Surface-induced ordering effect in one antiferroelectric liquid crystal compound

LiDong Pan,[1] Shun Wang,[1] C. S. Hsu,[2] and C. C. Huang[1]
[1]*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455, USA*
[2]*Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan*
(Received 16 September 2008; published 18 March 2009)

Null transmission ellipsometer was employed to study the surface-induced tilt transition of an antiferroelectric liquid crystal compound in the bulk smectic-*A* (Sm*A*) temperature range. The data of the surface tilt transition can be fitted with an extended mean-field model. These results indicate the transition is near a mean-field tricritical point. The surface layers' tilt directions are found to be in different planes several degrees above the bulk Sm*A*-SmC^*_α transition.

DOI: 10.1103/PhysRevE.79.031704 PACS number(s): 61.30.Hn, 64.70.M−, 77.84.Nh

I. INTRODUCTION

Since the discovery of ferroelectricity [1] and antiferroelectricity [2] in smectic liquid crystals, a considerable amount of research effort has been devoted to this field. Among the various smectic liquid crystal phases, smectic-*A* (Sm*A*) and smectic-*C* (Sm*C*)/smectic-C^* (SmC^*) are the most studied ones. Earlier heat capacity [3–6] and x-ray diffraction [7] studies of the Sm*A* to Sm*C* (SmC^*) transition showed classical mean-field behavior. The data can be described by an extended mean-field free-energy expansion including a sixth-order term in the order parameter (tilt angle). Among antiferroelectric liquid crystal compounds, in many cases, the smectic-C^*_α (SmC^*_α) phase is found below Sm*A* instead of the SmC^* phase. The SmC^*_α exhibits an incommensurate nanoscale helical pitch [8]. Near the Sm*A*-SmC^*_α transition calorimetric studies [9] and layer compression modulus measurements [10] yield a crossover from three-dimensional (3D) *XY* critical to tricritical behavior.

Among liquid crystals, surface-induced ordering effects were often observed [11]. For smectic liquid crystals, free standing film geometry has been widely used in experiments. Films with thickness ranging from 2 to several hundred layers can be obtained. Thus smectic liquid crystal films are perfect systems to study the surface-induced ordering effect. For most materials showing a Sm*A*-Sm*C* (SmC^*) transition, surface-induced ordering appears as surface-induced tilts at temperatures in the bulk Sm*A* range. Thus far, most studies yield that surface layers tilt in a synclinic or anticlinic arrangement, i.e., the surface layers tilt in the same plane [12–15]. Earlier studies using the extended mean-field model to analyze the tilt angle data from thin films ($\leq$10 layers) yielded good fitting results [12,13]. However, in recent studies, synclinic-anticlinic-synclinic-anticlinic double reentrance surface transitions were reported in two different liquid crystal compounds [14,16]. Meanwhile nonplanar arrangements of surface tilt directions were discovered, in which the surface layers' tilt directions are in different planes [17,18]. So far, the general understanding of these complex surface-induced ordering effects has been limited. In this paper, we report the ellipsometric study of surface-induced ordering effect found in an antiferroelectric liquid crystal compound. Despite the fact that the underlying bulk transition shows a crossover behavior from 3D *XY* to tricritical, order parameter of the surface transition can be well described by an extended mean-field model.

II. EXPERIMENTAL METHOD

The liquid crystal compound used in this study is (R)-MHPBC. Its molecular structure is shown at the top of Fig. 1. The phase sequence found in bulk is isotropic (109 °C)-Sm*A* (76 °C)-SmC^*_α (71 °C)-SmC^*_{FI2} (66 °C)-SmC^*_{FI1} (62 °C)-SmC^*_A [19,20]. Free standing films were prepared in our null transmission ellipsometer (NTE). Two optical parameters, Δ and Ψ, were acquired. Δ measures the phase difference between the *p* and *s* components of the incident light necessary to produce linearly polarized transmitted light, while Ψ defines the polarization angle of the transmitted light. A cover glass slide with a 4 mm diam-

