

# Structural transitions in thin free-standing films of an antiferroelectric liquid crystal exhibiting the smectic- $C_\alpha^*$ phase in the bulk sample

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Optical reflectivity studies have been conducted upon thin free-standing films of an antiferroelectric liquid crystal possessing the bulk phase sequence  $\text{Sm } C_A^* \text{-Sm } C_\alpha^* \text{-Sm } A$ . Electrically induced field independent and field dependent structural transformations were observed above the bulk  $\text{Sm } C_A^* \text{-Sm } C_\alpha^*$  transition temperature. The anisotropy of the reflectivity was measured for different states in thin films. Our data provide direct evidence of structures without the short-pitched helix in the temperature region between the antiferroelectric  $\text{Sm } C_A^*$  and untilted  $\text{Sm } A$  structures.

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## I. INTRODUCTION

Up to 1989 one polar structure composed of chiral molecules was found in liquid crystals. In the ferroelectric smectic- $C^*$  ( $\text{Sm } C^*$ ) phase [1] the molecules arrange in parallel layers in which the average orientation of the long molecular axes is tilted from the layer normal by an angle  $\theta$ . The spatial variation of the molecular tilt direction (tilt plane) is characterized by the azimuthal angle  $\phi$ . The direction of the in-layer spontaneous ferroelectric polarization  $\vec{P}$  is perpendicular to the tilt plane. Molecular chirality induces a change of the azimuthal angle  $\phi$  from layer to layer and a helical macrostructure is formed. The helical pitch in the  $\text{Sm } C^*$  phase is so much longer than the layer spacing that the azimuthal angle  $\phi$  is practically the same in adjacent layers (synclinc ordering,  $\Delta\phi=0$ ). Unlike the  $\text{Sm } C^*$  phase, the molecules in the  $\text{Sm } C_A^*$  structure [2] tilt in the opposite directions in adjacent layers (anticlinc structure,  $\Delta\phi=180^\circ$ ). The anticlinc ordering leads to antiferroelectricity (AF), because net spontaneous polarization cancels out.

Since the discovery of the  $\text{Sm } C_A^*$  and several  $\text{Sm } C^*$ -like phases (subphases) [2,3], it has become evident that multiple structures with polar ordering of smectic layers may exist in liquid crystals. In particular, the unusual  $\text{Sm } C_\alpha^*$  phase [2,3] may appear just below the untilted nonpolar  $\text{Sm } A$  phase. On the low-temperature side, it adjoins one of the several  $\text{Sm } C^*$ -like phases [3]:  $\text{Sm } C_A^*$  [ $\text{Sm } C_A^*(q=\frac{1}{2})$ ],  $\text{Sm } C_\gamma^*$  [ $\text{Sm } C_A^*(q=\frac{1}{3})$ ], AF [ $\text{Sm } C_A^*(q=\frac{1}{4})$ ], and  $\text{Sm } C^*$  [ $\text{Sm } C_A^*(q=0)$ ]. It could be assumed that the structure of the  $\text{Sm } C_\alpha^*$  subphase is intermediate between the structures of the fundamental  $\text{Sm } C^*$ ,  $\text{Sm } C_A^*$ , and  $\text{Sm } A$  phases. Several models have been proposed for the  $\text{Sm } C_\alpha^*$  phase [3–5]. In these models the  $\text{Sm } C_\alpha^*$  phase appears as a result of competing interactions, each stabilizing synclinc or anticlinc ordering. In the first explanation, based on the one-dimensional Ising model [3,4], only coplanar structures were assumed with both synclinc and anticlinc orientations of the molecules in adjacent layers. This assumption resulted from the

structure of the fundamental  $\text{Sm } C^*$  and  $\text{Sm } C_A^*$  phases in which the minima of energy correspond to the same direction of the tilt plane of the molecules ( $\Delta\phi=0^\circ$  or  $180^\circ$ ). In a “clock” (X-Y) model [5] intermediate orientations of the molecules are allowed with  $\Delta\phi\neq 0$  or  $\Delta\phi\neq 180^\circ$  between adjacent layers. This leads to the structure with a very short pitch of about several smectic layers. If the temperature changes, both  $\theta$  and  $\phi$  change continuously. The possibility of such ordering was shown in optical microscope observations of thin droplets [6,7].

