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Optical properties of antiferroelectric liquid crystals in free-standing films

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A theoretical explanation of the results of ellipsometric measurements, performed some time ago by Bahr and co-workers [Ch. Bahr, D. Fliegner, C. J. Booth, and J. W. Goodby, Phys. Rev. E **51**, R3823 (1995)] on free-standing films of antiferroelectric liquid crystal (R)-1-methylheptyl-4-(4′-*n*-dodecyloxybiphenyl-4-*yl* carbonyloxy)-3-fluorobenzoate (in the following 12F1M7), is given within a discrete phenomenological model of antiferroelectric liquid crystals. The structure of the smectic-C_α (Sm-C_α) phase is described as an incommensurate phase, an average dielectric tensor, in general biaxial, is determined and the ellipsometric parameter Δ is found for two orientations of the film structures, defined by external electric field. Results are in agreement with observations: we show that temperature induced changes of the structure of the Sm-C_α phase, as derived from the model, lead to the oscillatory dependence of the ellipsometric parameters Δ_- and Δ_+ on temperature. [S1063-651X(96)51410-8]

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Much attention has been paid already to the investigation of liquid crystalline phases with antiferroelectric properties, but there has not been developed a complete and consistent theory yet, which would explain the variety of different phases, their structure, properties and their sequence on the temperature scale. It is clear though that the structures in question are characterized by a layered smectic order and among many that appear below the smectic-*A* (Sm-*A*) phase, only the structures of ferroelectric and antiferroelectric phases are known [1,2]. Among the mysteries waiting to be cleared up, the structure of the Sm-C_α phase, which appears in several systems immediately below the smectic-*A* phase, aroused quite an interest. Two basically different pictures of the Sm-C_α phase were proposed so far. The first one [3] is within a devil's staircase model, where the Sm-C_α phase is constituted from an infinitely large number of different planar states (planar in the sense that all the molecules tilt in the same plane), which cannot proceed continuously one from another. The second picture of the Sm-C_α phase was introduced by a discrete phenomenological model [4–6]. As a consequence of competing interactions between nearest- and next-nearest neighboring smectic planes, the structure of the Sm-C_α phase is spatially modulated with a pitch, which is short in comparison to the pitch in other tilted phases, that is a consequence of the chirality of the liquid crystal. Within the discrete model the Sm-C_α phase develops continuously from the Sm-*A* phase and its structure changes continuously with lowering temperature, as in general in incommensurate systems, until it transforms into a commensurate ferroelectric Sm-C^*) or antiferroelectric phase (Sm-C_A^*). No abrupt changes of structure occur in contrast to the devil's staircase model.

Among experimental methods, which enable us to observe and study liquid crystal systems, a technique of ellipsometric measurements was used extensively on free-standing films of (anti)ferroelectric liquid crystals [7,8]. The latest report refers to the compound 12F1M7 [8]. In a film with 122 smectic layers oscillatory behavior of the ellipsometric parameter Δ as a function of temperature was observed and interpreted as a consequence of the devil's staircase structure. But in this paper we demonstrate that the results of ellipsometric experiments are in quite remarkable agreement with the predictions, deduced from the discrete model of antiferroelectric liquid crystals. In reference to the experimental results we shall only be concerned with thick films. In thin films the effects, which are due to the induced higher smectic order at the surfaces and beyond the scope of this paper, blur the typical picture of the oscillatory behavior.