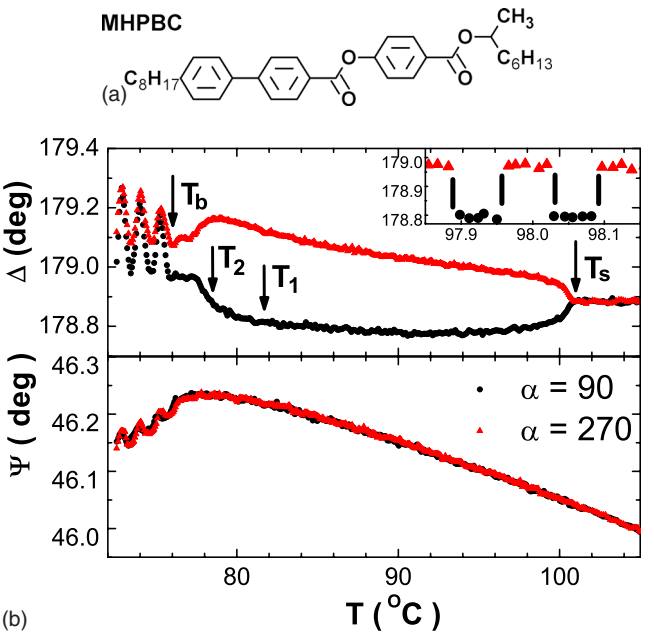

FIG. 1. (Color online) Δ and Ψ as a function of temperature upon cooling from an 81-layer film, with α=90° (black dots) and 270° (red triangles). Inset shows raw data obtained from a cooling run while switching the direction of *E*. On the top is the chemical structure of MHPBC

eter hole was used as the film plate. Applying a proper set of voltages to eight evenly spaced electrodes around the film hole creates a rotatable uniform in-plane dc electric field over more than 90% of the film. For films with nonzero in-plane polarization, the whole structure can be rotated smoothly about the layer normal by rotating the electric field (**E**). Variable α denotes the angle between **E** and the projection of **k** (wave vector of the laser beam) onto the film plate. Details of our experimental setup have been reported elsewhere [21].

The ellipsometric parameters Δ and Ψ were measured from about 50 films with thickness ranging from 2 to 200 layers at 104.9 °C where there are no surface tilts present. Data were fitted by a 4×4 matrix method [22]. By modeling each layer as a uniaxial slab with n_o, n_e, d being the principal indices of refraction and layer thickness, we obtained their values to be 1.481 ± 0.002, 1.626 ± 0.01, and 3.44 ± 0.05 nm, respectively [15]. Afterwards, the same fitting method was used to determine the thickness of all films studied.

III. DATA AND ANALYSES

For chiral smectic liquid crystals, polarization is perpendicular to the tilt plane due to symmetry of the molecule. By setting **E** field orientation $\alpha=90°/270°$, the molecules will tilt toward/away from the incident laser beam. So data collected at $\alpha=90°$ and 270° give important information concerning the average tilt and structural symmetry of the film studied [12,13,23]. Figure 1 shows Δ and Ψ as functions of temperature upon cooling from an 81-layer film, with $\alpha=90°$ (black dots) and 270° (red triangles). To minimize the complications caused by thermal degradation of the sample, data were collected in the following procedure. During the temperature ramps the direction of **E** was switched every 150 s between $\alpha=90°$ and $\alpha=270°$. The temperature ramping rate was set to be 40 mK/min in the region 10 K below the surface transition temperature (T_s) and 20 mK/min above it (for the films from which critical exponent β was measured, this rate was reduced to 10 mK/min). Since our ellipsometer collects one data point every 30 s, five data points are collected for one **E** field orientation before switching to the other orientation. These five raw data points are then averaged to obtain one single point. Data for the other field orientation of the same temperature window are obtained by linear interpolation of the ten raw data points in the two neighboring temperature windows. Since the optical parameters vary smoothly as temperature changes, with this procedure we are able to obtain a complete ramping data set with $\alpha=90°$ and 270° from a single cooling run.

