PHYSICAL REVIEW E, VOLUME 65, 010704(R)

Surface structures and transitions in the smectic-C* phase of one chiral liquid crystal compound

X. F. Han,[1] D. A. Olson,[1] A. Cady,[1] J. W. Goodby,[2] and C. C. Huang[1]
[1]*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455*
[2]*Department of Chemistry, University of Hull, Hull HU67RX, United Kingdom*
(Received 21 September 2001; published 19 December 2001)

Three optical probes have been employed on free-standing films to study surface structure and transitions of the SmC* phase of one liquid crystal compound. While the interior layers show the SmC* structure, the tilt in adjacent surface layers is found to be anticlinic. The number of anticlinic surface layers grows rapidly as the transition to the SmC^*_{FI2} phase is approached.

DOI: 10.1103/PhysRevE.65.010704 PACS number(s): 61.30.Gd, 77.84.Nh

Because of their well-aligned layers with a wide range of thicknesses, free-standing liquid crystal films have provided a unique system to study surface phenomena, bulk structures, and reduced dimensionality effects on phase transitions. Compared to the solid-air interfaces, which usually induce disorder, the surfaces of free-standing liquid crystal films in general favor lower-temperature order. Enhanced surface order has been demonstrated by numerous experimental investigations [1,2]. While enhanced surface order and surface structures are interesting in their own right, they are also important for the study of bulk structures using free-standing films. Recently Schlauf and Bahr [3] have employed ellipsometry to study the ordering in thin free-standing films in two compounds and have shown the occurrence of a sudden 180° rotation in the tilt azimuthal angle (tilt inversion) in single layers near the surfaces. They found that this tilt inversion transition exhibited a large thermal hysteresis and could occur at different temperatures for the two surfaces. To further study these phenomena, we employed differential optical reflectivity (DOR) [4], null transmission ellipsometry (NTE) [5], and depolarized reflected light microscopy (DRLM) [6] on the liquid crystal compound 12F1M7 (see Fig. 1).

Using pyroelectric effect, Shtykov *et al.* have reported the following transition sequence: SmA (94.2 °C) SmC^*_α (92.9 °C) SmC* (91.7 °C) FiLC (84.6 °C) SmC^*_{FI2} (80.3 °C) SmC^*_{FI1} (77.7 °C) SmC^*_A [7]. However, no specific feature of the SmC^*_α phase is given. In the FiLC phase, the pyroelectric signal as a function of the applied electric field shows two regions of steep increase, which are separated by a slow change region. Using our optical probes on free-standing films, first, we have clearly identified the SmC^*_α phase. Second, in the temperature window between the SmC^*_α and SmC^*_{FI2} phases, we characterize the phase as a SmC* phase with a short optical pitch, which is about 75 layers (300 nm). Third, upon cooling we have observed a rapid growth of the surface layers with an anticlinic arrangement between adjacent layers as the sample approaches the SmC^*_{FI2} phase.

In our DOR approach, linearly polarized laser light is reflected off the free-standing film. It is separated into two beams, the *P* and *S* components, by a polarizing beam splitter. Two currents, i_p and i_s, proportional to the intensity of these two components are produced by two similar photodetectors. To significantly reduce the common-mode noise, the difference of the two currents is taken immediately after the photodetectors. Then three currents, $i_p - i_s$, i_p, and $-i_s$, are converted to voltages. Lock-in amplifiers are used to measure the differential reflectivity $I_p - I_s$ and the total reflectivity $I_p + I_s$, where *I* represents voltage. A detailed description of our DOR has been reported [4].

Details of our NTE system are described in a recent paper [8]. In the polarizer-compensator-sample-analyzer configuration of our NTE, Δ measures the phase difference between the *P* and *S* components of the incident light, which is necessary to produce a linearly polarized light after the film. Ψ is the polarization angle of this linearly polarized light. The uniqueness of our technique is that a set of eight electrodes uniformly spaced around the hole creates an in-plane smoothly rotatable electric field. For a film with a net in-plane polarization, the whole structure can be rotated smoothly about the layer normal. In our experiment usually an electric field of 3 V/cm is applied. This field is too small to distort the internal structure or induce any flow in the film. Compared to the ellipsometer designed by another research group [9], in which the electric field can only be applied in two opposite directions, our approach is capable of giving us more optical information of the sample.

