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Direct layer-by-layer freezing of a smectic liquid-crystal surface into the crystalline phase

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Electron diffraction and optical reflectivity have provided the direct confirmation of the existence of layer-by-layer surface transitions from the smectic-*A* immediately to the crystal-*B* phase in a liquid-crystal material, without going through an intermediate hexatic phase. The molecular interactions are found to be through retarded van der Waals forces. Our results suggest that a smectic-*A* film can transform into a crystal-*B* through three possible scenarios.

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The phenomenon of surface freezing, which is somewhat unique in liquid crystals, has been studied extensively in recent years [1–7]. Most experiments on the surface phase transition of smectic liquid crystals have been conducted in materials that exhibit a hexatic phase either in the bulk or in thin films. Layer-by-layer surface freezing in liquid-crystal films have been identified near the smectic-*C* to smectic-*I* (Sm-*I*) [1], the smectic-*A* (Sm-*A*) to tilted hexatic [2,7], and the Sm-*A* to hexatic-*B* (Hex-*B*) [3,4,6] transitions. The involvement of a hexatic phase in these surface phase transitions is consistent with the occurrence of such a phase as predicted in the defect-mediated theory of two-dimensional (2D) melting [8]. A recent experiment on *N*-(4-*n*-butoxybenzylidene)-4-*n*-octylaniline (40.8) demonstrated that this material, which contains the Sm-*A* and crystal-*B* (Cry-*B*) phases but no hexatic phase in the bulk, nevertheless exhibits a two-stage Sm-*A*–Hex-*B*–Cry-*B* transition sequence in a layer-by-layer manner on the surface [9]. This discovery raises the intriguing possibility that the involvement of a hexatic phase is ubiquitous in surface layer-by-layer transitions in smectic liquid crystals, where the spatial dimension is effectively reduced. It is therefore important to test this hypothesis by studying the surface freezing in other materials that show a direct Sm-*A*–Cry-*B* transition in the bulk.

One promising candidate for such a study is 4-*n*-pentylbenzenethio-4′-*n*-tetradecyloxybenzoate (14S5), which transforms directly from the Sm-*A* to the Cry-*B* phase at 66.5 °C in the bulk [10]. Unfortunately, there have been conflicting reports on the surface-freezing behavior of this material. Mechanical and x-ray measurements on 14S5 free-standing films indicated that, upon cooling, the outermost layers of Sm-*A* films undergo a single freezing transition into the Cry-*B* phase, to be followed by the abrupt freezing of the entire interior at a lower temperature [10,11]. These studies also suggested that the three-layer film might be somewhat unique in that the interior layer appears to show a hexatic intermediate phase. However, a more recent study reported that 14S5 transforms from the Sm-*A* phase, not to the orthogonal crystalline Cry-*B*, but to the tilted hexatic Sm-*I* phase, and that the birefringence of the Sm-*I* made it possible to use video imaging to observe multiple layer-by-layer freezing of Sm-*A* films [7]. In an attempt to resolve these conflicting results and to ascertain the nature of the surface freezing in this material, we have conducted electron-diffraction and optical-reflectivity studies in free-standing 14S5 films. Our results indicate that the surface of Sm-*A* films of 14S5 undergoes a layer-by-layer direct Sm-*A*–Cry-*B* transition without any evidence of an intermediate hexatic phase. Our data also suggest that the molecular binding in 14S5 is due to retarded van der Waals forces.