Recent experiments [8–13] revealed various aspects of macro- and micro-structures of the  $\text{Sm } C_\alpha^*$  phase. Near the  $\text{Sm } C_\alpha^* \text{-Sm } A$  transition temperatures the sign and value of circular dichroism are the same in the  $\text{Sm } C_\alpha^*$  and the untilted  $\text{Sm } A$  phases [8]. Based on these observations a conclusion was made about macrostructure of the  $\text{Sm } C_\alpha^*$  phase: the circular dichroism results not from the structural helical pitch, as in the  $\text{Sm } C^*$  and  $\text{Sm } C_A^*$  phases, but from long wavelength fluctuation helical modes (“dynamical helical structure” in [8]), as in the nonhelical  $\text{Sm } A$  phase. On the other hand, resonant x-ray diffraction gave evidence for the short-pitch helical microstructure with periodicity from five to eight layers in the  $\text{Sm } C_\alpha^*$  phase [9,10]. These results on the  $\text{Sm } C_\alpha^*$  phase were confirmed by optical reflectivity and ellipsometry measurements [11–13] and are consistent with the “clock” model [5]. Bahr *et al.* [14] studied the  $\text{Sm } C_\alpha^*$  phase in free-standing films with the number of smectic layers  $N\geq 8$ . The results on thick films were interpreted [15] on the base of the short-pitch helicoidal structure. It should be noted, however, that to date there are no data about the microstructure of the  $\text{Sm } C_\alpha^*$  phase found between the antiferroelectric  $\text{Sm } C_A^*$  and  $\text{Sm } A$  phases.

Of particular interest is the investigation of the liquid crystalline phases in ultrathin films. It is known that the restricted geometry and surface ordering strongly influence the phase transitions. For the subphases it is not even clear whether they may appear in the films with thickness of a few layers that is the order of the period of their microstructures. Theoretical calculations for thin films, derived within the dis-

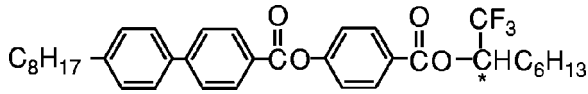


FIG. 1. Molecular structure of TFMHPBC. An asterisk indicates the chiral center.

crete phenomenological model, predict a possible existence of the  $\text{Sm } C_{\alpha}^*$  phase even for materials exhibiting only the  $\text{Sm } C^*$  ( $\text{Sm } C_A^*$ ), and  $\text{Sm } A$  phases in the bulk sample. It was predicted [16,17] that besides the  $\text{Sm } C_{\alpha}^*$  phase structures without the short-pitched helix appear in thin films below the transition from the  $\text{Sm } A$  phase.

In this paper we report the studies of thin free-standing films in a compound exhibiting the  $\text{Sm } C_A^*$ ,  $\text{Sm } C_{\alpha}^*$ , and  $\text{Sm } A$  phases in the bulk sample. The measurements of optical reflectivity of linearly polarized light enable us to observe structural transformations and determine the optical anisotropy of the film. A sequence of phases without any short-pitched helix is shown to appear above the  $\text{Sm } C_A^*$  phase in thin free-standing films. In the electric field experiment, the behavior of these structures depends on film thickness and differs in films with odd and even number of layers.

## II. EXPERIMENT

Experiments were carried out on the free-standing films of chiral TFMHPBC [3], whose chemical structure is given in Fig. 1. The bulk material has the following phase sequence:  $\text{Sm } C_A^*$ -(74.3 °C)- $\text{Sm } C_{\alpha}^*$ -(75.0 °C)- $\text{Sm } A$ . Free-standing films were prepared in a temperature controlled oven. The films were drawn across a 0.4-cm-diameter hole in a glass plate. In such films the smectic layers are parallel to the film surface. The electric field was applied to the film parallel to the smectic layers to align the structure. In our experiment, we may change the direction of both the light polarization and the electric field within the plane of the film. The film thickness was determined by optical reflectivity measurements. The incident light was perpendicular to the film surface (backward reflected light was observed). For thin films, the reflectivity is proportional to the number of layers  $N$  squared [18],

$$I \approx [\pi N d (n^2 - 1) / \lambda]^2, \quad (1)$$

where  $d$  is the thickness of a smectic layer ( $d \approx 3$  nm),  $n$  the refractive index, and  $\lambda$  the free-space wavelength. The knowledge of the exact number of layers in the film is essential for our measurements. Thus, first we prepared several thin films (more than five) of unknown thickness and measured their optical reflectivity. The number of layers was determined by comparing ratios among reflected intensities with ratios among different integers squared. After determining the reflectivity for several different film thicknesses, we were able to prepare the film with known  $N$ . The  $\text{Sm } C_A^*$  structure is optically anisotropic in the plane of the film. The larger refractive index  $n_{\parallel}$  is for light polarized in the tilt plane, and the smaller one  $n_{\perp}$  for a light polarized perpendicularly to the tilt plane. In the  $\text{Sm } C_A^*$