In Fig. 1, for $T>T_s$, the Δ data obtained with $\alpha=90°$ and 270° are the same, indicating the whole film is in the uniaxial Sm*A* phase. For $T_s>T>T_2$, a distinct difference develops continuously between Δ_{90} and Δ_{270} while Ψ_{90} and Ψ_{270} remain the same, indicating the surfaces begin to tilt synclinicly, while the bulk is still in a Sm*A* structure. Between T_2 and T_b, the temperature variations of Δ and Ψ show a noticeable deviation from the general trends obtained in the temperature range $T_2<T<T_s$; we will show in later discussion a nonplanar arrangement of the surface layers begins to develop in this temperature window. Here T_b is the bulk Sm*A*-SmC^*_α transition temperature. For $T<T_b$, the characteristic oscillations in Δ and Ψ indicate the presence of the SmC^*_α phase [8,24].

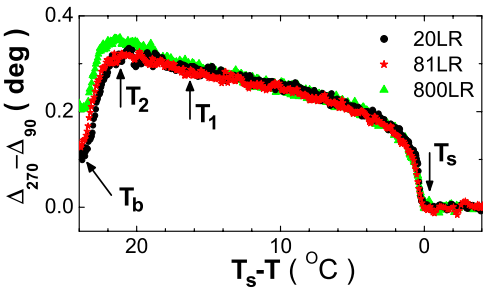

FIG. 2. (Color online) $\Delta_{270}-\Delta_{90}$ as a function of T_s-T from 20- (black dots), 81 ± 2- (red stars), and 800 ± 30- (green triangles) layer films obtained from cooling runs. $T_s=100.65$ °C for the films shown.

It has been demonstrated that for free standing smectic films with synclinic tilt, $|\Delta_{270}-\Delta_{90}|$ is proportional to the total tilt angle of the film [12,23]. Shown in Fig. 2 is $\Delta_{270}-\Delta_{90}$ as a function of temperature upon cooling from three films having 20 (black dots), 81 ± 2 (red stars), and 800 ± 30 (green triangles) layers in thickness, respectively. As can be seen, for $T_s>T>T_1$, $\Delta_{270}-\Delta_{90}$ is independent of film thickness for the range of film thickness studied, indicating the molecular tilts are localized in the surface layers. A smooth growth of $\Delta_{270}-\Delta_{90}$ from 0 at T_s indicates a well-defined continuous surface-induced tilt transition. Meanwhile, below T_1, $\Delta_{270}-\Delta_{90}$ shows a clear deviation from the trend found in the high-temperature region. This can be attributed to the changes in the surface molecular arrangements which will be addressed in detail later.

The data from the 800-layer film shows a higher $\Delta_{270}-\Delta_{90}$ value below T_1 than those from the other two films. This is most likely due to the fact that the interactions of the two surfaces are much weaker in thicker films, thus causing the change of surface structures to occur at a slightly lower temperature than those in thinner films.

First, a simple power-law equation $\Delta_{270}-\Delta_{90}=A[(T_s-T)/T_s]^\beta$ was employed to fit the data for $T>T_s-16$ K. The exponent β for the surface tilt transition was found to be 0.27 ± 0.02. The value of β is smaller than the associated value ($\beta=0.35$) for the 3D *XY* model. This strongly suggests that the surface-induced tilt transition is in the vicinity of a mean-field tricritical point ($\beta=0.25$). Consequently, we fitted our results to an equation derived from the extended mean-field model [3], i.e.,

$$(\Delta_{270}-\Delta_{90})^2=B\{[1+3(-t)/t_0]^{1/2}-1\}.$$

Here $t=(T-T_s)/T_s$ is the reduced temperature. Both B and t_0 are fitting parameters. The value of t_0 gives crossover temperature in the reduced temperature scale between the ordinary and tricritical mean-field behavior. Shown in Fig. 3 are the data and fitting result from the 800-layer film. The smallness of t_0 ($5\pm2\times10^{-4}$) demonstrates that the surface transi-

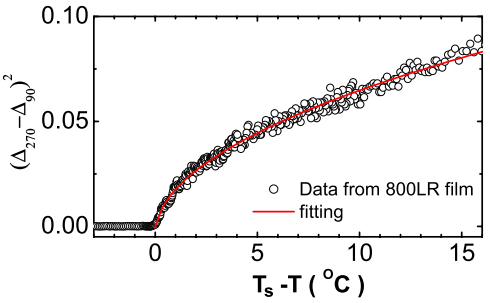

FIG. 3. (Color online) Extended mean-field theory fitting of $(\Delta_{270}-\Delta_{90})^2$ from the 800-layer film.

tion is in the close vicinity of a mean-field tricritical point. For comparison, the extended mean-field theory fitting from thin films of DOBAMBC gives t_0 about 1.8×10^{-2} and MBOOBC gives t_0 of 1.6×10^{-3}, while in earlier studies of bulk Sm*A*-Sm*C* (SmC^*) transition, a value on the order of 10^{-3} is often found for t_0 [5,6,9,13].

