RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 62, NUMBER 2 AUGUST 2000

Structural characterization of surface hexatic behavior in free-standing 4O.8 liquid-crystal films

C. Y. Chao,[1] T. C. Pan,[1] C. F. Chou,[2,*] and J. T. Ho[2]
[1]*Department of Physics, National Central University, Chung-Li, Taiwan 32054, Republic of China*
[2]*Department of Physics, State University of New York at Buffalo, Buffalo, New York 14260*

(Received 9 March 2000)

Electron diffraction in free-standing liquid-crystal films of *N*-(4-*n*-butoxybenzylidene)-4-*n*-octylaniline between 3 and 12 molecular layers thick reveals the unusual occurrence of the smectic-A' phase, a highly correlated isotropic liquid, on the surface of smectic-*A* films. The surface smectic-*A*–smectic-A' transition is found to be first order. Surprisingly, the temperature range of the subsequent surface hexatic-*B* phase is reduced with decreasing film thickness.

PACS number(s): 64.70.Md, 61.30.Eb

The theory of defect-mediated phase transitions in two dimensions (2D) by Kosterlitz and Thouless (KT) [1] has generated considerable interest and extensive research on the subject. Their original ideas were later extended by Halperin, Nelson, and Young [2,3] to describe a process by which a solid in 2D could melt, via two KT-type transitions, through an intermediate hexatic phase into the isotropic liquid. The hexatic phase in 2D is characterized by the existence of quasi-long-range bond-orientational order but short-range positional order. While much experimental effort has been undertaken to test these theoretical predictions, studies on several liquid-crystal systems have proven to be among the most fruitful [4].

The liquid-crystal compound *N*-(4-*n*-butoxybenzylidene)-4-*n*-octylaniline (4O.8) has been extensively studied from the point of view of phase transitions because it possesses several important phases in the bulk, including the nematic, smectic-*A* (Sm-*A*), and crystal-*B* (Cry-*B*). However, it is generally not expected to be a relevant system in which to study possible hexatic behavior [5,6]. On the other hand, recent electron-diffraction experiments have indicated that free-standing films of 4O.8 between 6 and 12 molecular layers thick do display an unexpected multistep surface-freezing phenomenon in which the outermost layers undergo phase transitions involving an intermediate hexatic-*B* (Hex-*B*) phase [7]. Furthermore, data on a two-layer 4O.8 film provided preliminary suggestions for the possible existence of, not only the Hex-*B* phase, but also a preceding phase with hexaticlike positional correlations but no long-range bond-orientational order [8]. This unexpected phase, which we call smectic-A' (Sm-A') [9], has also been tentatively identified in a two-layer film of *n*-pentyl-4′-*n*-pentanoyloxy-biphenyl-4-carboxylate (54COOBC) [10]. The existence of the Sm-A' phase, if confirmed, will significantly modify our understanding of 2D melting. It is also interesting to see whether the Sm-A' phase can be found in non-2D systems. In this study, we report electron-diffraction experiments that establish the occurrence and elucidate the phase-transitional properties of the Sm-A' phase on the surface of 4O.8 Sm-*A* films with different layer thicknesses.

Our experimental technique for making electron-diffraction measurements in free-standing liquid-crystal thin films has been described elsewhere [11]. Bulk 4O.8 shows the following phase sequence: isotropic (78 °C) nematic (64 °C) Sm-*A* (49 °C) Cry-*B*. Free-standing films of various thickness are spread in the Sm-*A* phase across a hole of 1 mm in diameter in a sample holder.