The wavelength of the light, commonly used in optical experiments, is two orders of magnitude larger than the smectic layers thickness. Therefore the structural details with a typical extension length of a few layers influence the measurements on the average: the dielectric tensor $\boldsymbol{\varepsilon}$, that determines reflectivity and refraction of light in the free-standing film of an antiferroelectric liquid crystal, is averaged over the film [9]. In general, the average $\boldsymbol{\varepsilon}$ is biaxial and gives rise to double refraction of the light in the film. The ellipsometric experiments were performed on the free-standing films to detect the phase shift between both partial refracted waves with perpendicular polarizations *s* and *p* [7]. The inverse surface of wave normals, which helps us to visualize the refraction of light at an interface of two media, is a complicated surface of the fourth degree. But the setup (fully described in [7,8]) and the geometry of the ellipsometric measurements were such that they simplify the evaluation of double refraction a lot. Light from a He-Ne laser was incident on a film under an angle $\theta_0 = 45°$ and linearly polarized with an azimuthal angle of 45° with respect to the plane of incidence. The external electric field was applied to the film parallel to the smectic layers and perpendicular to the plane of the light incidence which was so weak, that did not distort the structure but only fixed its orientation in space through the coupling with the residual permanent polarization of the liquid crystal film. By selecting such a geometry they had chosen just a special simple cross section of the inverse surface of the wave normals, a circle and an ellipse for two perpendicular components of polarizations, s and p, respectively. Considering the experimental geometry the following calculations are simplified much. Bearing in mind the angles that define the incidence of polarized light we see that s and p components of polarization in the incident light were equally shared and had the same phases.

If d is the film thickness, $\lambda_0 = 633$ nm is the free-space wavelength of the incident light and $n_{s,p}$ is the refractive index for refraction of s and p waves in the film under refraction angles $\theta_{s,p}$, then a phase difference that a particular wave gains at the passage through the film is [7,10]

$$\Delta_{s,p} = -\beta_{s,p} - \arctan\frac{r_{s,p}^2 \sin 2\beta_{s,p}}{1 - r_{s,p}^2 \cos 2\beta_{s,p}} \tag{1}$$

where $\beta_{s,p} = (2\pi d/\lambda_0)\sqrt{n_{s,p}^2 - \sin^2\theta_0}$ is the film phase thickness. Refraction indices $n_{s,p}$ and refraction angles $\theta_{s,p}$ are obtained as solutions of the law of refraction

$$\frac{\sin\theta_0}{\sin\theta_{s,p}} = n_{s,p}, \tag{2}$$

coupled to the nonlinear equations of the circular and elliptical cross sections of the inverse surface of the wave normals. In a chosen geometry the refractive index n_s for the s wave is independent of the refraction angle θ_s and equals the principal value n_1, which is the square root of the first eigenvalue of the average dielectric tensor,

$$n_s = n_1 = \sqrt{\varepsilon_1}. \tag{3}$$

For the p-wave determination of the refractive index n_p and refraction angle θ_p is nontrivial and numerical, from Eq. (2) and

$$\frac{1}{n_p^2} = \frac{\sin^2(\theta_p - \Theta_\varepsilon)}{n_3^2} + \frac{\cos^2(\theta_p - \Theta_\varepsilon)}{n_2^2}. \tag{4}$$

Two other principal values of the refractive index ellipsoid n_2 and n_3 are square roots of the second and the third eigenvalues of $\boldsymbol{\varepsilon}$, ε_2 and ε_3. An angle Θ_ε is the angle between the principal axis of the dielectric tensor, which corresponds to eigenvalue ε_3, and the normal to the smectic layers. The reflection coefficients $r_{s,p}$ are given by Fresnel formulas,

$$r_s = -\frac{\sin(\theta_0 - \theta_s)}{\sin(\theta_0 + \theta_s)}, \qquad r_p = \frac{\tan(\theta_0 - \theta_p)}{\tan(\theta_0 + \theta_p)}. \tag{5}$$

The phase shift between both partial waves is

$$\Delta = \Delta_s - \Delta_p \tag{6}$$

and can be evaluated.

