

Ferroelectric-Antiferroelectric Phase Transition in a Two-Molecular-Layer Free-Standing Liquid-Crystal Film

Ch. Bahr and D. Fliegner

Iwan-N.-Stranski-Institute for Physical and Theoretical Chemistry, Technical University of Berlin, D-1000 Berlin 12, Germany
(Received 1 December 1992)

Free-standing films of a smectic liquid crystal possessing the bulk phase sequence smectic A , ferroelectric smectic C , antiferroelectric smectic C_A are studied. Using ellipsometric measurements, we show that the bulk phases still exist in films consisting of only four, three, and even two smectic layers, i.e., the phase transition from the ferroelectric smectic- C phase to the antiferroelectric smectic- C_A phase in the three- and two-layer films is characterized by the inversion of the tilt and polarization direction in a single smectic layer.

PACS numbers: 64.70.Md, 61.30.Eb, 77.80.Bh

The discovery of ferroelectricity in chiral smectic- C liquid crystals by Meyer *et al.* [1] has generated a lot of interest concerning these materials from both fundamental and technological points of view [2]. A smectic- C (Sm- C) liquid crystal is a fluid in which the rodlike molecules tend to align their long axes along a common direction, the so-called director, and form a one-dimensional density wave with a periodicity of about 1 molecular length. The director is inclined by a tilt angle θ with respect to the density wave vector. In many compounds the Sm- C phase undergoes at higher temperatures a phase transition to the Sm- A phase where θ equals zero. The density wave in Sm- C and Sm- A phases may also be described as an arrangement of the molecules in layers, the wave vector corresponding to the layer normal. If the molecules are chiral (i.e., without mirror plane), the reduced symmetry leads in the Sm- C phase to the appearance of a ferroelectric spontaneous polarization \mathbf{P}_s provided that a transverse permanent molecular dipole moment exists. The direction of \mathbf{P}_s is always normal to the plane containing the director \mathbf{n} and the layer normal \mathbf{z} . Depending on the molecular structure, $(\mathbf{z}, \mathbf{n}, \mathbf{P}_s)$ forms either a right-handed or a left-handed system, i.e., for a given compound only one of these possibilities is realized and the polarization direction is definitely coupled to the tilt direction [3].

Recently [4], three new modifications (Sm- C_A , Sm- C_α , Sm- C_γ) of the Sm- C phase were observed in the chiral compound MHPOBC [5] showing for the first time in liquid crystals antiferroelectric (Sm- C_A) and ferroelectric (Sm- C_α , Sm- C_γ) properties. The main argument for the antiferroelectricity of the Sm- C_A phase in MHPOBC consists of the electro-optic behavior in a dc electric field \mathbf{E} applied along the smectic layers: There are three clearly distinguishable states for $\mathbf{E} \gg 0$, $\mathbf{E} = 0$, and $\mathbf{E} \ll 0$ and field-induced transitions between these states occur discontinuously, afflicted with hysteresis, at well-defined threshold fields. On the basis of these results and results from x-ray and conoscopic studies [6], which showed that all three states are optically biaxial and that the molecules must be tilted in the layers, a structural model was

proposed which assumes, for the zero-field state, an alternation of the tilt direction (and thus of the spontaneous polarization direction) by $\pm 180^\circ$ when going from layer to layer. There is, however, no direct evidence that tilt and polarization in the Sm- C_A phase alternate really in this layer-by-layer fashion. On the other hand, such a structure was proved for another liquid-crystal phase, the so-called Sm- O phase which occurs in the compound MHTAC [7]. By studying thin (i.e., a few smectic layers thick) Sm- O films floating on the free surface of isotropic MHTAC droplets the layer-by-layer alternation of tilt and polarization in the Sm- O phase was confirmed [8,9]. It is not clarified, however, whether the Sm- O phase in MHTAC and the Sm- C_A phase in MHPOBC belong to the same phase type [10].

Free-standing films [11] provide samples with an exactly defined number of smectic layers and can be varied in thickness between thousands and only two layers. In this Letter, we present the first study of the Sm- C_A phase in free-standing films at the two-dimensional limit (i.e., in films only a few layers thick). Using ellipsometric measurements, we show that the bulk phase sequence Sm- A -Sm- C_A still exists in films consisting of only four, three, and even two molecular layers, i.e., at the Sm- C -Sm- C_A transition of the three- and two-layer film the tilt direction in a single smectic layer is inverted. Our results thereby strongly support the model of a layer-by-layer alternation of the directions of tilt and polarization in the Sm- C_A phase.