We have studied in detail free-standing films of 4O.8 with thicknesses of 3, 4, 5, 6, 8, 9, 10, and 12 molecular layers and found similar behavior among them. We will use the results of a ten-layer film as a typical example. Above 62 °C, the film is in the Sm-*A* phase. Its diffraction pattern shows a diffuse ring of constant intensity, signifying the liquid nature of this phase. The positional correlation length ξ derived from the radial linewidth ($Q_\parallel$-scan) is of the order of 10 Å. When the film is cooled to about 62 °C, a temperature which coincides with the location of the heat-capacity anomaly reported in a eight-layer 4O.8 film [12], a diffraction pattern shown in Fig. 1(a) is observed, which is characterized by the occurrence of a sharper ring coexisting with the diffuse ring. The coexistence of the two diffraction rings is best seen in a plot of the integrated intensity along a radial direction, as shown in Fig. 2(a). The broad peak is similar to that of the diffuse ring observed above 62 °C, and can be fitted by a Lorentzian function whose linewidth implies a positional correlation length of 10.5 Å, indicative of Sm-*A* diffraction. On the other hand, the narrower peak, after subtraction of the Sm-*A* signal, can be fitted to a square-root Lorentzian function, which is typically applicable in a hexatic phase [13,14]. The fitting function is $I(Q_\parallel)=A\xi[1+\xi^2(Q_\parallel-Q_0)^2]^{-1/2}$, where Q_0 is the peak position. The value of ξ derived from the linewidth of the narrower peak is 50 Å. Because it is a general rule that the surface of a smectic film is more ordered than the interior [15,16], this unexpected diffraction pattern shown in Fig. 1(a) suggests a higher degree of in-plane positional correlations (comparable to some hexatic phases) in the two surface layers than in the interior Sm-*A* phase. However, the lack of sixfold modulation of the diffraction intensity around the sharper ring indicates the absence of long-range bond-orientational order on the surfaces within our probing electron beam of diameter 50 μm. The unusual characteristics of the surface layers in this ten-layer film of 4O.8 are similar to those of the Sm-A' phase tentatively suggested in two-layer films of 4O.8 [8] and 54COOBC [10].

---

[*] Present address: Department of Physics, Princeton University, Princeton, NJ 08544.

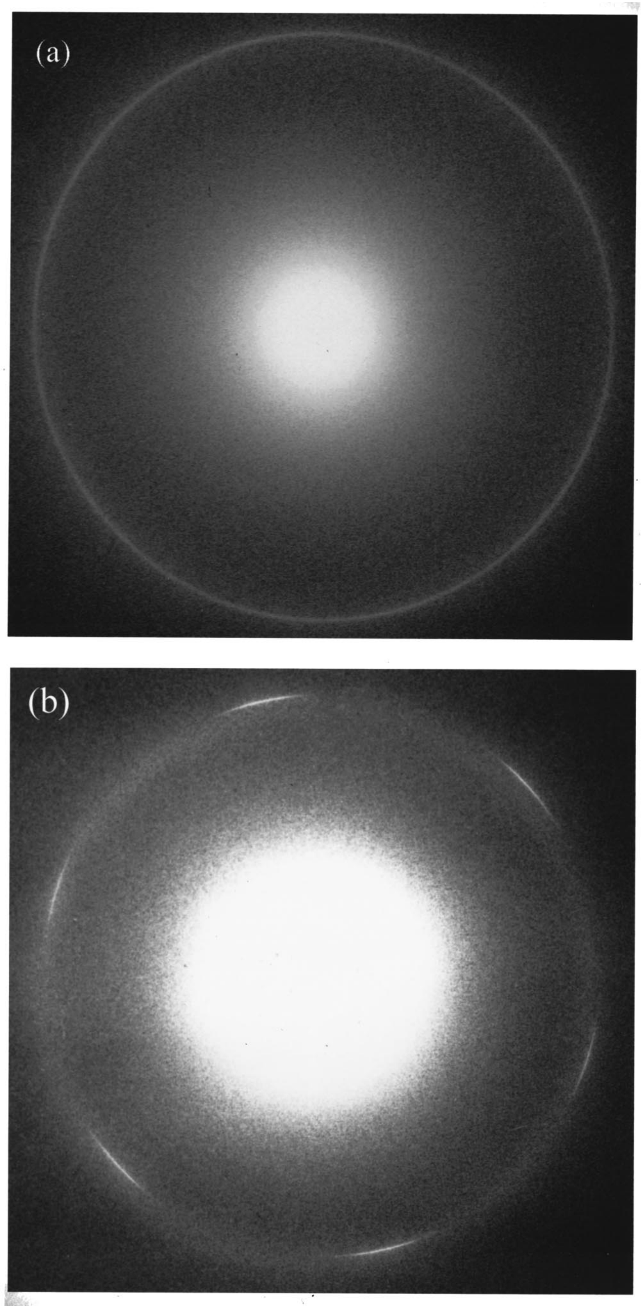

FIG. 1. Electron-diffraction pattern from a ten-layer 4O.8 film at (a) 59.5 °C, indicating surface Sm-A' (sharp ring) and interior Sm-A (diffuse ring) phases, and (b) 57.5 °C, indicating surface Hex-B (six arcs) and interior Sm-A (diffuse ring) phases.

