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NON-ORTHOGONAL PHASES IN FERRIELECTRIC LIQUID CRYSTALS

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Abstract Two ferrielectric structures in a liquid crystal composed of asymmetric dimers are discussed. The anomalies of the physical properties at the phase transitions are studied.

INTRODUCTION

The recent progress in studies of tilted smectic phases in chiral liquid crystals like MHPOBC and its family[1,2], tolane series[3,4] and thiobenzoate derivatives[5] has revealed a whole number of new structures with complex dipolar order. Among them the antiferroelectric SmC_A^* phase with molecules tilted in nearly opposite directions in adjacent layers[6], ferrielectric phase which is supposed to be also two-layer structure but with an angle between the neighbouring layers varying with temperature[7]. Such kind of structure can have at least two different modifications which differ by their pitch length and sense and by the value of the azimuthal angle between the layers[8] which is well seen in optical experiments like Grandjean-Cano method and selective band reflection[4], or optical rotatory power measurements and Raman scattering[9,10]. The conoscopic observations under an external electric field permit also to suppose the existence of some additional ferrielectric phases[11], with the structures which are not precised yet. This reach variety of phases and unusual properties of the new type of chiral smectics favour strongly the construction of new models of liquid crystals with complex dipolar order.

Among the substances which show antiferroelectric and ferrielectric phases in their polymorphism there is a particular class of materials constituted of dimers[12]. In the case of symmetric dimers, their thermodynamic behaviour, dielectric and optical responses do not differ from those of usual monomer liquid crystal. By contrast, in the case of a molecule constituted of *two different rigid parts* (monomers) connected by a

soft junction, the difference can be significant. The aim of the present work is to give a classification of *tilted smectic phases with* dipolar order in a system of *asymmetric dimers*. We demonstrate that such a system shows two different ferrielectric phases and neither ferroelectric nor antiferroelectric one. In addition, in one of these ferrielectric phases the projections of big molecular axes of different monomers are not collinear and macroscopic polarization is not perpendicular to the optic plane (so-called non-orthogonal phase). It is shown that asymmetric chiral dimers are *true ferrielectrics* according to the classification of ferroics[13] in contrast with usual ferrielectric phases in liquid crystals constituted of monomers.

The paper is organized as follows: in Section I the structure analysis and corresponding thermodynamical model of tilted smectic phases in the system of asymmetric dimers is given. Possible ordered structures are classified. Theoretical phase diagram is calculated. Section II is devoted to the anomalies of physical properties of true ferrielectric liquid crystals, especially at the transition between orthogonal and non-orthogonal ferrielectric phases. In Section III a brief discussion is proposed.

I. FERRIELECTRIC STRUCTURES AND THEIR RELATIVE STABILITY

First, let us focus our attention on the basic unwound structures which can exist in a system of asymmetric dimers. Helicoidal phases can be obtained then by simple addition of Lifshitz term (and other inhomogeneous terms) in the free energy. Possible tilted phases can be easily derived from the group theory analysis of parent SmA phase. In the system of dimers the symmetry group of SmA phase is the same as in the case of monomers[14] : $G_0 = D_\infty \otimes T_Z$ for chiral molecules. The main difference in properties of tilted smectics between monomers and dimers comes from the asymmetry of dimers themselves. To illustrate this fact let us introduce tilt characteristics $\vec{\xi}_i$ in the i-th layer in the form : $\vec{\xi}_i = (n_{iy}n_{iz}, n_{ix}n_{iz})$ where n_j (j = x, y, z) are the components of the director ; i = 1, 2 for dimers. Then, one can introduce two order parameters characterizing two principal types of tilt order in smectics[6] : i) $\vec{\eta}_p = \vec{\xi}_1 + \vec{\xi}_2$ which favours the same sense of tilting and transforms as macroscopic polarization $\vec{P}$; ii) $\vec{\eta}_A = \vec{\xi}_1 - \vec{\xi}_2$ which is responsible of the tilting in opposite directions and transforms

as a vector of antipolarization $\vec{A} = \vec{P}_1 - \vec{P}_2$, where $\vec{P}_i$ (i = 1, 2) is the polarization of the i-th layer. In the case of monomers or symmetric dimers consisting of two identical monomers, $\vec{\eta}_P$ and $\vec{\eta}_A$ axial vectors span two different irreducible representations of G_0 group. This leads to the possibility of existence in this system of ferroelectric phase ($\vec{\eta}_P \neq 0; \vec{\eta}_A = 0$), or antiferrolectric phase ($\vec{\eta}_P = 0; \vec{\eta}_A \neq 0$), as well as mixed ferrielectric one ($\vec{\eta}_P \neq 0; \vec{\eta}_A \neq 0$). By contrast, if the monomers in a dimer are not identical then $\vec{\eta}_P$ and $\vec{\eta}_A$ span the same irreducible representation of G_0.