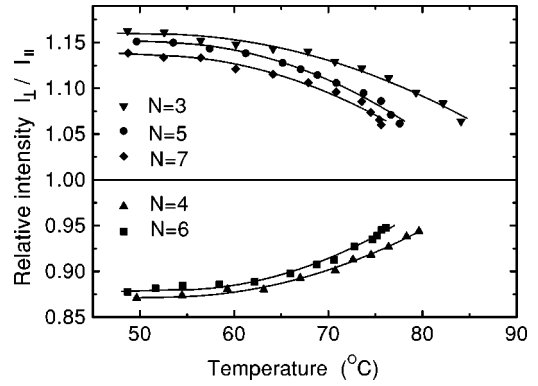


FIG. 2. Relative optical reflectivity ( $I_{\perp}/I_{\parallel}$ ) vs temperature for thin films in the  $\text{Sm } C_A^*$  phase.  $I_{\perp}$  and  $I_{\parallel}$  are reflectivities for the light polarization perpendicular and parallel to the direction of the electric field.

phase, the two reflected intensities were measured for the light polarizations parallel  $I_{\parallel}$  and perpendicular  $I_{\perp}$  to the direction of the electric field. As the refractive index  $n_{\parallel} > n_{\perp}$  ( $n_{\perp}$  is the ordinary refractive index), the reflected intensity is larger for the light polarization parallel to the tilt plane. The measurement of the reflectivity with the linearly polarized light gives information about the optical anisotropy in the plane of the film and about the orientation of the tilt plane with respect to the electric field.

## III. EXPERIMENTAL RESULTS

First we measured the optical reflectivity in the oriented  $\text{Sm } C_A^*$  phase. These measurements are needed not only for the investigation of the  $\text{Sm } C_A^*$  phase but also for studies of the transitions at higher temperatures, as the change of the reflectivity at the transition is determined by the reorientation of the tilt planes with respect to the field direction. Figure 2 shows the temperature dependence of the relative reflected intensities  $I_{\perp}/I_{\parallel}$ , where  $I_{\perp}$  is the reflectivity for the light polarization perpendicular to the direction of the electric field and  $I_{\parallel}$  is the reflectivity for the light polarization parallel to the electric field. The measurements gave two types of dependencies for the relative reflected intensities. In films with an odd number of layers, the reflected intensity is larger for the light polarization perpendicular to the direction of the electric field ( $I_{\perp}/I_{\parallel} > 1$ ). In films with  $N$  even, inverse behavior is observed ( $I_{\perp}/I_{\parallel} < 1$ ). The odd/even effect in the intensity (Fig. 2) is connected with nonzero transverse and longitudinal polarizations, respectively, in odd- and even-layer films [19,20]. According to the model of Link and co-workers [19,20] an alternation of the polarization direction in neighboring layers leads to zero transverse polarization in  $N$ -even films; however, net surface longitudinal polarization  $P_L$  is nonzero. Conversely, transverse net polarization  $P_T$  is nonzero for  $N$  odd and equal to the polarization of a single layer  $P_1$ , but, as the molecules near surfaces tilt in the same direction, net longitudinal polarization is zero [19]. So longitudinal polarization in  $N$ -even films leads to the orientation of the tilt plane parallel to the field direction ( $I_{\perp}/I_{\parallel} < 1$ , Fig. 2). Transverse polarization in  $N$ -odd films leads to the orien-