DRLM is another optical technique that enables us to directly visualize the average *c*-director of tilted liquid crystal phases. It is also very sensitive to the change of this direction. The capability of DRLM has been demonstrated by the extensive work of Link [10].

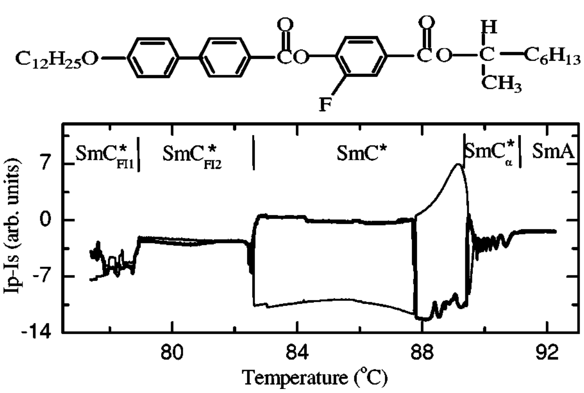

FIG. 1. Temperature dependence of the differential optical reflectivity from a 156-layer film on cooling: thick line: $E = +2$ V/cm: thin line: $E = -2$ V/cm. Electric field was applied in the incident plane.

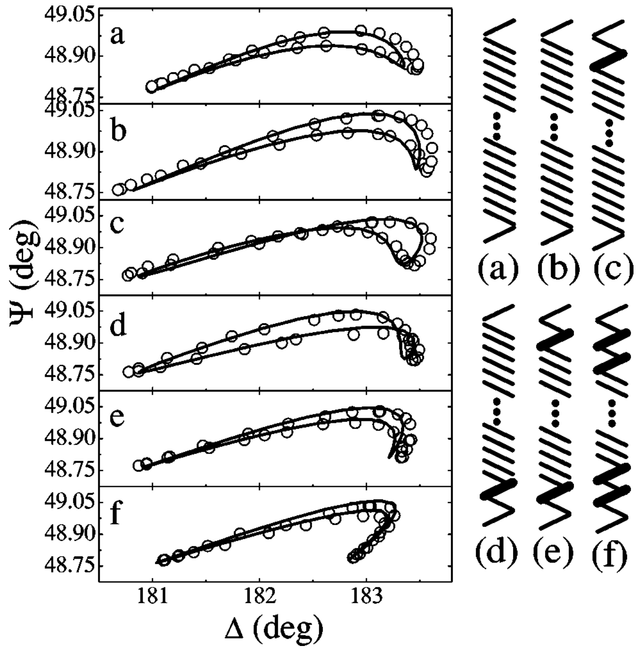

FIG. 2. The Ψ vs Δ data (circles) and simulations (solid lines) for 24-layer films of 12F1M7. The data in (a) were taken at 87.0 °C. The others were at 85.0 °C. The corresponding tilt directions of the smectic layers used in the simulation are shown schematically in the cartoon. Starting from the structure in (a), there is no surface transition in (b). The third layer from the top and the third layer from the bottom are inverted in (c) and (d), respectively. In (e) and (f) two and four surface layers are inverted, respectively. The layers that invert their tilt directions are depicted with heavier lines.

Many films with thicknesses ranging from 14 to 465 layers have been studied using our DOR, NTE, and DRLM. The phase diagram can be determined using the DOR data obtained under opposite orientations of applied electric field. The data from a 156-layer film upon cooling are shown in Fig. 1. Below the SmA phase, the characteristic oscillations in $I_p - I_s$ [11] indicates the existence of the SmC$^*_\alpha$ phase. The SmC* phase is identified by the large difference in $I_p - I_s$ signal found under opposite electric field, which is consistent with its ferroelectric nature [12]. In the SmC$^*_{FI2}$ phase, within the four-layer unit cell there exists a 180° rotational symmetry [13]. Thus the $I_p - I_s$ signal remains almost the same upon field orientation reversal. In the SmC$^*_{FI1}$ phase, we always encounter numerous domain walls and defect lines in the film and obtain noisy signals. These DOR data acquired upon cooling yield the following phase sequence: SmA (91.0 °C) SmC$^*_\alpha$ (89.5 °C) SmC* (82.7 °C) SmC$^*_{FI2}$ (79.0 °C) SmC$^*_{FI1}$.