We have conducted electron-diffraction (ED) studies on free-standing films of 14S5 with thickness from two to tens of molecular layers in an electron microscope equipped with a pressurized and temperature-controlled sample chamber [12]. For films thicker than two molecular layers, there is an initial surface transition at about 75 °C, above which the films are entirely in the Sm-*A* phase. Their ED pattern consists of a uniform diffuse ring, as exemplified in Fig. 1(a) for a 40-layer film at 78.4 °C. When cooled below about 75 °C, the films exhibit an ED pattern, illustrated in Fig. 1(b) for the 40-layer film at 72 °C, consisting of six bright Bragg spots with equal intensity, in addition to the uniform diffuse ring. We interpret the diffraction spots and the diffuse ring as indicative of Cry-*B* surfaces and a Sm-*A* interior, respectively. It can be further inferred from previous x-ray studies [11] and our additional optical-reflectivity (OR) results that the frozen Cry-*B* surfaces consist of a single outermost layer on either side of the films. For films thicker than four molecular layers, there are additional layer-by-layer Sm-*A*–Cry-*B* transitions upon further cooling, which are most easily seen in the OR results presented below. At a sufficiently low temperature (66.6 °C for films with tens of layers), the entire film eventually freezes to the Cry-*B* phase, producing an ED pattern composed entirely of the characteristic Bragg spots and no diffuse ring. Our most significant observation is that there is no evidence whatsoever of a hexatic phase in all our films of various thickness as they undergo layer-by-layer freezing. This represents an important definitive result on the existence of direct Sm-*A*–Cry-*B* layer-by-layer freezing without involving a hexatic phase, since single-crystal ED is a much more sensitive technique to discern hexatic behavior than the previous studies on 14S5 films using a torsional oscillator [10], x-ray intralayer powder diffraction [11], or video observation of birefringence changes [7]. In particular, we see no evidence of an intermediate phase with no positional order but with bond-

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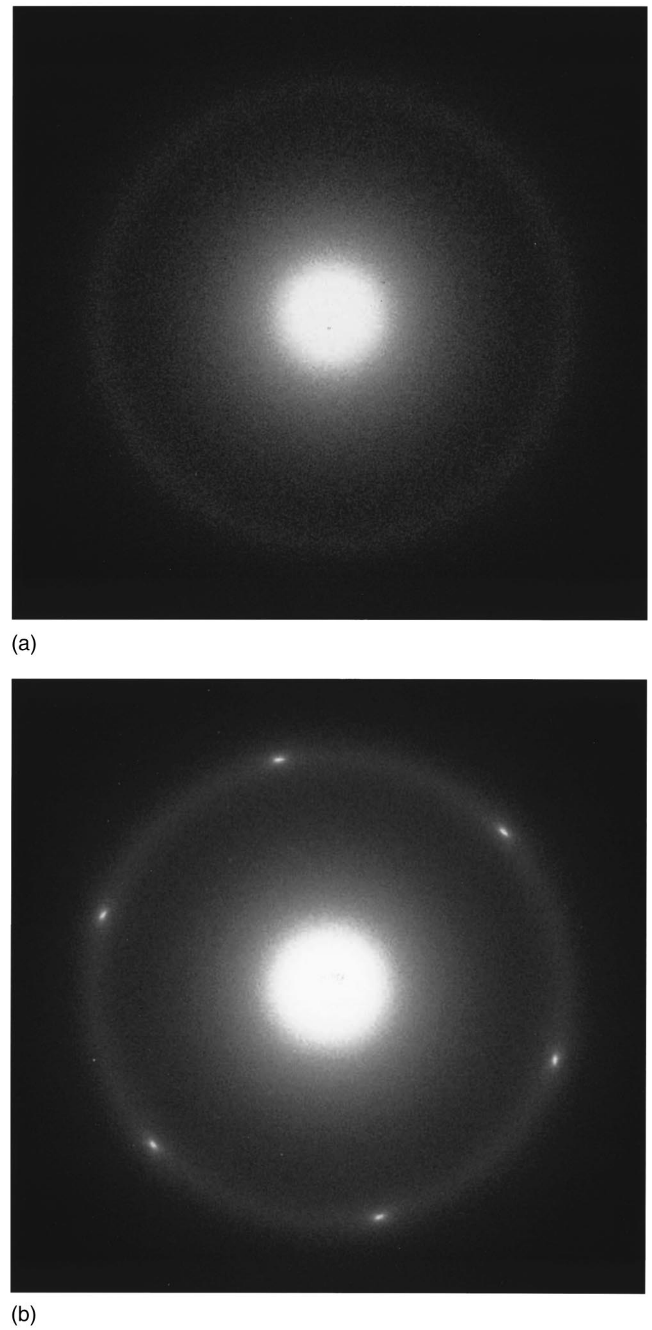
(a)

(b)

FIG. 1. Electron-diffraction pattern from a 40-layer film of 14S5 at (a) 78.4 °C and (b) 72 °C.

orientational order in the interior layer of the three-layer film that was suggested earlier [10,11].