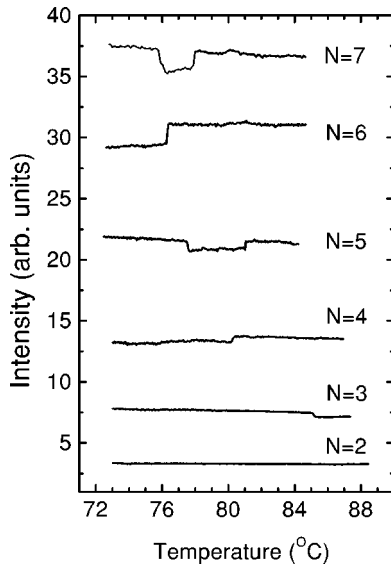


FIG. 3. Reflectivity from thin films at high temperatures. The light polarization is perpendicular to the electric field (50 V/cm). Films with  $N$  even ( $N > 2$ ) show one transition, while films with  $N$ -odd show two transitions (for a three-layer film the second transition could be observed at  $96^\circ\text{C}$ ). Temperature of the transitions (steps in the reflectivity, upward in  $N$  even and downward in  $N$  odd) increases with decreasing the film thickness. The ramp rates are 0.3 K/min.

tation of the tilt plane perpendicular to the electric field direction ( $I_\perp/I_\parallel > 1$ , Fig. 2). An increase in  $I_\perp/I_\parallel$  for  $N$ -odd (a decrease in  $I_\perp/I_\parallel$  for  $N$  even) films (Fig. 2) results from the surface ordering. The higher tilt angle  $\theta$  at the film surfaces than that in the interior layers leads to an increase in the reflection anisotropy in thinner films. As  $P_L < P_T$  [19], due to the chirality, the contribution to the net longitudinal polarization resulting from the rotation of the transverse polarization from layer to layer should be taken into account in antiferroelectric films [21]. For a six-layer film with helical pitch of 100 smectic layers ( $\Delta\phi = 3.6^\circ$ ) this part of the longitudinal polarization should be about  $0.18P_1$ . At the same time an additional in-plane spontaneous polarization that is parallel to the tilt plane emerges at each smectic layer boundary [22]. The transverse polarization changes its sign from layer to layer and the parallel one does so from boundary to boundary. In  $N$ -even films this parallel polarization may give rise to nonzero net longitudinal polarization.

Figure 3 shows the temperature dependence of the reflected intensity for linearly polarized light at higher temperatures. In the bulk  $\text{Sm} C_A^*$  temperature region no pronounced features in the intensity were observed in thin films. The transitions are shifted above the bulk transition temperature. This shift is correlated with the phase transitions between smectic phases in which the surface ordering effect leads to the increase of the transition temperature [23–25]. The change of the reflectivity at the steps (Fig. 3) is connected with the reorientation of the tilt planes with respect to the direction of the electric field. Two different behaviors were observed in  $N$ -odd and  $N$ -even films: whereas the first low-temperature step in  $N$ -odd films leads to the decrease of

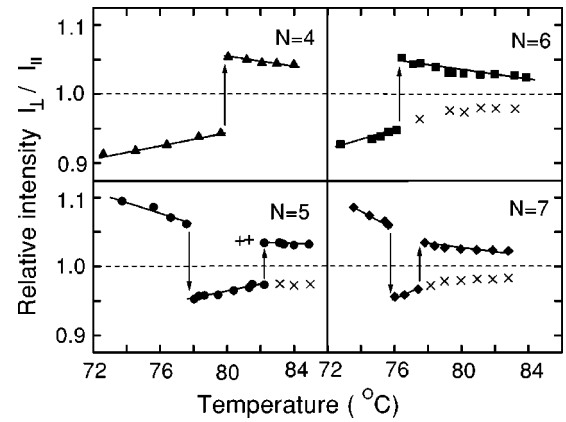


FIG. 4. Relative optical reflectivity  $I_\perp/I_\parallel$  in the temperature range of the transitions. The arrows indicate transitions on heating. Solid symbols stand for data obtained at the electric field 35 V/cm. Crosses show the results at low ( $\times$ ) and high ( $+$ ) electric field values.  $N$  is the number of smectic layers. Points with  $I_\perp/I_\parallel > 1$  ( $I_\perp/I_\parallel < 1$ ) correspond to structures with transverse (longitudinal) polarization.

the intensity, it increases in  $N$ -even films. Another distinguishing feature of the transitions is the number of the steps. In the  $N$ -odd films there is a second high-temperature transition with the increase of the intensity (in the  $N=3$  film, this transition occurs above  $96^\circ\text{C}$  in the high electric field, 600 V/cm). In thin  $N$ -even films one transition was observed except for the superthin two-layer film in which no abrupt change was found in the temperature range of the film stability (up to  $98^\circ\text{C}$ ).