Our liquid-crystal sample consists of a 8:2 mixture [12] of R - and S -configured MHPOBC possessing the following bulk phase sequence: Sm- $C_A \leftarrow 114^\circ\text{C} \rightarrow$ Sm- $C \leftarrow 120^\circ\text{C} \rightarrow$ Sm- $A \leftarrow 150^\circ\text{C} \rightarrow$ isotropic. Free-standing films are prepared by drawing the liquid crystal in the Sm- A state across a $3 \times 12 \text{ mm}^2$ rectangular opening in a 0.15 mm thick glass plate. In a free-standing film, the smectic layers align parallel to the film surface and the film normal corresponds to the layer normal. The long sides of the hole are conductively coated and an electric field can be applied along the film plane in order to align the tilt direction in the ferroelectric Sm- C phase by fixing

the polarization direction by the external field.

The principles of our measurement are the same as in previous ellipsometric studies of free-standing films [13-15]. The film is maintained in a one-stage oven (temperature stability ≈ 0.05 K) which allows transmission of the beam of a HeNe laser ($\lambda = 633$ nm) through the film under an angle of incidence of 45° . The incident light is linearly polarized with an azimuth of 45° with respect to the plane of incidence, i.e., the *s*- and *p*-polarized components of the incident light have the same values of amplitude and phase. Using a null ellipsometer in the PCSA configuration [16] we determine the phase difference $\Delta = \Delta_p - \Delta_s$ between the *s* and *p* components of the transmitted light. The experimental details of our measurement are given in [15].

The value of Δ is in general a complicated function of the refractive indices of the liquid crystal, the angle of incidence, the wavelength, the film thickness, and the tilt of the optical axis of the film. For thin films (below ≈ 12 smectic layers) and zero tilt (i.e., in the Sm-*A* phase), Δ is nearly proportional to the film thickness. Since the film thickness *h* is quantized as $h = Nd$ (*d* being the thickness of a single Sm-*A* layer and *N* an integer), the Δ values of thin Sm-*A* films are also quantized. By measuring many thin films (in our case ≈ 40), one can easily construct a Δ vs *N* diagram and thereby determine the number of smectic layers of a given film in a similar way as by the often used reflectivity method [11].

At the transition from the Sm-*A* to the Sm-*C* phase the director, and thus the optical axis of the film, tilts within the plane of incidence either towards the incoming laser beam or away from it, depending on the polarity of the applied dc orienting field. The value of Δ will be either increased or decreased compared to the Sm-*A* phase. In our experiment, we determined the temperature dependence of Δ for both polarities, i.e., for each film two data sets, $\Delta_+(T)$ and $\Delta_-(T)$, were produced (cf. Fig. 1). After the drawing of each film a small dc electric field (6 V/cm) was applied. The films were observed through a telescope while they were allowed to thin to uniform thickness. We started each measurement near the Sm-*A*-isotropic transition temperature (150°C) lowering the

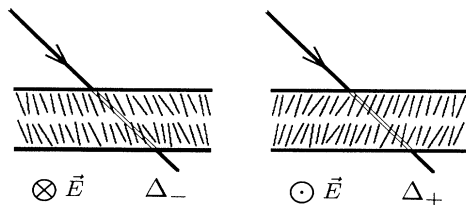


FIG. 1. Experimental geometry for measuring Δ_+ and Δ_- (shown here for a two-layer film). Depending on the polarity of the orienting field **E**, the molecules (and thus the optical axis) tilt in the Sm-*C* phase either towards (Δ_-) or away from (Δ_+) the incident laser beam.

temperature [17] at a rate of 0.25 K/min while the computer controlled ellipsometer continuously determined the Δ values; each run was repeated with the opposite polarity of the applied orienting field [18].