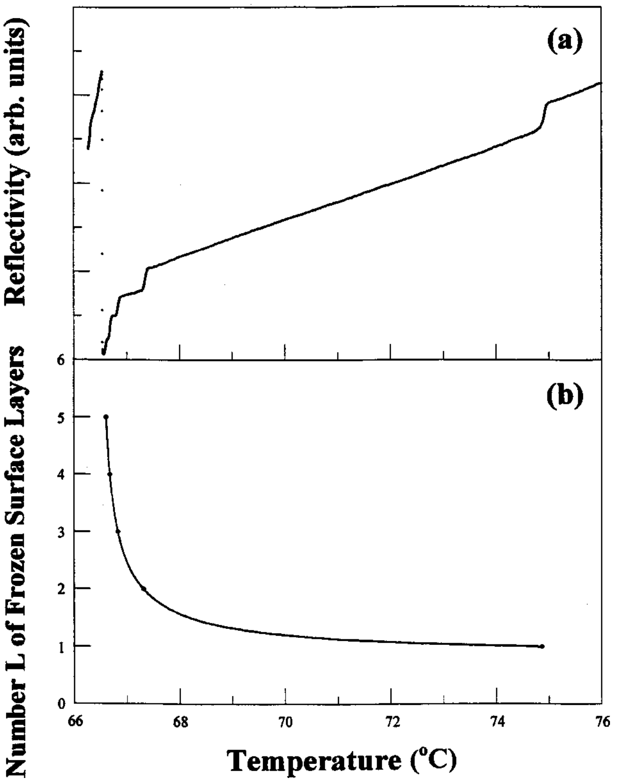

FIG. 2. Temperature dependence of (a) the optical reflectivity and (b) the number of frozen surface layers L for a 64-layer film. The solid line in (b) is a fit to the long-range power-law dependence.

The free-standing two-layer smectic film is of particular interest because of its possible use as a prototype to test the defect-mediated theory of 2D melting [8]. Previous studies on *n*-pentyl-4′-*n*-pentanoyloxy-biphenyl-4-carboxylate (54COOBC), which possesses the Sm-*A*–Hex-*B*–Cry-*B* transitions in the bulk, show that the bond-orientational order in the Hex-*B* phase in a two-layer 54COOBC film is indeed 2D in nature [13]. Furthermore, there is evidence for the existence of an intermediate phase between the Sm-*A* and the Hex-*B* [14]. In 40.8, which has a direct Sm-*A*–Cry-*B* transition in the bulk, a two-layer film also exhibits two intermediate phases, including the Hex-*B* [15]. In contrast, our current ED experiment shows that the two-layer 14S5 film transforms directly from the Sm-*A* to the Cry-*B* phase at 77 °C, in agreement with previous x-ray results [11]. Thus a two-layer 14S5 film represents an important example of a 2D liquid-crystalline system that does not melt via the hexatic phase, and demonstrates that defect-mediated theory offers a likely but not unique mechanism for 2D melting.