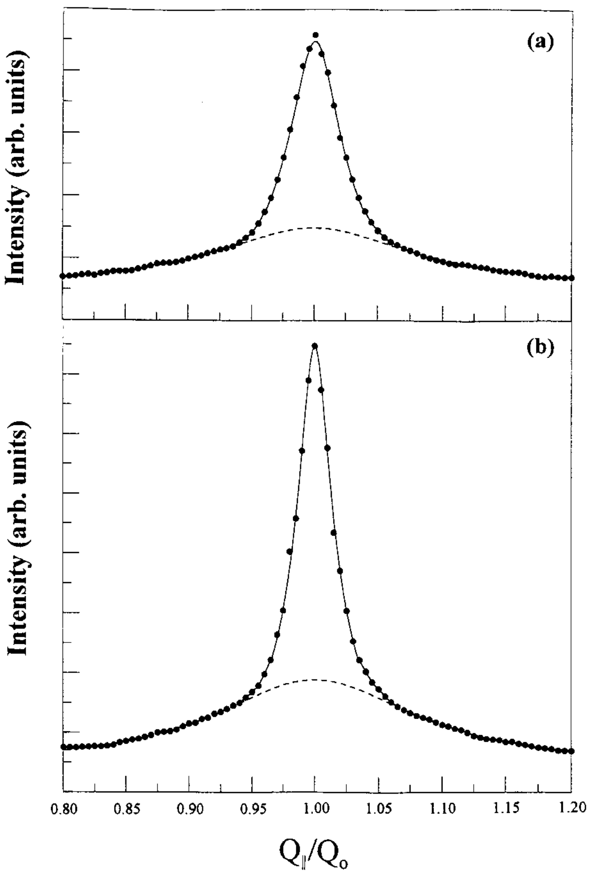

FIG. 2. Integrated intensity along a radial wave vector $Q_{\parallel}$ at (a) 59.5 °C and (b) 57.5 °C, where Q_o is the peak position. The dashed and solid lines are fits to a Lorentzian and square-root Lorentzian function, respectively.

At around 59 °C, the outermost layers undergo a transition to a single-domain Hex-B phase while the interior still remains the Sm-A phase, giving a diffraction pattern exemplified by Fig. 1(b), in which six identical arcs coexist with a diffuse ring. The aximuthal width of arcs diminishes gradually with decreasing temperature, indicating an increase in the bond-orientational order in the surface layers. The coexistence of the Hex-B and Sm-A diffraction can be seen in the intensity plot along the radial direction in Fig. 2(b). The linewidths of the sharper surface Hex-B and the broader interior Sm-A signals indicate positional correlation lengths of 80 and 12 Å, respectively. The outermost layers make another transition at about 55 °C to the Cry-B phase, while the interior layers remain in the Sm-A phase, with an electron-diffraction pattern consisting of two sets of six Bragg spots coexisting with a diffuse ring.

To yield detailed information about the temperature dependence of both the bond-orientational and positional orders in the surface layers of the ten-layer 4O.8 film, we analyze the electron-diffraction data by fitting the intensity of the hexatic arcs (χ-scan) as a function of the azimuthal angle to obtain the sixfold bond-orientational order parameter C_6, and by fitting the integrated intensity as a function of the wave vector along the radial direction ($Q_{\parallel}$-scan) to obtain the in-plane positional correlation length of the surface phases. Between 59 °C and 53 °C, the higher-harmonic $6n$-fold bond-orientational order parameters $C_{6n}=\mathrm{Re}\langle\exp(i6n\theta)\rangle$ in the surface Hex-B and Cry-B phases are determined from the diffraction intensity $I(\chi)$ along an arc over an angular range χ of 60° by fitting to the expression

$$I(\chi)=I_o\left[1/2+\sum_{n=1}^{\infty}C_{6n}\cos[6n(\chi-30°)]\right]+I_{\mathrm{BG}}$$

where I_{BG} is a fitting parameter representing the background intensity. The temperature dependence of the bond-orientational order parameter C_6 of the surface hexatic phase in the ten-layer 4O.8 film is thus obtained and shown in Fig. 3(a). The analysis of the $Q_{\parallel}$-scan is done by fitting to a Lorentzian line shape in the Sm-A phase and to a square-root