Figure 2 shows the temperature dependence of Δ_+ and Δ_- for a four-layer film. For $T > 136^\circ\text{C}$, the Δ values are constant and there is no influence of the polarity of the orienting field as is expected for the Sm-*A* phase. At 136°C obviously the transition to the Sm-*C* phase takes place: Depending on the polarity of the applied orienting field either a decrease (Δ_+) or an increase (Δ_-) of the Δ values occurs, corresponding to a tilt of the optical axis either away from or towards the incoming laser beam. The tilt process seems to take place in two steps: Some degrees kelvin below the first occurrence of a tilt at 136°C a second sudden decrease (increase) of Δ is discernible. From earlier studies [13,14] of the Sm-*A*-Sm-*C* transition in the compound DOBAMC [19] it is known that in free-standing films—when the temperature is lowered starting in the Sm-*A* phase—first the two surface layers tilt (at a temperature about 20-30 K above the bulk temperature) while all interior layers remain untilted. Thus, our results for the four-layer film indicate that at 136°C the two surface layers of the film start to tilt and at 127°C the two interior layers. It is remarkable that in our four-layer film the interior layers show a distinct separate transition whereas in a four-layer film of DOBAMC the tilt in the interior layers seems to set in smoothly without a distinct transition [13,14].

On cooling the four-layer film further, another phase transition, characterized by an abrupt discontinuous

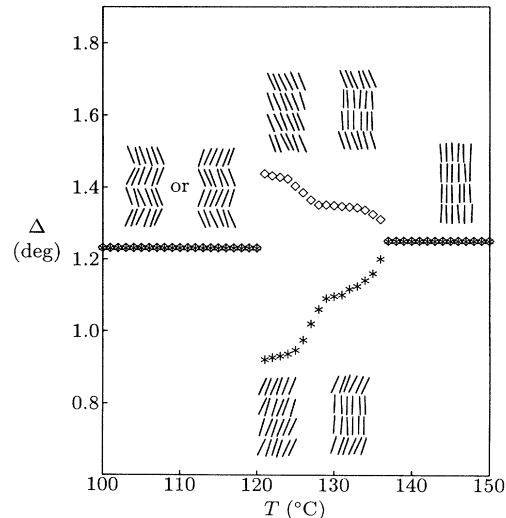


FIG. 2. Temperature dependence of the phase difference Δ for a four-layer film of MHPOBC (8:2 mixture of *R* and *S* enantiomer) and schematic drawings of the corresponding molecular arrangements in the Sm-*A* ($T > 136^\circ\text{C}$), Sm-*C* ($121^\circ\text{C} < T < 136^\circ\text{C}$), and Sm-*C_A* phase ($T < 121^\circ\text{C}$); * symbols correspond to Δ_+ and \diamond symbols to Δ_- (cf. Fig. 1).

change of Δ , occurs at 120°C . Below 120°C , the difference between Δ_+ and Δ_- vanishes again, the amount of Δ then being similar (but not equal) to the value of the Sm-A phase. Two observations indicate that this phase has a structure proposed for the antiferroelectric Sm- C_A phase: First, optical observation of the film by the eye using polarized reflected light microscopy clearly shows that a tilt of the molecules must be present within the layers because typical defects like π walls [20] are frequently observed in this phase [21]. Second, because the polarity of the orienting field has no effect, there is obviously no net spontaneous polarization as is expected if two layers tilt to one direction and the other two layers tilt to the opposite direction. In principle we cannot distinguish between the case that each two adjacent layers of the four-layer film exhibit the same tilt direction and the case that the tilt direction alternates in a layer-by-layer fashion. On the other hand, the results reported in the following for the three- and a two-layer film strongly support the assumption of a layer-by-layer alternation.

Figure 3 shows the temperature dependence of Δ for a three-layer film. The phase sequence Sm-A-Sm-C transition in the interior layer as in the case of the four-layer film; obviously, the immediate proximity of the two free surfaces induces a tilt in the interior layer simultaneously to the tilt in the surface layers.

The three-layer film shows, as the four-layer film, a second phase transition at a lower temperature (125°C) characterized by a discontinuous jump of the Δ values; in contrast to the four-layer film, the polarity of the orienting field has still a significant influence on the amount of Δ . This is exactly what is to be expected for a three-layer film (or any film with an odd number of layers), which must always retain a nonzero net spontaneous polariza-