The questions arise, about the anisotropy and the relative orientations of the tilt planes in different layers (with or without the short-pitched helix) in the phases above the  $\text{Sm} C_A^*$  temperature range. To answer these questions, we measured the anisotropy of the reflected intensity for these structures (Fig. 4). The main result is that the anisotropy exists in the whole temperature range of the tilted structures. The smooth decrease of the anisotropy with temperature is connected with the decrease of the tilt angle. The temperatures of the first low-temperature transitions practically do not depend on the electric field. This means that the transitions are only determined by the intrinsic structure of the film. By contrast, at higher temperatures the reflectivity and the transition temperatures depend on the electric field.

The examples of the electric field dependence of the reflected intensity are given in Fig. 5 for a five-layer film. Two states were observed in the electric field [Fig. 5(a)]. The film can be switched between these structures by changing the electric field. These states correspond different change of the intensity to the  $90^\circ$  switch of the field in the film plane [Fig. 5(b)]. The lower field state (Fig. 5, state 1) has the longitudinal electric polarization ( $I_\parallel > I_\perp$ ), and the film changes into state 2 with transverse polarization ( $I_\perp > I_\parallel$ ) at a higher field. The change in the type of dominant net polarization is illustrated in Fig. 6. The field at which the film structure changes between states with transverse and longitudinal polarization is determined by a step in the relative reflection intensity  $I_\perp/I_\parallel$ . The stepwise transitions take place with hysteresis in

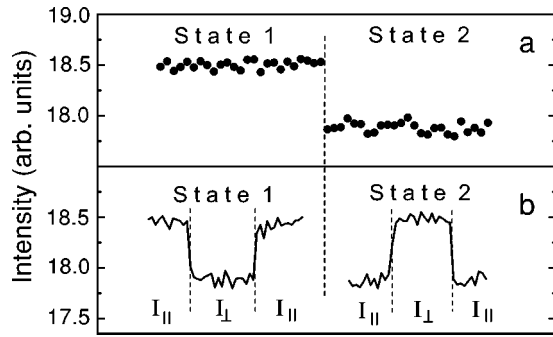


FIG. 5. Reflected intensity (solid circles) for light polarized parallel to the field direction  $I_{\parallel}$  (a). Two states are observed in the electric field: state 1 (low field state) and state 2 (high field state). Transition from state 1 to state 2 on increasing the electric field is followed by a decrease of the reflected intensity  $I_{\parallel}$  (a). Optical response on the  $90^\circ$  switching of the electric field orientation differs in the two states (b). In state 1 the tilt plane is parallel to the field direction, in state 2 the tilt direction is perpendicular to the electric field. Measurements were carried in electric fields 23 V/cm (state 1) and 45 V/cm (state 2).  $N=5$ ,  $T=81.3^\circ\text{C}$ .

the electric field. The closed symbols in Fig. 6 denote the transition at increasing field; decreasing  $E$  leads to the reciprocal transition but at lower fields (open symbols). There is no universal behavior for films of different thickness. In a five-layer film the field magnitude for reorientation increases considerably with decreasing temperature. In a six-layer film the reorienting field changes smoothly in the high-temperature range and then decreases abruptly at about  $78.6^\circ\text{C}$ . In the lower temperature state the field-induced

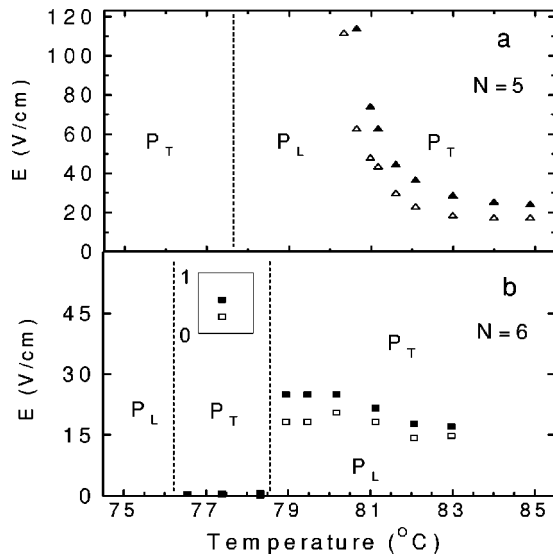


FIG. 6. Temperature dependence of the field-induced transitions from longitudinal to transverse polarization (solid symbols, increasing field) and from transverse to longitudinal polarization (open symbols, decreasing field) for five- and six-layer films. The inset for the  $N=6$  film shows the data at  $77.5^\circ\text{C}$  on an enlarged scale from 0 to 1 V/cm. The dotted lines indicate the transitions on change of the temperature.  $P_L$  and  $P_T$  are longitudinal and transverse polarizations, respectively.

transition is observed at extremely small voltages. The inset of Fig. 6(b) shows the data at  $77.5^\circ\text{C}$  on an enlarged scale. The step in voltage inducing reorientation may indicate the change in the film structure at  $78.6^\circ\text{C}$ .