The bulk heat-capacity data of MHPBC near the Sm*A*-SmC^*_α transition can be fitted to a crossover expression for 3D *XY* critical to tricritical behavior, with a large crossover temperature suggesting pronounced critical behavior [9]. Layer compression measurement also yields the same type of crossover behavior [10]. Since the surface-induced tilts occur in a constrained dimensional space, intuitively the tilt fluctuations should be much enhanced. However, x-ray reflectivity experiments have shown that surface tension suppresses the surface fluctuations significantly and enhances the surface ordering [26]. Our results clearly indicate that surface tension dominates the surface-induced tilt transition.

A noticeable deviation from the general trend of $\Delta_{270}-\Delta_{90}$ below T_1 is visible from the data shown in Fig. 2. Thus our low-temperature cutoff of the fitting is at about $T_s-T=16$ K. In Fig. 2, the $\Delta_{270}-\Delta_{90}$ data show a maximum near T_2. If we limit ourselves to synclinic surface arrangements, this would imply a decrease in the surface-induced tilt angle for $T<T_2$, which is highly unlikely. Based on our previous experience, the decrease of $\Delta_{270}-\Delta_{90}$ is most likely due to the development of a nonplanar structure in the film. In order to get the surface structures for T_s-16 K$>T>T_b$, rotations of **E** through 360° with steps of 15° were performed at constant temperature. To minimize the effect of defects such as 2π walls, a clockwise rotation was done after a counterclockwise one and vice versa.

Shown in Fig. 4(a) is the α dependence of Δ and Ψ from a 20-layer film at (a) 81.5 °C (black dots) and (b) 76 °C (red triangles). Data were fitted by using the 4×4 matrix method [22] along with the previously determined parameters (n_o, n_e, and d). To simplify our fitting, a model with two tilted surface layers was used [27], with the outermost layers always in a synclinic arrangement and $\delta\phi$ denoting the azimuth difference between the outermost layers and the adjacent layers. From the fitting, the following values of θ_{surf}, θ_{AS}, and $\delta\phi$ are obtained: (a) $15°\pm1°$, $5°\pm1°$, $50°\pm15°$; (b) $18°\pm1°$, $7.5°\pm1°$, $180°\pm15°$. θ_{surf} denotes the tilt angle of the surface layers and θ_{AS} the tilt angle of the layers adjacent to the surfaces.

As shown in Fig. 4(a), the Ψ versus α curve evolves from an asymmetric shape to having a twofold symmetry at