At this point we shall briefly review the properties of the discrete model [4,6] and the properties of the film structures as proposed within the discrete model, with emphasis on the structure of the Sm-C_α phase. Assuming the system is homogeneous inside each layer and therefore disregarding the (x,y) dependence, in the discrete phenomenological model the ordering of the liquid crystal in the film with N layers is described by the set of N two-dimensional layer-tilt vectors $\boldsymbol{\xi}_i = (\xi_{i,x}, \xi_{i,y})$, which are the projections of the layer directors to the plane of the smectic layers. Magnitude of the tilt is described by the tilt angle Θ_i and the orientation of the layer tilt vector by the phase angle Φ_i. Index i stands for the ith layer. The following expression is formally correct if we take $\boldsymbol{\xi}_i = 0$ for $i < 1$ or $i > N$. Expansion of the free energy in the tilt order parameters $\boldsymbol{\xi}_i$ is [4–6]

$$\begin{aligned} G = \sum_{i=1}^{N} \Bigg[& \frac{1}{2} a_0 \boldsymbol{\xi}_i^2 + \frac{1}{4} b_0 \boldsymbol{\xi}_i^4 + \left(\frac{1}{4} a_1 + \frac{1}{4} c_1 \boldsymbol{\xi}_i^2 \right) \\ & \times (\boldsymbol{\xi}_{i-1} \cdot \boldsymbol{\xi}_i + \boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_{i+1}) + \frac{1}{8} a_2 (\boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_{i+2}) \\ & + \frac{1}{2} f (\xi_{i+1,x} \xi_{i,y} - \xi_{i,x} \xi_{i+1,y}) \Bigg]. \end{aligned} \tag{7}$$

The only temperature dependent parameter is $a_0 = a(T - T_0)$, a is positive and T_0 would be the temperature of the transition to the tilted phase if there was no interaction between the layers. Parameter b_0 is positive as always in the theory of the second order phase transitions. Terms with parameters a_1 and c_1 describe interactions between the nearest layers [6]. The coefficient f of the Lifshitz term is of chiral origin and equals zero in racemic mixtures or achiral compounds. The a_2 term is due to polar interactions between the next-nearest layers. If a_2 is positive, interactions between nearest and next-nearest layers compete, which may, as a frustration effect, lead to the appearance of the Sm-C_α phase in a certain temperature range.

In a bulk sample the structure of the Sm-C_α phase turns out to be characterized by the constant magnitude of the tilt, $\Theta_i = \Theta$, and by the rotation of the layer-tilt vector for a certain constant angle $\alpha = \Phi_{i+1} - \Phi_i$, as we proceed from the ith layer to the next. The angle α may have any value. The resulting helicoidal modulation of the structure, with a pitch that equals $2\pi/\alpha$ smectic layers, is a consequence of the competing nearest and next-nearest layers interactions alone, disregarding a weak additional modulation due to the eventual chirality of the liquid crystal. Due to the presence of the c_1 term in the free energy expansion [Eq.(7)], the structure of the Sm-C_α phase changes continuously, as the temperature is varied, if $c_1 < 0$ towards a ferroelectric with $\alpha = 0$ and if $c_1 > 0$ towards an antiferroelectric with $\alpha = \pi$. In the case of compound 12F1M7, decrease of temperature leads to the transition from the Sm-C_α phase to the ferroelectric phase. A temperature dependence of angle α in the bulk structure of the Sm-C_α phase is presented in Fig. 1.

In the following we shall concentrate on the systems with a limited number of smectic layers. When determining a temperature evolution of the film structure far from the Sm-$A \leftrightarrow$ Sm-C_α transition temperature, a constant amplitude approximation (CAA), assuming a constant magnitude of the tilt everywhere in the film, is adopted. Within the CAA the number of minimizing components of the tilt vector is reduced by two and replaced by the unique magnitude of the tilt Θ and $N-1$ phase angle differences $\alpha_i = \Phi_{i+1} - \Phi_i$. In the bulk sample α_i is the same everywhere as well as the magnitude of the tilt Θ, while in the finite size films there are discrepancies at the free surfaces, due to the fact that the surface layers may have neighboring layers, which they interact with, just on one side. As an example, the structure of

