)\ c^*$ ($n>2$) changes from $C_{\infty v}$ to C_{∞}. This leads to the fact that two vectors η_{A1} and η_{A2} characterizing 4-layer ordering span not one but two irreducible representations of the SmA chiral space group. Namely x-component of η_{A1} and y-component of η_{A2} form one OP and x-component of η_{A2} and y-component of η_{A1} form another OP. These two OP are always coupled, so that in chiral case there appears an invariant $I_D=[\eta_{A1} \times \eta_{A2}]$, vector product of the planar vectors η_{A1} and η_{A2}. This invariant is similar to those, introduced by Dzyaloshinskii to the explain the phenomenon of the weak ferromagnetism of antiferromagnetics [37]. Its value defines the angle between different sublattices, in our case it is the azimuthal angle between the tilt vectors of even and odd layers.

The homogeneous part of Landau-de Gennes free energy of the 4-layer antiferroelectric ordering depends on three basis invariants :

$$F_{hom}^* = F(I'_1, I'_2, I'_3) \qquad (7)$$

where $I'_1=(\eta_{A1})^2 + (\eta_{A2})^2$; $I'_2=(\eta_{A1})^2\,(\eta_{A2})^2$ and $I'_3=[\eta_{A1} \times \eta_{A2}]=\eta_{A1}\,\eta_{A2}\,\sin\alpha$. Thus, one can expect as in the nonchiral case the existence of three soft modes and one Goldstone mode. Possible low symmetry structures are defined by the minima of F_{hom}^*. It is evident that the absence of mirror planes in the chiral SmA phase and the existence of the Dzyaloshinskii type invariant $I_D=I'_3=[\eta_{A1} \times \eta_{A2}]$ do not permit the existence of the 4-layers phases with the molecules lying in the same plane. As it is easy to show using the method mentioned in the section II.C in the chiral case there exist five different 4-layer antiferroelectric basic structures, namely the phases noted as I, IV, VI and VII in (6)and presented in Fig. 3, A, D, F, G, respectively. The fifth possible phases can be noted as I'. It has the same symmetry as the phase I, but in the phase I' four vectors of the tilt form right spiral, whereas in the phase I they form left one. The energies of these phases are quite different because of the different signs of I'_3 which correspond to the left and to the right 4-layer spirals. Usually such kind of phases are called antiisostructural [38,39,31]. These two phases are the most probable 4-layer antiferroelectric phases, because there is only one component of the OP which varies with temperature in these phases. Let us note again that the phase II with a planar structure is not permitted by the symmetry of the chiral smectic A phase.

One can generalized the description presented hereabove to the case of any even value of n. Actually, for any even n, the phase transition will be described by two vectors η_{A1} and η_{A2}. The only difference consists in the fact that for n layers η_{A1} and η_{A2} are

the symmetric combinations of n layers and not of 4-layers. However, for any n there will be always 7 antiferroclinic phases in the non chiral case, described by the same relations between η_{A1} and η_{A2} as in Eq. (6). Analogously, there will be always five antiferroelectric basic structures for any even value of n, similar to the phases I, I', IV, VI and VII.

E. Case n=3.

We will discuss multilayer tilt ordering with odd number of layers using the example of the 3-layer structures.

Three layers involved in the ordering are characterized by three axial vectors of the tilt η_1, η_2, η_3. They form three symmetric vector combinations :

$$\begin{aligned} \eta_P &= (\eta_1 + \eta_2 + \eta_3) / 3^{1/2} \\ \eta_{A1} &= (2\eta_1 - \eta_2 - \eta_2) / 6^{1/2} \\ \eta_{A2} &= (\eta_2 - \eta_2) / 2^{1/2} \end{aligned} \qquad (8)$$

The first vector is responsible of the ordering of the SmC-type. Vectors η_{A1} and η_{A2} in their turn are associated with the wave vector $\mathbf{k}=1/3c^*$. As in the previous section one can show that in nonchiral case these two vectors form one four dimensional OP and in chiral case there exists two coupled OP $(\eta_{A1}^x, \eta_{A2}^y)$ and $(\eta_{A2}^x, \eta_{A1}^y)$ with Dzyaloshinkii type invariant $I_D=[\eta_{A1} \times \eta_{A2}]$. As in the previous case there will be seven low symmetry phases in the non chiral case and five low symmetry phases in chiral one, but there is a slight difference in the expression of the structures of the phases with respect to the case of n even :