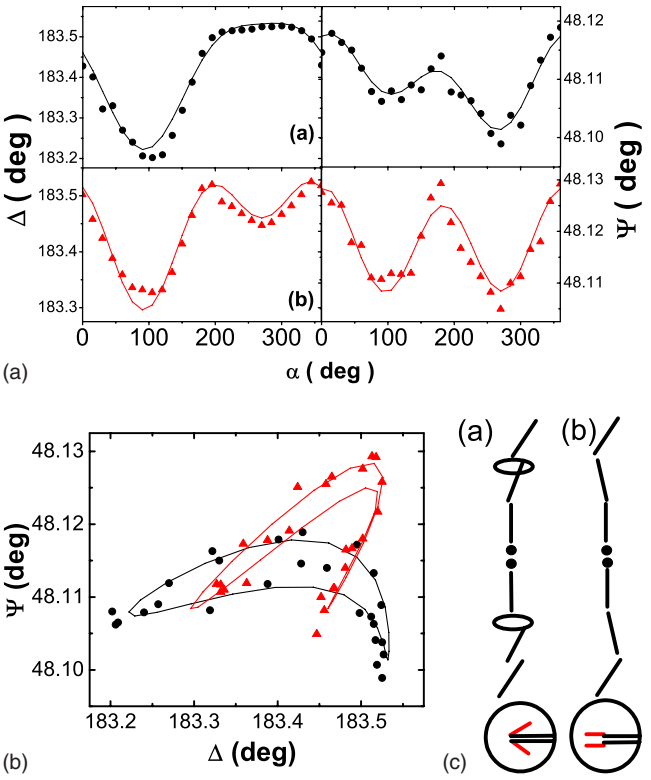

FIG. 4. (Color online) (a) Δ, Ψ vs α data (symbols) and fits (solid lines) from a 20-layer film at (a) 81.5 °C (black dots) and (b) 76 °C (red triangles). (b) Δ vs Ψ plot for the rotation data. (c) Cartoons and top views of the corresponding layer structures from the fitting. In the top view, black (longer) rods represent the outermost surface layers while red rods (shorter) represent the layers adjacent to the surfaces. Note: the change in Ψ over the whole range of α is extremely small (approximately 0.02°). Our resolution in Ψ is about 0.002°. This is the main reason for the scattering of the Ψ vs α data.

76 °C, just above T_b. This indicates the structure is nonplanar for $T=81.5$ °C. However the shapes of Δ versus α curves at these temperatures show the typical features of a synclinic structure, i.e., a global minimum at $\alpha=90°$ and a plateau/local minimum around $\alpha=270°$. These results suggest that the major tilted parts (the outermost layers) of the film are in a synclinic arrangement in the temperature window studied. The layers adjacent to the surface evolve from synclinic to nonplanar and finally to anticlinic arrangements with respect to the outermost layers just above T_b.

In Fig. 4(b), plots of Δ versus Ψ for the two rotations are shown. The distinct shapes of the curves clearly indicate different surface structures at these two temperatures. The cartoons and top views of the molecular arrangements used in the fittings are given in Fig. 4(c).

IV. DISCUSSION AND SUMMARY

We have demonstrated that while the underlying bulk Sm*A*-SmC^*_α transition shows a crossover from 3D *XY* to tricritical behavior, the surface-induced tilt transition can be well described with an extended mean-field theory. The non-

planar surface structure of MHPBC appears to be the intermediate state between the high-temperature synclinic and lower temperature anticlinic structure, as seen from the smooth evolution of $\Delta_{270}-\Delta_{90}$ around T_1. To the best of our knowledge, this complex surface structure is most likely induced by the underlying SmC^*_α structure occurring at the bulk transition temperature (T_b). However, the relationship between the nature of the surface transition and the underlying bulk transition as well as the effect of the underlying bulk structure on the surface structure remain to be important topics for further studies. It would be interesting to compare the behavior of surface-induced tilt transition of MHPBC to the group of materials showing significantly different crossover behavior in the bulk, such as MHPOBC, 12BIMF10, and MHPOCBC as reported in Ref. [9].

From earlier studies of thin smectic liquid crystal films, it was found that the structure of the tilted surfaces may depend on the strength of in-plane **E** field [15,25]. In all the experiments reported in this paper, **E** field was fixed at 1.25 V/mm, which is strong enough to align the film, while too weak to cause any change in the tilt angle, thus the results of the surface tilt transition are not affected by our applied **E** field.

In conclusion, a nonplanar-anticlinic surface transition was observed at temperatures higher than the bulk Sm*A*-SmC^*_α transition for MHPBC. The power-law and extended mean-field fittings show the synclinic surface tilt transition is close to a mean-field tricritical point, even though the bulk results yield 3D *XY* behavior.

ACKNOWLEDGMENT

The research was supported in part by the National Science Foundation, Solid State Chemistry Program, under Grant No. DMR-0605760.