While these temperature ramps are capable of detecting phase changes, we would like to acquire more detailed information of the molecular arrangements in the temperature window of the SmC* phase, in which the FiLC phase was identified by previous studies on bulk samples. Employing our NTE, we have performed detailed studies with two different procedures. (a) The film was heated up to 100 °C in the SmA phase, and cooled to a lower temperature, where data were taken while the electric field was rotated through 360° with 12° steps. To check reproducibility, an opposite sense of rotation of the field was performed. The above procedure was repeated many times on the same film. One 22-layer and two 24-layer films were studied in this way. (b) The film temperature was decreased from 87 °C with a step size of 0.1 K or 0.25 K into the SmC$^*_{FI2}$ phase region. At each temperature, we took data while rotating electric field through 360° with 12° or 22.5° steps. The whole procedure was repeated three times for each of three films with thicknesses of 14, 109, and 130 layers.

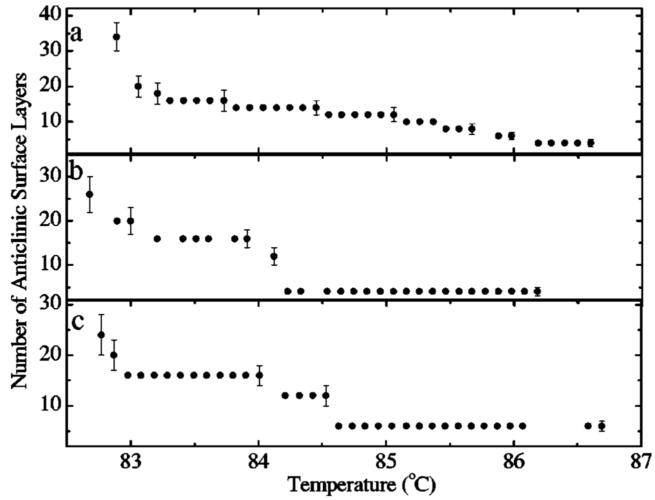

FIG. 3. The total number of anticlinic surface layers vs temperature in the SmC* phase for a 109-layer film from three separate cooling runs described in the text. In one plot, data with the same value have the same error bars. For clarity, error bar is shown only for one of them.

Simulations of our NTE results are done using the 4×4 matrix method [14], in which each layer is modeled as a uniaxial slab with extraordinary index of refraction (n_e) along the long axis of the molecule, and ordinary index of refraction (n_o) along the other two principal axes. n_e, n_o and layer spacing are measured in the SmA phase [9]. The tilt profile is assumed to be $\theta_j = (\theta_{\rm surf} - \theta_{\rm bulk})\cosh([2j-(N-1)](N/2\lambda)/(N-1))/\cosh(N/2\lambda) + \theta_{\rm bulk}$, where $\theta_{\rm surf}$, $\theta_{\rm bulk}$, N, and λ are the surface tilt, bulk tilt, film thickness, and extrapolation length, respectively [15]. Both N and λ have the unit of layer spacing. The index j denotes the layer number.

As shown in Fig. 1, in the SmC$^*_\alpha$ phase, the $I_p - I_s$ data change little under the inversion of the electric field. This is similar to what Johnson *et al.* observed in another compound [16]. Such behavior indicates that the arrangement of the surface layers is anticlinic between adjacent layers. This suggests that the surface layers in the SmC* phase should also have such arrangements. From comparison of simulation to our NTE results, we have found that the anticlinic surface layer structure matches the data much better than the synclinic one. We have also found that the SmC* phase has a short optical pitch of 75 layers (300 nm).

For the first 24-layer film, we cycled the film from 100.0 °C to 87.0 °C six times using method (a) described