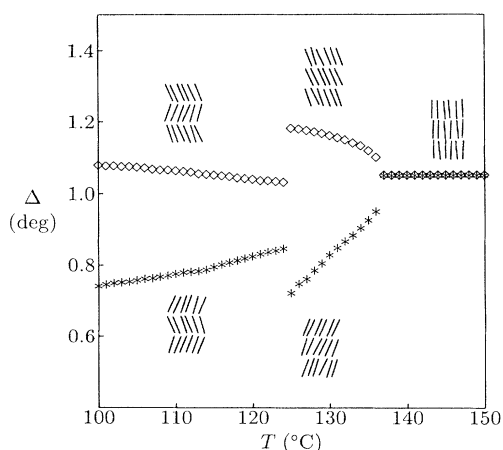


FIG. 3. Temperature dependence of Δ_+ (* symbols) and Δ_- (\diamond symbols) for a three-layer film and schematic drawings of the corresponding molecular arrangements in the Sm-A ($T > 137^\circ\text{C}$), Sm-C ($125^\circ\text{C} < T < 137^\circ\text{C}$), and Sm- C_A phase ($T < 125^\circ\text{C}$).

tion (if the tilt direction of all layers is restricted to be within a common plane). The behavior of Δ_+ and Δ_- below 125°C is thus consistent with a phase transition where the tilt in two of the three smectic layers remains in the direction favored by the orienting field while the tilt in a *single* smectic layer turns to the opposite direction thereby leading to a layer-by-layer alternation of the tilt.

In Fig. 4 our results for a two-layer film are shown. Obviously, all three phases are still present: At 142°C the transition from Sm-A to Sm-C takes place, Δ showing the usual splitup in different values of Δ_+ and Δ_- . At 130°C both Δ_+ and Δ_- show an abrupt change and the difference between their values vanishes, i.e., the polarity of the orienting dc field has no effect (as is expected for films with an even number of smectic layers). Optical observation of the film indicates again the presence of a tilt. Thus, the two-layer film also shows, by inverting the tilt direction in a single smectic layer, a phase transition from the ferroelectric Sm-C phase to the antiferroelectric Sm- C_A phase.

Comparing the transition temperatures of the two-layer film and the bulk sample it is obvious that both the Sm-A-Sm-C and the Sm-C-Sm- C_A transitions are shifted considerably to higher temperatures in the free-standing film. The shift of the Sm-A-Sm-C transition (22 K) is comparable to the behavior found in earlier studies [13, 14] of the compound DOBAMBC and can be understood as a result of the ordering field of the free surface; this effect (the stabilization of the low-temperature phase by the surface field) is frequently observed for phase transitions in free-standing liquid-crystal films. However, the interactions which lead to the transition from the Sm-C to the Sm- C_A phase require the existence of adjacent smectic layers. A free surface may therefore be expected to suppress or, at least, not to stabilize the Sm- C_A phase. On the other hand, we can expect that the Sm- C_A phase appears when the tilt angle in the Sm-C phase exceeds a certain value (the Δ values in the Sm-C phase just above the transition to the Sm- C_A phase correspond in all three

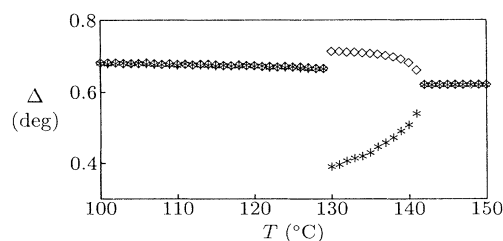


FIG. 4. Temperature dependence of Δ_+ (* symbols) and Δ_- (\diamond symbols) for a two-layer film. The amount of Δ in the Sm- C_A phase ($T < 130^\circ\text{C}$) is larger than expected: In the first approximation, it should amount to the mean of the Δ_+ and Δ_- values of the Sm-C phase. We have no explanation why we find experimentally a significantly larger value.

films to a tilt value of 15° – 20° [22]), i.e., since the surface-induced shift of the Sm-*A*–Sm-*C* transition temperature is coupled to a shift of the whole tilt versus temperature function, it is likely to produce also a shift of the Sm-*C*–Sm-*C_A* transition temperature.

In conclusion, we have presented an ellipsometric study of thin free-standing films of a liquid crystal showing the phase sequence smectic-*A*–ferroelectric smectic-*C*–antiferroelectric smectic-*C_A*. This phase sequence is still present in films consisting of only two smectic layers, the temperatures of both transitions being shifted to higher values. We find that the transition from the ferroelectric smectic-*C* phase to the antiferroelectric smectic-*C_A* phase takes place in three- and two-layer films by inverting the tilt and polarization direction of a single smectic layer. Our results thereby strongly support the structural model of a layer-by-layer alternating tilt direction proposed for the bulk smectic-*C_A* phase.