#### IV. DISCUSSION

Reflectivity of the linearly polarized light gives information about the azimuthal orientation of molecules in the smectic films. According to the “clock” model the  $\text{Sm} C_A^*$  has a structure with very short helical pitch. Films with such structure should be almost uniaxial in the plane of the film if the pitch is of the order of or less than the film thickness. Optical anisotropy may exist, but its value should be essentially less than that in the  $\text{Sm} C_A^*$  phase. We consider two possible scenarios of the transition to the structure with a short pitch: continuous and discontinuous changes of azimuthal angles. When the azimuthal angles change continuously, the reflectivity anisotropy should vanish ( $I_{\perp}/I_{\parallel}=1$ ) as the helical pitch becomes about twice the film thickness. At further increasing  $\Delta\phi$  the anisotropy appears again but its value  $|I_{\perp}/I_{\parallel}-1|$  should be essentially less than that in the  $\text{Sm} C_A^*$  phase. We did not observe such continuous evolution of the reflectivity (Fig. 4). The smooth decrease of the anisotropy  $|I_{\perp}/I_{\parallel}-1|$  on heating is connected with the well-known decrease of the angle  $\theta$  in tilted phases above the bulk transition [23,26]. At discontinuous transition to the short-pitch structure the anisotropy above the transition may exist both with  $I_{\perp}/I_{\parallel}>1$  and  $I_{\perp}/I_{\parallel}<1$ , but again its magnitude should be considerably smaller than that in the  $\text{Sm} C_A^*$  structure before the transition. The change of the anisotropy at the transition should also depend on the film thickness. In the experiment we observed only a small change of the reflectivity anisotropy  $|I_{\perp}/I_{\parallel}-1|$  at the transition (Fig. 4). In this way, our data are inconsistent with the short-pitch structure above the  $\text{Sm} C_A^*$  phase. From the change of the anisotropy we may evaluate the lower bound of the helical pitch in the temperature range above the transition. Its value is more than 50 layers. Consequently, the directions of molecular tilt in different layers may be considered coplanar as in the Ising type model of the  $\text{Sm} C^*$ -like phases. Points with  $I_{\perp}/I_{\parallel}>1$  ( $I_{\perp}/I_{\parallel}<1$ ) correspond to structures with transverse (longitudinal) polarization.

Figure 7 shows the temperature of the first low-temperature transition  $T_N$  vs the film thickness. As noted above, these temperatures do not practically depend on the value of the electric field. As in the case of layer-by-layer [25] and thinning [27] transitions in thin smectic films, the data in Fig. 7 can be fitted with a power law expression  $N=N_0[T_0/(T_N-T_0)]^\beta$ . The fit yields for  $\beta=0.46\pm 0.04$ . For the quantitative description of the thickness dependence of transitions in antiferroelectric films, the theory should be developed considering the discrete structure of the films with surface ordering. Now we only may speculate that the transitions occur when at heating the tilt angle  $\theta$  in the interior of the film reaches some critical value  $\theta_c(0)$ . The tilt angle in the center of the film  $\theta(0)$  may be represented by the average tilt  $\theta_a$  in the film [23,28],



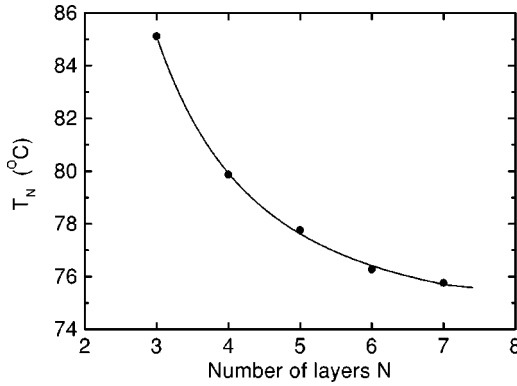


FIG. 7. Temperatures of low-temperature transitions vs film thickness. The solid line is a power law function  $N=N_0[T_0/(T-T_0)]^\beta$ .  $\beta=0.46$ .