Homogeneous part of the free energy density in this case depends on three independent invariants $F = F(I_1, I_2, I_3)$, where $I_1 = \eta_P^2$; $I_2 = \eta_A^2$; $I_3 = (\vec{\eta}_P \cdot \vec{\eta}_A) = \eta_P \eta_A \cos\alpha$. First invariant expresses the energy of parallel tilting, second one stands for the energy of antiparallel ordering and the last one represents the energy of coupling of the ferro-antiferro type. The bilinear form of the coupling has an evident consequence : the tilting of one monomer always induces the tilting of another one, though the temperatures of proper tilt ordering of the monomers are different. The stable phases of this system can be obtained by minimization of the free energy F. Using the general method proposed in [7] one can show that in the system of asymmetric dimers there exist three stable states :

I. Paraelectric SmA phase with $\vec{\eta}_P = 0; \vec{\eta}_A = 0$. II. Orthogonal ferrielectric phase with $\vec{\eta}_P \neq 0; \vec{\eta}_A \neq 0$ and $\vec{\eta}_P // \vec{\eta}_A$ (Fig. 1,a). Both monomers are tilted in this phase. Tilt angles have *a priori* different values Θ_1 and Θ_2. The projections of big molecular axes are parallel or antiparallel (there is no qualitative difference between these two situations). Macroscopic polarization is perpendicular to the optic plane. III. The most low-symmetry phase of the system with $\vec{\eta}_P \neq 0; \vec{\eta}_A \neq 0$ and $0 \neq (\vec{\eta}_P \cdot \vec{\eta}_A) \neq \eta_P \eta_A$ (Fig. 1,b). In this non-orthogonal ferrielectric phase the projections of big molecular axes on the smectic plane form an angle β different from 0 or π. Though macroscopic polarization $\vec{P}$ remains perpendicular to $\vec{\eta}_P$ axial vector, it becomes non-orthogonal to the optic plane because of the individual dimer asymmetry.

There cannot exist any region of stability of ferroelectric or antiferroelectric phase in the case when polarization $\vec{P}$ and antipolarization $\vec{A}$ span the same representation of

the parent phase symmetry group. According to the classification of ferroics[13] the class of substances satisfying this condition is called *true ferrielectric*.

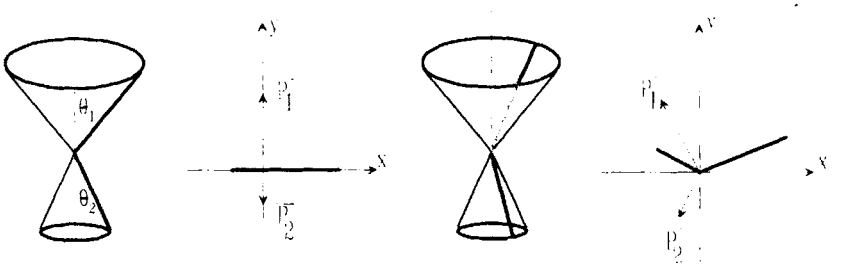

FIGURE 1 Ferrielectric structures in asymmetric dimers

Let us follow the thermodynamics of th e system of asymmetric dimers using the minimal non-degenerated model of Landau - de Gennes free energy :

$$F = a_1\eta_P^2 + a_2\eta_A^2 + a_3(\vec{\eta}_P \cdot \vec{\eta}_A) + (1/2)\eta_P^4 + (1/2)\eta_A^4 + (1/2)(\vec{\eta}_P \cdot \vec{\eta}_A)^2 \qquad (1)$$

where $a_1 = \alpha(T - Tc_1)$, $a_2 = \alpha(T-Tc_2)$, Tc_1 and Tc_2 being the temperatures of ordering of different monomers. Calculated theoretical phase diagram is shown in Fig. 2.