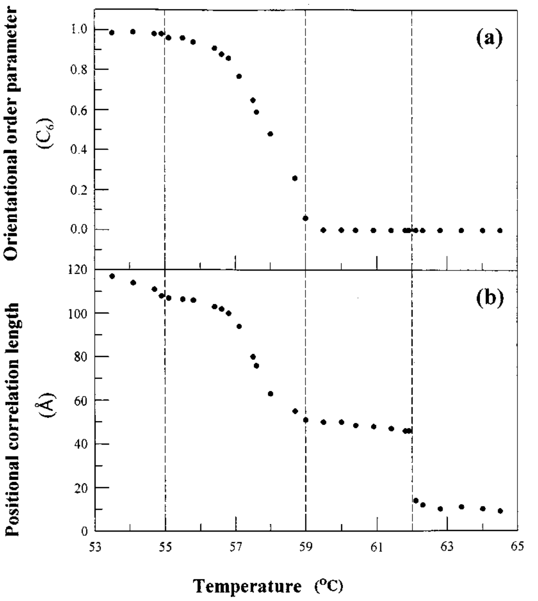

FIG. 3. Temperature dependence of (a) the bond-orientational order parameter C_6 and (b) the in-plane positional correlation length of the surface phase in a ten-layer 4O.8 film.

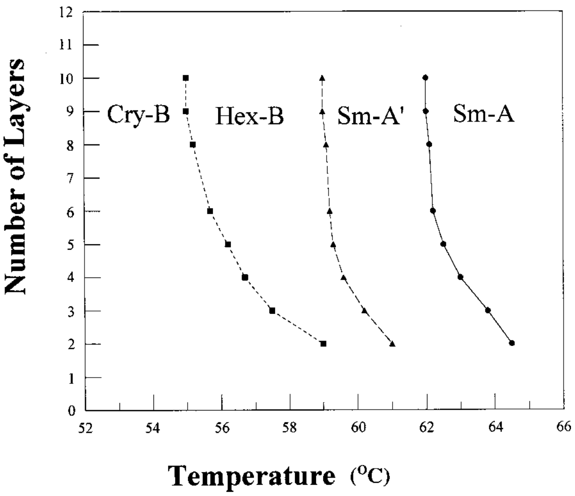

FIG. 4. Phase diagram of the two outermost layers in 4O.8 films with different thicknesses obtained by electron diffraction. The transition temperatures of the two-layer film are from Ref. [8].

Lorentzian in the surface Sm-*A′* and Hex-*B* phases. We have not applied any deconvolution to correct for instrumental resolution, thus resulting in the apparent saturation of the positional correlation length near the surface Hex-*B*–Cry-*B* transition at 55 °C. The temperature dependence of the in-plane positional correlation length ξ of the surface phases in the ten-layer 4O.8 film is shown in Fig. 3(b), in which ξ exhibits a sudden jump near 62 °C, indicating that the surface Sm-*A*–Sm-*A′* transition is first order. Over the 3 °C temperature range of the surface Sm-*A′* phase, ξ increases very slowly upon cooling. Below 59 °C, however, ξ increases much more rapidly in the surface Hex-*B* phase. The behavior of the order parameter C_6 in Fig. 3(a) suggests no long-range bond-orientational order above 59 °C, and a monotonic increase in the bond-orientational order in the surface Hex-*B* phase with decreasing temperature from 59 °C to 55 °C. The surfaces undergo an apparently continuous transition at about 55 °C to the Cry-*B* phase. The temperature dependence of the in-plane positional correlation length between 65 °C and 53 °C reveals four distinct phase regions, corresponding to the Sm-*A* (above 62 °C), the surface Sm-*A′* (62 °C to 59 °C), the surface Hex-*B* (59 °C to 55 °C), and the surface Cry-*B* (below 55 °C) phases. The most important observation here is the existence of the surface Sm-*A′* phase. On the basis of the electron-diffraction pattern shown in Fig. 1(a) alone, one might argue that the Sm-*A′* signal could be the result of powder diffraction from a multidomain Hex-*B* sample spatially averaged by the electron beam of diameter 50 μm. However, our temperature-dependence data reveal (i) an abrupt jump at 62 °C in the positional correlation length and (ii) the simultaneous occurrence at 59 °C of both the emergence of bond-orientational order and a sharp increase in the positional correlation length. These results strongly point to the existence of a surface Sm-*A′* phase between 62 °C and 59 °C, while the interior remains in the Sm-*A*. Our data suggest that the Sm-*A′* is indeed a distinct phase in the surfaces that can be characterized as a 2D isotropic liquid with a higher degree of positional correlations than an ordinary liquid but no long-range bond-orientational order.