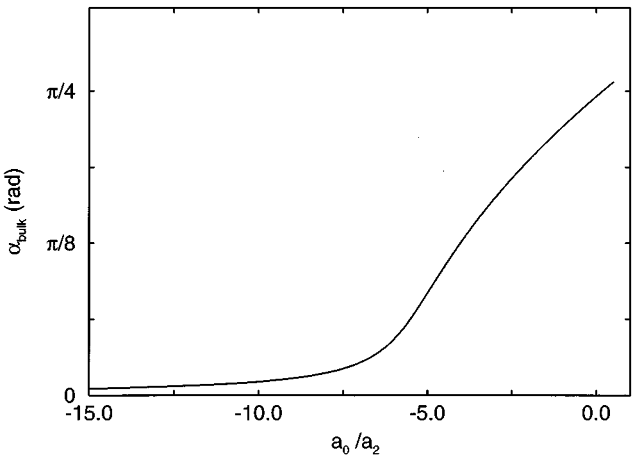

FIG. 1. Phase angle difference α in the bulk in dependence on normalized temperature a_0/a_2, for a set of model parameters corresponding to a compound 12F1M7, $a_1/a_2=-0.7$, $b_0/a_2=100$, $c_1/a_2=-5$, and $f/a_2=0.01$. The temperature of the Sm-A↔Sm-C_α phase transition corresponds approximately to $a_0/a_2=0.5$.

the Sm-C_α phase, as obtained within the CAA at different temperatures, is presented in Fig. 2. We may notice that the phase angle differences α_i in the major middle part of the film approach the bulk value α and are smaller at the surfaces. This effect is due to greater influence of the nearest-neighbor interactions at the surface layers, favoring ferroelectric ordering [see Eq. (7), $a_1<0$ in the case of compound 12F1M7], in comparison to the opposite next-nearest-neighbor interactions ($a_2>0$), because there is one less a_2 term in the free energy expansion (7) than there are a_1 terms.

Optical properties of the free-standing film are determined by the average dielectric tensor [9]. Once we know the structures of the phases appearing in the phase diagram we can easily find the average dielectric tensor for each of them and study the refraction of polarized light in the film, as well as predict the results of other optical experiments.

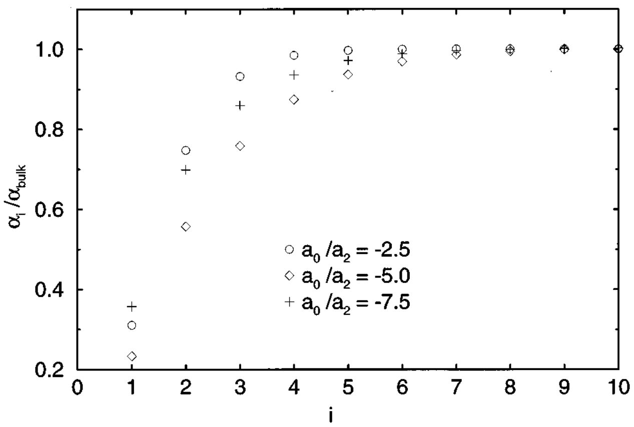

FIG. 2. The structure of the Sm-C_α phase, represented by the phase angle differences α_i, in a 122-layer film of compound 12F1M7, as obtained within the CAA at different temperatures. Phase angle differences α_i in the surface layers at the bottom side are shown only, the structure being symmetrical with respect to the middle of the film. In the middle of the film $\alpha_i\approx\alpha_{bulk}$ holds true.