[1] R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris), Lett. **36**, L69 (1975).
[2] A. D. L. Chandani, E. Gorecka, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys., Part 2 **28**, L1265 (1989).
[3] C. C. Huang and J. M. Viner, Phys. Rev. A **25**, 3385 (1982).
[4] C. C. Huang and S. Dumrongrattana, Phys. Rev. A **34**, 5020 (1986).
[5] C. C. Huang and S. C. Lien, Phys. Rev. A **31**, 2621 (1985).
[6] M. Meichle and C. W. Garland, Phys. Rev. A **27**, 2624 (1983).
[7] R. Shashidhar, B. R. Ratna, Geetha G. Nair, S. K. Prasad, Ch. Bahr, and G. Heppke, Phys. Rev. Lett. **61**, 547 (1988).
[8] D. Schlauf, Ch. Bahr, and H. T. Nguyen, Phys. Rev. E **60**, 6816 (1999); P. Mach, R. Pindak, A.-M. Levelut, P. Barois, H. T. Nguyen, H. Baltes, M. Hird, K. Toyne, A. Seed, J. W. Goodby, C. C. Huang, and L. Furenlid, *ibid.* **60**, 6793 (1999).
[9] K. Ema and H. Yao, Phys. Rev. E **57**, 6677 (1998).
[10] S. Shibahara, J. Yamamoto, Y. Takanishi, K. Ishikawa, H. Takezoe, and H. Tanaka, Phys. Rev. Lett. **85**, 1670 (2000).
[11] B. Jerome, Rep. Prog. Phys. **54**, 391 (1991).
[12] S. Heinekamp, R. A. Pelcovits, E. Fontes, E. Y. Chen, R. Pindak, and R. B. Meyer, Phys. Rev. Lett. **52**, 1017 (1984).
[13] Ch. Bahr, C. J. Booth, and D. Fliegner, Ferroelectrics **178**, 229 (1996).
[14] X. F. Han, S. T. Wang, A. Cady, M. D. Radcliffe, and C. C. Huang, Phys. Rev. Lett. **91**, 045501 (2003).
[15] P. M. Johnson, D. A. Olson, S. Pankratz, Ch. Bahr, J. W. Goodby, and C. C. Huang, Phys. Rev. E **62**, 8106 (2000).
[16] B. K. McCoy, Z. Q. Liu, S. T. Wang, V. P. Panov, J. K. Vij, J. W. Goodby, and C. C. Huang, Phys. Rev. E **73**, 041704 (2006).
[17] X. F. Han, D. A. Olson, A. Cady, D. R. Link, N. A. Clark, and C. C. Huang, Phys. Rev. E **66**, 040701(R) (2002).
[18] S. T. Wang, X. F. Han, Z. Q. Liu, A. Cady, M. D. Radcliffe, and C. C. Huang, Phys. Rev. E **68**, 060702(R) (2003).
[19] K. Miyachi, M. Kabe, K. Ishikawa, H. Takezoe, and A. Fukuda, Ferroelectrics **147**, 147 (1993).
[20] A. Cady, Z. Q. Liu, X. F. Han, S. T. Wang, M. Veum, N. Janarthanan, C. S. Hsu, D. A. Olson, and C. C. Huang, Phys. Rev. E **66**, 061704 (2002).
[21] D. A. Olson, X. F. Han, P. M. Johnson, A. Cady, and C. C. Huang, Liq. Cryst. **29**, 1521 (2002).
[22] D. W. Berreman, J. Opt. Soc. Am. **62**, 502 (1972); H. Wohler, G. Hass, M. Fritsch, and D. A. Mlynski, J. Opt. Soc. Am. A **5**, 1554 (1988).
[23] Ch. Bahr and D. Fliegner, Phys. Rev. A **46**, 7657 (1992).
[24] P. M. Johnson, S. Pankratz, P. Mach, H. T. Nguyen, and C. C. Huang, Phys. Rev. Lett. **83**, 4073 (1999).
[25] D. R. Link, G. Natale, N. A. Clark, J. E. Maclennan, M. Walsh, S. S. Keast, and M. E. Neubert, Phys. Rev. Lett. **82**, 2508 (1999).
[26] D. J. Tweet, R. Holyst, B. D. Swanson, H. Stragier, and L. B. Sorensen, Phys. Rev. Lett. **65**, 2157 (1990); R. Holyst, D. J. Tweet, and L. B. Sorensen, *ibid.* **65**, 2153 (1990).
[27] From our two-layer film results, $\Delta_{270}-\Delta_{90}$ above the synclinic-anticlinic transition matches with the data obtained from other films nicely if plotted in T_s-T scale. Thus we concluded that the major contribution of the surface-induced tilt comes from the outermost layers.