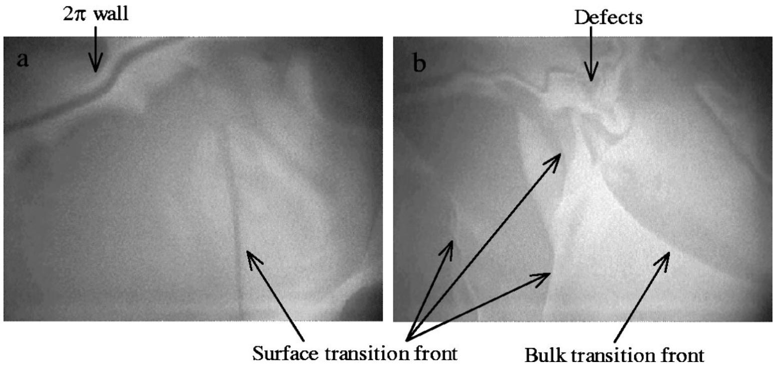

FIG. 4. Video frames from a 60±10 layer film. There is a 1 K/cm temperature gradient in the film. (a) shows the surface transition at 86 °C. The front moves slowly to the left, the hotter side. (b) shows the bulk transition from the SmC* phase to SmC^*_{F12} phase near 83 °C. This transition changes the defects dramatically and moves quickly to the hotter side.

above. At 87.0 °C, one set of Ψ versus Δ data was obtained upon rotating the electric field. The data from one of such runs are shown in Fig. 2(a) as circles [17]. At 87.0 °C a similar behavior was also observed for the 22-layer film, where the data were identical during all 15 runs. However, cooling this 24-layer film from 100.0 °C to 85.0 °C, we have observed four different metastable states at 85.0 °C after repeating the procedure six times. The results are shown in Fig. 2(b), (c), (e), and (f) as circles. They appeared 2, 2, 1, and 1 time(s), respectively. The data in Fig. 2(d) are from the second 24-layer film. The simulation results using the corresponding tilt structure in the cartoon of Fig. 2 are presented as solid lines. For the five states at 85.0 °C, θ_{bulk}, θ_{surf}, λ and the optical pitch were assumed to be 22°, 26°, 5 layers and 75 layers, respectively. Moreover, the simulations were done under the constraint that only the surface state was allowed to be changed as shown in the cartoon. The data in Figs. 2(a) and 2(b) are very similar, indicating that during this cooling, the surface state did not change. In (c), (d), (e), and (f) of the cartoon, the anticlinic surface layers grow by inverting single layers in the surfaces. Although the fit is not perfect, the simple physical picture that explains all the features of the data is still worth being emphasized. Due to our limited repeated times of the experiment and the complexity of this first order tilt inversion transition, we did not observe two metastable states between (e) and (f).

Figure 3 shows the temperature dependence of the total number of anticlinic surface layers in the SmC* phase from simulating both Ψ and Δ data acquired from a 109-layer film using method (b) described above [18]. The three plots are from the three separate cooling runs. Surface transition occurs when there is a change of the total number of surface layers. The data also show that tilt inversion transitions are not reproducible upon cooling. In the run corresponding to Fig. 3(a), we have observed the growth of the anticlinic surface layers by inverting single layers when the temperature is between 83.0 °C and 86.0 °C. In the other two runs, such a growth is replaced by larger changes in the number of surface layers. Near the transition to the SmC^*_{F12} phase, surface transitions become more significant. Around 82.7 °C [19], the total number of anticlinic surface layers can be as large as 34±4. Although our data can be well modeled by the SmC* phase with anticlinic surface layers, at temperatures near the SmC^*_{F12} phase we cannot rule out the possibility that the arrangement of the surface layers is SmC^*_{F12} type whose structure has been given by Johnson *et al.* [13].

Our DRLM observations support our conclusion that in thick free-standing films between the SmC^*_{α} and SmC^*_{F12} phases, the structure is the SmC* phase with anticlinic surface layers and there are surface transitions. In the study of a 60±10 layer film [20], a field of 0.6 V/cm was applied. The temperature was decreased from 100 °C to 70 °C at a rate of 0.07 K/min. Nine transitions were observed in the SmC* phase window. A video frame of the one that occurred at 86 °C is shown in Fig. 4(a). There was a temperature gradient of 1 K/cm in the film. In Fig. 4, the left-hand side is hotter. We observed that the front of these nine transitions moved slowly from the colder side to the hotter side. They had a small effect on defect structures and brightness of the image, which indicated that the change of the overall optical properties was small. For comparison, a transition observed near 83 °C is shown in Fig. 4(b). This transition changed defect structures dramatically and moved quickly across the film. Thus, we believe that the former ones are due to surface transitions that involve a few layers and the latter is due to the bulk transition from the SmC* to SmC^*_{F12} phase. Moreover, in Fig. 4(b) there are three surface transitions, indicating that more surface transitions occurred as the transition to the SmC^*_{F12} phase was approached on cooling.