The dielectric tensor $\boldsymbol{\varepsilon}_i$ in a particular layer is weakly biaxial with two of the three eigenvalues almost equal. Therefore in practice it may be considered as uniaxial [9,11] with eigenvalue $\varepsilon_\parallel$ corresponding to the eigenvector in a direction parallel to the long molecular axis and double eigenvalue $\varepsilon_\perp$ corresponding to two eigenvectors in a plane perpendicular to it. In a chosen laboratory frame orientation of the principal axis of the dielectric tensor in a layer is determined by the tilt and the phase angles Θ_i and Φ_i, which are the same as the angles that describe the layer tilt vector $\boldsymbol{\xi}_i$. The elements of the $\boldsymbol{\varepsilon}_i$ are

$$\varepsilon_{11}=\varepsilon_\perp+\tfrac{1}{2}(\varepsilon_\parallel-\varepsilon_\perp)\sin^2\Theta_i(1+\cos2\Phi_i),$$

$$\varepsilon_{22}=\varepsilon_\perp+\tfrac{1}{2}(\varepsilon_\parallel-\varepsilon_\perp)\sin^2\Theta_i(1-\cos2\Phi_i),$$

$$\varepsilon_{33}=\varepsilon_\perp\sin^2\Theta_i+\varepsilon_\parallel\cos^2\Theta_i,$$

$$\varepsilon_{12}=\varepsilon_{21}=\tfrac{1}{2}(\varepsilon_\parallel-\varepsilon_\perp)\sin^2\Theta_i\sin2\Phi_i,$$

$$\varepsilon_{13}=\varepsilon_{31}=(\varepsilon_\parallel-\varepsilon_\perp)\sin\Theta_i\cos\Theta_i\cos\Phi_i,$$

$$\varepsilon_{23}=\varepsilon_{32}=(\varepsilon_\parallel-\varepsilon_\perp)\sin\Theta_i\cos\Theta_i\sin\Phi_i. \tag{8}$$

The average dielectric tensor in the film is then

$$\varepsilon=\frac{1}{N}\sum_{i=1}^{N}\varepsilon_i. \tag{9}$$

To meet the available experimental data, which are the observed phase sequence in compound 12F1M7, used in ellipsometric experiments, as well as the temperature interval of stability of the Sm-C_α phase, we have chosen the model parameters $a_1/a_2=-0.7$, $b_0/a_2=100$, $c_1/a_2=-5$, and $f/a_2=0.01$. The choice is to a certain extent arbitrary due to the lack of additional information such as the temperature dependences of the magnitude of the tilt, the pitch in the bulk ferroelectric phase, the dielectric response, etc., in compound 12F1M7. Material parameters, also needed at evaluation of the phase shift Δ, are a thickness of a single layer $d_0=4.0$ nm and the principal refractive indices in the uniaxial Sm-A phase $n_\perp=1.477$ and $n_\parallel=1.60$.

Results of our theoretical predictions are presented in Figs. 3 and 4 for the film of 12F1M7 with $N=122$ smectic layers. Temperature dependence of the eigenvalues of the average dielectric tensor is shown in Fig. 3. The ferroelectric phase below the ferroelectric–Sm-C_α transition is almost uniaxial, exhibiting this fact in almost equality of the first two eigenvalues ε_1 and ε_2 of $\boldsymbol{\varepsilon}$ (deviations are due to chirality of the liquid crystal and resulting helicoidal structure of the ferroelectric phase). After the transition to the Sm-C_α phase, the structure distorts and the film becomes biaxial. How strong the biaxiality is depends on a twist of the structure. To get an insight into this phenomenon, a simplified picture of the Sm-C_α phase will serve: let us assume that the twist is regular, i.e., the phase angle difference α_i is the same all over the film. If the thickness of the film is a multiple of the pitch, the average dielectric tensor will be uniaxial and its longest axis will be parallel to the plane normal. Such situations correspond to the points where two of the eigenvalues are the same. But for all the other values of the pitch $\boldsymbol{\varepsilon}$ will