The surface phase sequence seen in the ten-layer film is also observed by electron diffraction in the other films of different thicknesses that we have studied. The temperatures of the three distinct surface phase transitions as a function of film thickness are summarized in Fig. 4. As usual, there is a general increase in the transition temperatures as the thickness is reduced. However, the temperature range in which the surface Sm-*A′* phase exists does not change significantly with film thickness. On the other hand, the temperature range of the surface Hex-*B* phase decreases noticeably with decreasing film thickness. This trend is somewhat surprising, since the hexatic phase is generally expected to be more prevalent as the effective dimension becomes closer to 2.

Since our electron-diffraction data in the ten-layer 4O.8 film suggest that the surface transition at around 62 °C corresponds, not to the Sm-*A*–Hex-*B* transition, but to the Sm-*A*–Sm-*A′* transition, which is not expected to be KT-like, the power-law anomaly observed in the heat capacity at that temperature [12] is no longer surprising. Because there is no symmetry breaking involved, the surface Sm-*A*–Sm-*A′* transition should be first order, which is consistent with the discontinuity of the positional correlation length shown in Fig. 3(b).

In summary, we report the occurrence on the surface of a liquid-crystal material of the Sm-*A′* phase, an isotropic liquid with an enhanced positional correlation length (~50 Å) that has not been anticipated. This affirmation of the existence of this unusual phase, hitherto identified tentatively only in 2D films, could fundamentally alter our understanding of melting in reduced dimensions.

One of us (C.Y.C.) acknowledges support from the National Science Council, Taiwan, Republic of China, under Grant Nos. NSC87-2112-M-008-035, NSC 88-2112-M-008-029, and NSC889-2112-M-008-004.

[1] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973).
[2] B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978); D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).
[3] A. P. Young, Phys. Rev. B **19**, 1855 (1979).
[4] C. C. Huang and T. Stoebe, Adv. Phys. **42**, 343 (1993), and references therein.
[5] D. E. Moncton and R. Pindak, Phys. Rev. Lett. **43**, 701 (1979).
[6] P. S. Pershan, G. Aeppli, J. D. Litster, and R. J. Birgeneau, Mol. Cryst. Liq. Cryst. **67**, 205 (1981).
[7] C. Y. Chao, C. F. Chou, J. T. Ho, S. W. Hui, A. J. Jin, and C. C. Huang, Phys. Rev. Lett. **77**, 2750 (1996).
[8] C. F. Chou, A. J. Jin, C. Y. Chao, S. W. Hui, C. C. Huang, and J. T. Ho, Phys. Rev. E **55**, R6337 (1997).
[9] This phase was previously named the hexatic-B_1 in Ref. [8].
[10] C. F. Chou, A. J. Jin, S. W. Hui, C. C. Huang, and J. T. Ho, Science **280**, 1424 (1998).
[11] M. Cheng, J. T. Ho, S. W. Hui, and R. Pindak, Phys. Rev. Lett. **59**, 1112 (1987).
[12] A. J. Jin, T. Stoebe, and C. C. Huang, Phys. Rev. E **49**, R4791 (1994).
[13] S. C. Davey, J. Budai, J. W. Goodby, R. Pindak, and D. E. Moncton, Phys. Rev. Lett. **53**, 2129 (1984).
[14] G. Aeppli and R. Bruinsma, Phys. Rev. Lett. **53**, 2133 (1984).
[15] B. D. Swanson, H. Stragier, D. J. Tweet, and L. B. Sorensen, Phys. Rev. Lett. **62**, 909 (1989).
[16] R. Geer, T. Stoebe, C. C. Huang, R. Pindak, J. W. Goodby, M. Cheng, J. T. Ho, and S. W. Hui, Nature (London) **355**, 152 (1992).