$$\theta(0) = \theta_a \frac{dN}{2\xi} \frac{1}{\sinh(dN/2\xi)}, \quad (2)$$

where  $\xi$  is the bulk correlation length of  $\theta$ . From our reflectivity data it follows that the reflectivity anisotropy  $|I_\perp/I_\parallel - 1|$  is practically the same before the first transition (about 0.06). This means that the transitions occur at about the same average tilt angle  $\theta_a$ . On the assumption that  $\theta_c(0)$  are the same at the transitions,  $N/\xi$  should be constant at the transition temperatures  $T_N$  [Eq. (2)]. So, at  $T_N$  the correlation length  $\xi$  and  $N$  in various films should follow the same behavior. The correlation length  $\xi$  is usually described by a power law function of temperature  $\xi(T) = \xi_0 [T^*/(T - T^*)]^\alpha$ . It is well known that fluctuation modes result in pretransitional phenomena. The optical activity due to fluctuations in the SmA phase of chiral compounds may be described with an exponent for the correlation length  $\alpha$  of about 0.5 [29]. Consequently, the temperature dependence of the low-temperature transitions correlates with the temperature behavior of the correlation length. Our consideration is simplified, but gives a qualitative agreement with experiment.

The average tilt  $\theta$  in the film is easily determined from the optical reflectivity data. The details of the calculation of the tilt angle for anticlinic and synclinic structures can be found in [30]. For these calculations we used the value of birefringence  $\Delta n = n_e - n_\perp$  ( $n_e$  is the extraordinary index) [31] for molecules whose shapes are similar to those of TFMHPBC. Figure 8 shows the average tilt angle as a function of temperature for 2-, 4-, and 7-layer films. The average tilt increases with decreasing film thickness. This means that the surface ordering is essential at the transition in anticlinic structure, as it is for the SmC\*-SmA phase transition (synclinic structure). Large value of the tilt in the  $N=2$  film and its smooth temperature dependence mean that the transition to the untilted state is shifted far above the temperature of the bulk transition. Sharper decrease of  $\theta$  in thicker films is mainly determined by decreasing of the tilt angle in the interior layers. As mentioned above, this means that on heating transitions should start in the interior of the film.

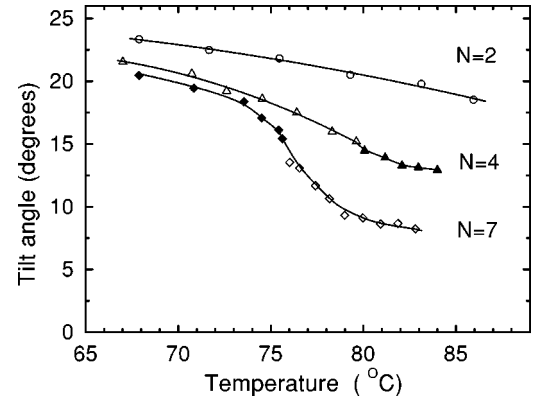


FIG. 8. Temperature dependence of the tilt angle  $\theta$  resulting from optical reflectivity data for two-, four-, and seven-layer films. Open and solid symbols are for structures with longitudinal and transverse polarization, respectively.

Transitions should be connected with the  $180^\circ$  reorientation of the tilt direction in single layers and formation of synclinic interlayer structures in the film. Some possible structures of three-, four-, five-, and six-layer films at high temperature are shown in Fig. 9(a)–(d). Common feature of the first transition is the change of the tilt plane orientation in the electric field (Fig. 3 and 4). In a three-layer film there is only one structure with formation of single synclinic pair [Fig. 9(a)]. In this structure the surface layers tilt in the opposite directions and the film has the longitudinal polarization as observed in the experiment. For a four-layer film the structure forming a synclinic pair in the interior of the film is shown in Fig. 9(a). This structure has no longitudinal polarization (the same tilt direction in the surface layers), but should possess transverse polarization due to the difference in the tilt magnitude (and hence polarization) in the surface and interior layers. The structure with transverse polarization was observed actually (Fig. 4).