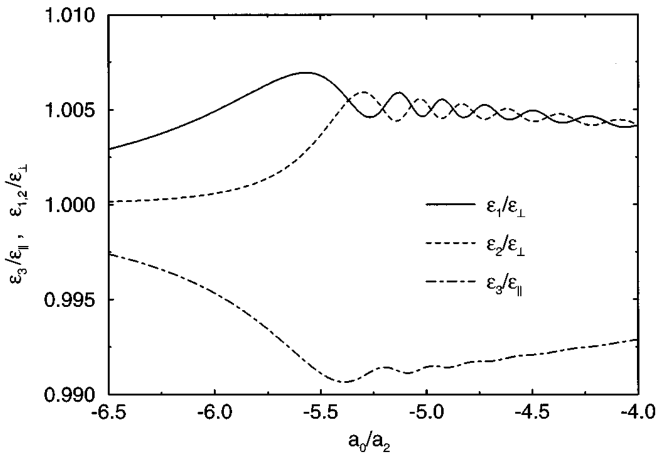

FIG. 3. The oscillatory dependence of the eigenvalues $\varepsilon_{1,2,3}$ of the average dielectric tensor on temperature (a_0/a_2) is presented for a free-standing film of compound 12F1M7 with 122 smectic layers.

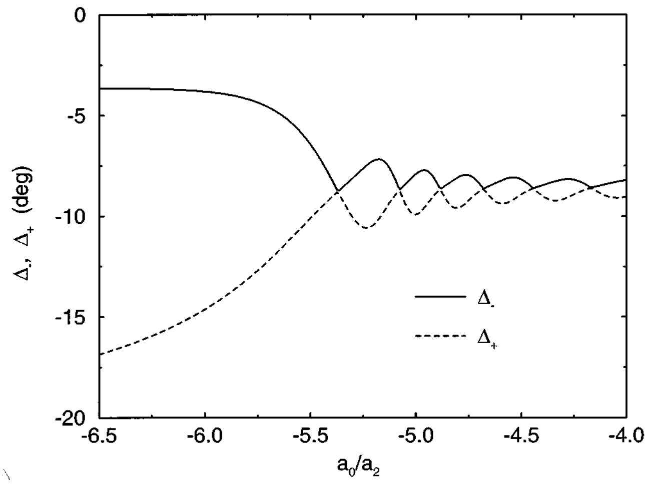

FIG. 4. Temperature dependences of the ellipsometric parameters Δ_- and Δ_+ are shown, which reflect oscillatory behavior of the dielectric tensor eigenvalues.

appear biaxial due to the residual nonclosed pitch. Since the pitch changes continuously by varying the temperature, $\boldsymbol{\varepsilon}$ also changes continuously and every time pitch is $1/m$th of the film thickness, $\boldsymbol{\varepsilon}$ is uniaxial. The closer to the ferroelectric phase, the longer pitch and residual nonclosed pitch characterize the structure of the Sm-C_α phase. Consequently oscillations of the eigenvalues of $\boldsymbol{\varepsilon}$ are more and more pronounced, as can be seen in Fig. 3.

How the phase shift Δ changes is, for two orientations of the longest principal axis of $\boldsymbol{\varepsilon}$, towards the incident light (Δ_-) and away from it (Δ_+), presented in Fig. 4. Switching between these two directions is induced by the external electric field, which couples with residual permanent polarization of the nonclosed pitch and which can be applied in two opposite directions perpendicular to the plane of the incidence. We may notice that the direction of the electric field does not affect the phase shift at temperatures where $\boldsymbol{\varepsilon}$ is uniaxial because there is no net polarization present in the film there. In general the phase shift reflects the oscillation behavior of $\boldsymbol{\varepsilon}$.

Out of two assumed structures of the Sm-C_α phase [3,4,6], the one with the planar structure [3] has been shown to be in disagreement with the symmetry properties of the higher temperature Sm-*A* phase [12]. Here we showed that the experimental data on the optical properties of smectic films are consistent with the short pitch helicoidal structure of the Sm-C_α phase, resulting from the discrete phenomenological model of antiferroelectric liquid crystals. The explanation of the proposed structure and optical properties of the Sm-C_α phase was given. Temperature evolution of the Sm-C_α phase as it influences the optical measurements was determined for a special case of the compound 12F1M7. Experimental data obtained by ellipsometry for the same liquid crystal seem to support the discrete model, nevertheless some further research is needed to prove its reliability.

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