This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 335). It is a pleasure to thank G. Heppke for stimulating discussions and his always kind and encouraging support. Thanks are also due to D. Löttsch and M. Wolff for supplying us with both enantiomers of MHPOBC.

-
- [1] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. (Paris)*, Lett. **36**, L69 (1975).
- [2] For recent reviews, see, e.g., K. Skarp and M. A. Handschy, *Mol. Cryst. Liq. Cryst.* **165**, 439 (1988); S. T. Lagerwall, N. A. Clark, J. Dijon, and J. F. Clerc, *Ferroelectrics* **94**, 3 (1989).
- [3] In a very small number of compounds the polarization direction in the ferroelectric Sm-*C* phase is temperature dependent and undergoes an inversion at a certain temperature; see J. S. Patel and J. W. Goodby, *Philos. Mag. Lett.* **55**, 283 (1987).
- [4] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **28**, L1265 (1989).
- [5] MHPOBC is the 4-(1-methylheptyloxy)phenyl-ester of 4-octyloxybiphenyl-4'-carboxylic acid.
- [6] E. Gorecka, A. D. L. Chandani, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **29**, 131 (1990).
- [7] MHTAC is the 1-methylheptylester of terephthalidene-bis-4-aminocinnamic acid.
- [8] Y. Galerne and L. Liebert, *Phys. Rev. Lett.* **64**, 906 (1990).
- [9] Y. Galerne and L. Liebert, *Phys. Rev. Lett.* **66**, 2891 (1991).
- [10] A recent study has shown that the Sm-*C_A* phase and the Sm-*O* phase show complete miscibility in a binary phase diagram of MHPOBC and MHTAC. This is a strong indication for structural likeness; G. Heppke, P. Kleineberg, D. Löttsch, S. Mery, and R. Shashidhar, *Mol. Cryst. Liq. Cryst.* (to be published).
- [11] C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **40**, 773 (1978).
- [12] We are using this partly racemic mixture and not the optically pure enantiomer of MHPOBC because the pure enantiomers show a more complicated phase sequence with two additional phases in which we are not interested in this study; a direct Sm-*C*–Sm-*C_A* transition is obtained only in the partly racemic mixture [H. Takezoe, J. Lee, A. D. L. Chandani, E. Gorecka, Y. Ouchi, A. Fukuda, K. Terashima, and K. Furukawa, *Ferroelectrics* **114**, 187 (1991)]. Since the transition temperatures do not change within 0.2 K during successive runs of a given film, a demixing process does not seem to occur.
- [13] S. Heinekamp, R. A. Pelcovits, E. Fontes, E. Y. Chen, R. Pindak, and R. B. Meyer, *Phys. Rev. Lett.* **52**, 1017 (1984).
- [14] S. M. Amador and P. S. Pershan, *Phys. Rev. A* **41**, 4326 (1990).
- [15] Ch. Bahr and D. Fliegner, *Phys. Rev. A* **46**, 7657 (1992).
- [16] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, Amsterdam, 1989).
- [17] In a few cases we carried out heating runs and obtained the same results as for cooling runs. However, because films have to be drawn in the Sm-*A* phase (to avoid defects), we performed almost only cooling runs.
- [18] We should note here that switching the polarity of the orienting field in the Sm-*C* and Sm-*C_A* phase causes a change of Δ corresponding exactly to the difference between Δ_+ and Δ_- measured at constant polarity. Because switching created additional defects, we carried out rather two successive runs with constant polarity, then a single run in the presence of a switching orienting field.
- [19] DOBAMBC is the 2-methylbutylester of 4-decyloxybenzylidene-4'-aminocinnamic acid.
- [20] J. MacLennan, *Europhys. Lett.* **13**, 435 (1990).
- [21] These defects can lead, if they appear in the part of the film which is transmitted by the laser beam, to an irregular scattering of the measured Δ values. The number of defects seems to depend strongly on the film thickness: Whereas in two- and three-layer films only few defects appear, they make about half of the measurements of four-layer films useless. In films thicker than four layers, they practically prevent correct measurements in the Sm-*C_A* phase.
- [22] These are only approximate tilt values. A more exact determination of the tilt from the Δ values would require the knowledge of the refractive indices and the spacing of a single Sm-*A* layer which we have not measured yet.