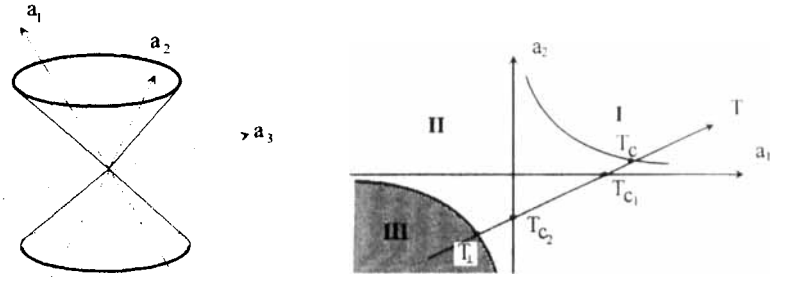

FIGURE 2 Phase diagram of the model (1) and its 2D section a_3 = const.

Paraelectric phase I is stable inside the upper part of the cone given by equation $a_1a_2 - a_3^2 = 0$. Orthogonal ferrielectric phase II is stable everywhere between two parts of the cone. Finally, the phase III has its stability region inside the lower part of the cone. Let us note that the necessary condition of stability of the phase III is $a_1 < 0$ and $a_2 < 0$

simultaneously. It means that such a state becomes stable only when both monomers are already ordered ($T < Tc_1$ and $T < Tc_2$). Both I-II and II-III phase transitions are of the second order in the model (1).

II.ANOMALIES OF PHYSICAL PROPERTIES AT THE PHASE TRANSITIONS

Second order of both phase transitions defines the behaviour of physical quantities in the vicinities of the transitions. Thus, at the transition from paraelectric to the orthogonal ferrielectric phase the tilt angle Θ_1 of one monomer is critical $\Theta_1 \sim (Tc - T)^{1/2}$ (Fig. 3,a),

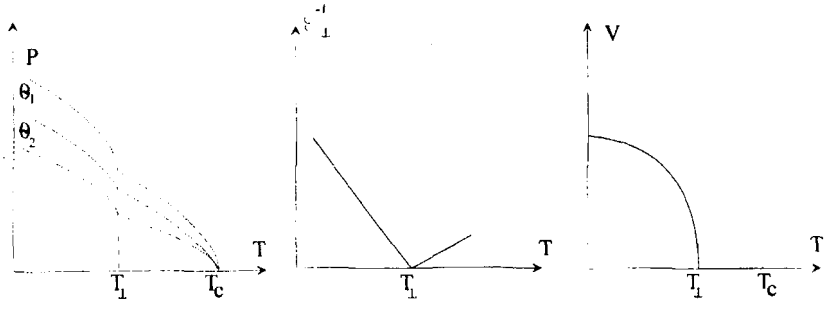

FIGURE 3 Anomalies of ferrielectric liquid crystal properties

where Tc is the temperature of I - II transition. The tilt angle Θ_2 of the second monomer as well as macroscopic polarization P are induced by Θ_1 as pseudoproper order parameters. Analogously, the antipolarization vector $\vec{A}$ is also induced by the tilting. At the transition II - III the angle α between $\vec{\eta}_P$ and $\vec{\eta}_A$ vectors can be taken as a critical variable $V \sim (-a_2 + a_3^2/a_1)^{1/2} \sim (T_\perp - T)^{1/2}$, where $T_\perp$ is the temperature of II - III transition (Fig. 3,c). At the same time the temperature dependencies of Θ_1 and Θ_2 become quite different at $T = T_\perp$ (Fig. 3,a) because of the proper ordering of the second monomer. The dielectric response at the transition paraelectric - true ferrielectric (I - II) is similar to that of SmA* - SmC* transition (Of course, the behaviour in an external electric field is more complicated than in usual ferroelectric ; the detailed analysis of this problem will be published elsewhere[15]). By contrast, one can show that at the transition II-III there appears an additional anomaly of *dielectric*

constant as a function of temperature. In a homogeneous structure the contribution in $\varepsilon_\perp$ component of dielectric tensor diverges at the transition II-III : $(\delta\varepsilon_\perp)^{-1} \sim 4\ (-a_2 + a_3^2/a_1) \sim (T_\perp - T)$ (Fig. 3,b). In corresponding helicoidal structure the direction of the tilt varies along the helix, so that $\delta\varepsilon_\perp$ gives its contribution in the average value of dielectric constant ε, which should undergo rather sharp maximum at the transition into non-orthogonal ferri-phase

III.DISCUSSION

In this work only the basic unwound structures of ferrielectric dimers were presented. The helicoidal structures of the true ferrielectric liquid crystals are much more complicated and bring new physical phenomena. Another important questions which are omitted in this short paper are : i) possible change of the polarization sign with temperature and corresponding existence of compensation temperature ; ii) behaviour of true ferrielectric in an external electric field which shows the existence of a non-collinear state between two critical fields E_{low} and E_{high}. All these problems will be discussed in the forthcoming paper[15].

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