More complex situation is in thicker films in which successive transitions to different structures in the interior of the film may take place. In a five-layer film the heating leads to the transition to a state with longitudinal polarization. This state is observed at low external field over a wide tempera-

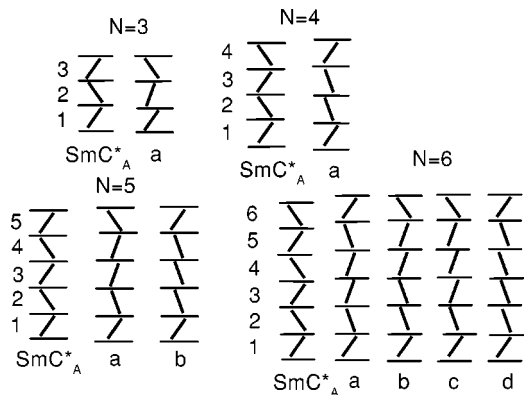


FIG. 9. Schematic representation of the anticlinic ( $\text{Sm}C_A^*$ ) phase and structures at higher temperatures (a,b,c,d) in films with three, four, five, and six layers.

ture range (Fig. 6). The structures with longitudinal and transverse polarization are shown in Fig. 9(a) and (b). The field required to switch between the states with different polarization increases with decreasing temperature. This behavior is connected with the temperature change of the local minima of the energy for synclinc and anticlinc order and of the relative value of the longitudinal and transverse polarization. In a six-layer film we observed the transition to the state with transverse polarization. However at small heating the state with the longitudinal polarization becomes the low-field state. There are several structures with transverse [Fig. 9(a) and (d)] and longitudinal [Fig. 9(b) and (c)] polarization having different number of synclinc pairs. We assume that the sharp change of the reorientation field of more than 20 times at 78.6 °C [Fig. 6(b)] is connected with the transition between two states with longitudinal polarization with different values of the energy minima and polarization. For thick films in the high temperature range the low-field states show longitudinal polarization. This behavior is similar to that of materials without the  $\text{Sm} C_A^*$  phase in the bulk sample [20]. In a recent paper by Chao *et al.* [32] field-induced transitions were investigated above the bulk  $\text{Sm} C^*$ - $\text{Sm} A$  transition temperature. They observed synclinc state in the temperature interval of more than 5 K above the bulk  $\text{Sm} C^*$  phase. In this temperature range no reorientations of the tilt plane were observed. In the same temperature range above the  $\text{Sm} C_A^*$  phase we observed transitions from the state with transverse polarization to the state with the longitudinal polarization and conversely. At the same time at higher temperatures the behavior of the field-induced transitions is similar to that observed in [32], in spite of the difference in the bulk phase sequences. According to the model proposed in Ref. [33] above the bulk  $\text{Sm} C^*$ - $\text{Sm} A$  transition temperature the state with longitudinal polarization results from the interaction between the polarization fluctuations near the film surfaces. The nature of the long-range interactions above the  $\text{Sm} C_A^*$  phase is not well understood by now.

Ellipsometry and optical reflectivity studies [11,13] gave evidence for the short-pitched structure of the  $\text{Sm} C_A^*$  phase

in thick films. It was suggested that two sets of anticlinc surface layers exist near the film surfaces. The  $\text{Sm} C_A^*$  phase in the investigated compounds emerges above the  $\text{Sm} C^*$  or the  $\text{Sm} C_{F12}^*$  phases. Oscillations of both optical reflectivity and ellipsometry data as functions of temperature observed in [11,13] are due to the temperature variations of the short-pitched helix. In thin films we observed transitions from the  $\text{Sm} C_A^*$  phase to other structures without the short-pitched helix. In the discrete phenomenological model [5,17] the short-pitch structure results from the competition between nearest-neighbor and next-nearest-neighbor layers interactions. This structure may appear above the  $\text{Sm} C_A^*$  phase when the order parameter reaches some small value. At least several molecular layers are needed for realization of the “clock” structure. Upon heating the tilt angles reach small values at first only in the center layers, and are too large near the surfaces due to the surface ordering. Furthermore, the variation of the tilt angle results in the large polarization near the surfaces and the polarization-induced charges [33]. In our opinion these prevent the formation of the short-pitch structure in thin films.

In summary, we report optical investigations of thin free-standing films of a material possessing the  $\text{Sm} C_A^*$  phase in the bulk sample. Stepwise transitions with the change of the film orientation were observed at high temperature. The temperatures of the transitions increase with decreasing film thickness. The measured values of optical anisotropy provide evidence that temperature and field-induced states above the  $\text{Sm} C_A^*$  phase possess structures without any short-pitched helix.

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