$$\begin{aligned}
&\textbf{I.}\ (\eta_{A1})^2 = (\eta_{A2})^2 \text{ and } \eta_{A1} \perp \eta_{A2} \\
&\quad \text{or } (\eta_i)^2 = (\eta_m)^2 \text{ and } (\eta_i \cdot \eta_{i+1}) = 1/2(\eta_m)^2 ; && \eta_P = 0 \\
&\textbf{II.}\ \eta_{A1} = 0 ;\ \eta_{A2} \neq 0 \quad \text{or} \quad \eta_2 = -\eta_3 ; && \eta_1 = 0 ; \\
&\qquad && \eta_P = 0 \\
&\textbf{III.}\ \eta_{A1} \neq 0 ;\ \eta_{A2} = 0 \text{ or } \eta_2 = \eta_3 \neq \eta_1 ; && \eta_P \neq 0 \\
&\textbf{IV.}\ \eta_{A1} \perp \eta_{A2} ;\ (\eta_{A1})^2 > (\eta_{A2})^2 \text{ or } (\eta_1)^2 > (\eta_2)^2 = (\eta_3)^2 ; && \eta_P \neq 0 \\
&\qquad \text{and } \eta_1 \perp (\eta_2 - \eta_3) && \\
&\textbf{V.}\ \eta_{A1} \perp \eta_{A2} ;\ (\eta_{A1})^2 < (\eta_{A2})^2 \text{ or } (\eta_1)^2 < (\eta_2)^2 = (\eta_3)^2 ; && \eta_P \neq 0 \\
&\qquad \text{and } \eta_1 \perp (\eta_2 - \eta_3) && \\
&\textbf{VI.}\ \eta_{A1} \parallel \eta_{A2} \quad \text{or} \quad \eta_1 \parallel \eta_2 \parallel \eta_3 ; && \eta_P \neq 0 \\
&\textbf{VII.}\ \text{no relation between } \eta_{A1} \text{ and } \eta_{A2} ; && \eta_P \neq 0 .
\end{aligned} \qquad (9)$$

The projections of the tilt vectors of the three layers on the (x,y) plane is presented in Fig. 4. In the chiral case the symmetry of the SmA phase permits : two antiisostructural

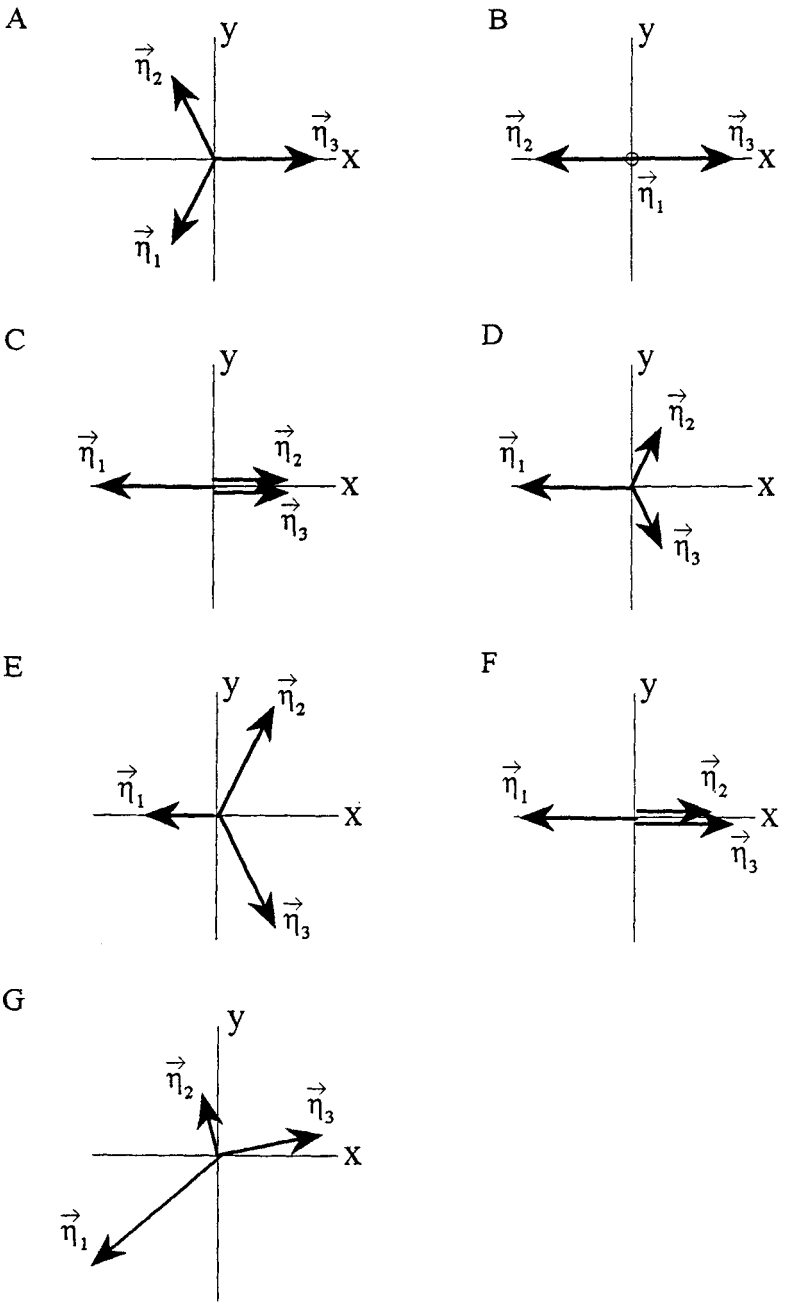

FIGURE 4 Structures of the different tilted three-layer smectic phases. The projection of the vectors of the tilts in three successive layers on the smectic plane are presented. Relations between modules and directions of corresponding vectors are given by Eq. (9).