In conclusion, from our DOR, NTE, and DRLM studies on free-standing films of 12F1M7 with thicknesses ranging from 14 to 465 layers, we have found that the structure between the SmC^*_{α} and SmC^*_{F12} phase is the SmC* phase with coexistent anticlinic surface layers. With decreasing temperature, the anticlinic surface layers grow from the surfaces toward the interior of the film. The rapid growth of the number of surface layers near the SmC*-SmC^*_{F12} transition may suggest some pretransitional phenomena. Also in this temperature window, whether the short pitched SmC* phase can explain the pyroelectric effect observed by Shtykov *et al.* [7] is not known yet.

The research was supported in part by the National Science Foundation, Solid State Chemistry Program, under Grants Nos. DMR-9703898 and 9901739.

[1] Ch. Bahr, Int. J. Mod. Phys. B **8**, 3051 (1994).
[2] T. Stoebe and C. C. Huang, Int. J. Mod. Phys. B **9**, 2285 (1995).
[3] D. Schlauf and Ch. Bahr, Phys. Rev. E **57**, R1235 (1998).
[4] S. Pankratz, P. M. Johnson, and C. C. Huang, Rev. Sci. Instrum. **71**, 3184 (2000).
[5] R. M. A. Azzam and N. M. Bashara. *Ellipsometry and Polarized Light* (North Holland, Amsterdam, 1989).
[6] R. Pindak, C. Y. Young, R. B. Meyer, and N. A. Clark, Phys. Rev. Lett. **45**, 1193 (1980).
[7] N. M. Shtykov, J. K. Vij, R. A. Lewis, M. Hird, and J. W. Goodby, Phys. Rev. E **62**, 2279 (2000).
[8] P. M. Johnson, D. A. Olson, S. Pankratz, Ch. Bahr, J. W. Goodby, and C. C. Huang, Phys. Rev. E **62**, 8106 (2000).
[9] Ch. Bahr and D. Fliegner, Phys. Rev. A **46**, 7657 (1992).
[10] D. R. Link, Ph.D. thesis, University of Colorado at Boulder, 1998.
[11] D. A. Olson, S. Pankratz, P. M. Johnson, A. Cady, H. T. Nguyen, and C. C. Huang, Phys. Rev. E **63**, 061711 (2001).
[12] The jump at 87.8 °C as seen in Fig. 1 is not due to phase transition. In the SmC* and SmC^*_α phases, when the net polarization passes zero as the helical pitches evolve with temperature, the whole film structure reorients by 180°. This reorientation causes the jump [11].
[13] P. M. Johnson, D. A. Olson, S. Pankratz, T. Nguyen, J. W. Goodby, M. Hird, and C. C. Huang, Phys. Rev. Lett. **84**, 4870 (2000).
[14] D. W. Berreman, J. Opt. Soc. Am. **62**, 502 (1972); H. Wöhler, G. Haas, M. Fritsch, and D. A. Mlynski, J. Opt. Soc. Am. A **5**, 1554 (1988).
[15] K. Binder, *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Liebowitz (Academic, London, 1986), Vol. 8; P. O. Andreeva, V. K. Dolganov, C. Gors, R. Fouret, and E. I. Kats, Phys. Rev. E **59**, 4143 (1999).
[16] P. M. Johnson, S. Pankratz, P. Mach, H. T. Nguyen, and C. C. Huang, Phys. Rev. Lett. **83**, 4073 (1999).
[17] While both Ψ and Δ are dependent on the orientation of the field, in practice we have found that the Ψ versus Δ plot is more useful in detecting the structural change.
[18] No detailed optical data were acquired in the temperature range between 86.6 °C and 89.5 °C. However, our data from $T > 89.5$ °C (in the SmC^*_α) and $T < 86.6$ °C (in the SmC*) yield anticlinic surface layers. Thus we believe that our free-standing films should have the same surface arrangement in this temperature window.
[19] For this film, the transition to the SmC_{FI2} phase occurred at 82.3 °C.
[20] The thickness of this film was estimated by the color. See E. B. Sirota, P. S. Pershan, L. B. Sorensen, and J. Collett, Phys. Rev. A **36**, 2890 (1987).