A) Phase **I** ; B) Phase **II** ; C) Phase **III** ; D) Phase **IV** ; E) Phase **V** ; F) Phase **VI** ; G) Phase **VII**

phases I, I' which differ by the sense of the three layers spirals and phases IV, V and VII, all the structures being, of course, non planar. The main difference of the odd value of n with respect to the case of even n, consists in appearance of the *nonzero value of* η_P *induced by antiferroelectric (or antiferroclinic) OP as improper secondary OP, due to the nontrivial coupling which exists always between* η_P *and* η_{A1} *and* η_{A2}. So that only two phases in Eq. (9) can be *truly antiferroclinic* : the phase I and the phase II with one frustrated layer. All the other phases can be only *ferriclinic*. Analogously, in the chiral case the phases I and I' are *truly antiferroelectric*, but the phases IV, V and VII are *ferrielectric* ones *with improper polarization P induced by the antiferroelectric ordering*. Let us emphasize that in the layer model of the SmCγ* phase proposed by Takezoe et al [17] the molecules are assumed to possess the same values of the tilt angle in three successive layers, but two of them are tilted in one sense and the third one in the opposite sense. Such situation cannot exist in the nonzero temperature range even in nonchiral substance, because the symmetry of the corresponding phase III in Eq. (9) (Fig. 4.c) doesn't impose the same values of the tilt in the first two similar layers and in the third different layer. The symmetry elements of the structure, (z,x)-plane, two- fold axis passing between two similar layers and another two- fold axis passing through the third different layer remain even when the tilt angles are different ($\eta_2 = \eta_3 \neq \eta_1$).

The generalization of the case n=3 to the case of any odd value of n can be done in the same manner as in previous section for n=4. Let us finally analyse a possible relaization of the Devil's staircase in such kind of structures. As it is mentioned hereabove, for any value of n in the chiral case the only phases with one component of OP varying with temperature are the phases I and I', representing right- or left-handed spiral. These phases are the most probable from the thermodynamic point of view. Such type of structure exists for any value of n, including irrational numbers for which it is an incommensurate structure of the spiral type. One can also suppose that only one of two possible spirals is realized for each given value of n, because the fixed sign of the Dzyaloshinskii interaction $I_D=[\eta_{A1} \times \eta_{A2}]$ favours fixed sense of the spiral.

Then the *Devil's staircase in multilayer chiral tilted smectics should express itself as progressive azimuthal reorientation of the molecules in successive layers*. Starting from antiferroelectric SmC_A^* phase with two layers in the unit cell (n=2) one should obtain a number of intermediate structures with $2 < n < \infty$, and with the ferroelectric SmC* phase as the end point ($n=\infty$). Actually, SmC* phase in the frame of this mechanism can be considered as a structure with the infinite number of layers in the unit cell. So long as the author is aware of, for a moment, there is no experimental data clearly speaking in favour of this mechanism and Devil's staircase in general.

III. Discussion.

Let us now briefly discuss the possibility of the fluctuational nature of several ordered tilted phases and of fluctuational mechanism of phase transitions between them.

As we have mentioned in the section II, the symmetry of the SmA phase in the non chiral case permits the existence of the phases with frustrated smectic layers (for example, phase III in Eq. (6) and phase II in Eq. (9)). In corresponding layers of these phases molecules have equal probability to be tilted to the angle $+\Theta$ or in the opposite sense (i.e. to the angle $-\Theta$), so that *statistical average tilt angle is equal to zero*. Let us note that some other phases of Eq. (6) and Eq. (9) and even ferrielectric phases of the bilayer model [22, 23, 24] can also be understood in these terms. Actually, when the probabilities to have a tilt angle equal to $+\Theta$ and $-\Theta$ in the same layer are different, the average tilt angle is different from zero and also from microscopic tilt angle. If the probability distribution varies with temperature the average tilt angle varies also. One can imagine a mechanism of the phase transition between SmC-type phase and Sm0-type phase through the intermediate phase in which in one of the two layers molecules spend different times in $+\Theta$ and $-\Theta$ positions on the cone with the fixed microscopic tilt angle, with rapid jumps between two stable positions.

However, in the chiral substances, the interaction of Dzyaloshinskii $I_D=[\eta_{A1} \times \eta_{A2}]$ destroys such kind of structures and favours azimuthal reorientation. Moreover, inhomogeneous Lifshitz interaction inducing helicoidal structures install a correlation between the layers which makes it very difficult for a molecule to effectuate thermally activated jumps between two equivalent positions on the cone. But this type of fluctuations can express itself in the helicoidal structures of the chiral smectics on the macroscopic level. For some balance between the elastic energy of the helix and the entropy of the frustrated smectic layers there can be more advantageous for a liquid crystal to break continuous helix, to form multiple defects of the disclination and dispiration type, which can in their turn fluctuate rather freely, being activated by the microscpic jumps of the molecules. Details of the calculations of the fluctuational dynamics of the defects of this type will be published elsewhere [40].

As a final remark, let us note that strong macroscopic fluctuations with multiple defects creation are noted experimentally in the SmCγ* phase in practically all types of optical experiments [18,27,41].

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