Our determination that the low-temperature phase in 14S5 is the orthogonal Cry-*B* phase is at variance with its earlier identification as the tilted Sm-*I* phase, whose birefringence facilitated the use of video imaging of textural changes to monitor the multiple layer-by-layer freezing of Sm-*A* films [7]. In fact, we conclude from the lack of birefringence in our 14S5 films that any tilt in the crystalline phase, if present, would be extremely small. Unable to observe textural changes associated with layer-by-layer freezing, we used instead high-resolution optical reflectivity [16] to monitor the phase transitions in 14S5 films. The temperature dependence of OR in a 64-layer film is shown in Fig. 2(a). The variation in OR is primarily due to changes in the average layer spacing. The five discontinuities in OR of roughly equal amount are associated with five separate phase transitions, each involving a pair of smectic layers undergoing the Sm-*A*–Cry-*B* transition inwardly from the surfaces as the temperature is decreased. The large abrupt change in OR near 66.6 °C occurs when all the remaining interior 54 layers make a transition to the Cry-*B* phase. Thus our OR data have revealed additional layer-by-layer transitions in 14S5 that were not detected in mechanical and x-ray studies [10,11]. From the results in Fig. 2(a), the total number L of frozen layers on each surface as a function of the temperature T is plotted in Fig. 2(b). According to the long-range power-law model for the molecular binding force [17,18], the behavior can be described by $T-T_c \propto L^{-n}$, where T_c is the bulk transition temperature. The value of n is expected to be 3 or 4 for either nonretarded or retarded van der Waals forces, respectively. The fitting of this expression to the data on 14S5 in Fig. 2(b) yields $n=3.81\pm0.02$. Hence, our results suggest that retarded van der Waals forces are the dominant long-range intermolecular interaction in 14S5 films [19]. This involvement of retarded van der Waals forces is in contrast to the nonretarded van der Waals forces (with values of n close to 3) that were reported in other materials exhibiting surface freezing from the Sm-*A* to hexatic phases [2,4]. It should be pointed out that $n=3.12$ was reported earlier for 14S5 [7]. However, Ref. [7] relied on the use of birefringence changes, which we found to be minimal. Furthermore, the value of T_c reported in Ref. [7] is significantly different from that of our sample, which in turn is in good agreement with that reported in other studies on 14S5 [10,11].

The first structural confirmation of the existence of direct Sm-*A*–Cry-*B* layer-by-layer freezing in 14S5 reported here, together with earlier observations in other systems, shows that there are three possible ways in which a Sm-*A* film can freeze into a Cry-*B* film upon cooling, as represented schematically in Fig. 3 for a six-layer film. For materials that exhibit the intermediate Hex-*B* phase in the bulk, such as 54COOBC [6], as shown in Fig. 3(a), the two outermost layers first freeze into the Hex-*B* phase, while the interior four layers remain in the Sm-*A* phase. Then the next-to-outermost layers transform into the Hex-*B* phase, while the interior two layers remain in the Sm-*A* phase. Finally, all six layers are in the Hex-*B* phase, after which the entire film transforms into the Cry-*B* phase. For materials that do not possess the Hex-*B* phase in the bulk, one class of materials exemplified by 4O.8 [9] would undergo the surface transitions depicted in Fig. 3(b), while another class of materials exemplified by 14S5 would exhibit the transitions shown in Fig. 3(c). In Fig. 3(b), the outermost layers undergo a two-stage Sm-*A*–Hex-*B*–Cry-*B* transition sequence before the next-to-outermost layers undergo a similar two-stage sequence. Finally, the two interior layers transforms into the Cry-*B* phase, either directly from the Sm-*A* phase or through an intermediate Hex-*B* phase. Figure 3(c) shows the phenomenon reported here in 14S5. The outermost layers first transform directly from the Sm-*A* phase into the Cry-*B* phase, to be followed by the next-to-outermost layers, and finally the interior layers. Since the Hex-*B* phase is essentially a two-dimensional phenomenon, we speculate that the role it plays, if any, in the surface freezing of the Sm-*A* phase depends primarily on the extent to which the smectic layers are coupled to each other. Additional studies on the correlation between the interlayer coupling and the type of surface transitions present would be needed to clarify this issue. In particular, it would be interesting to investigate whether the unusual presence of retarded van der Waals forces in 14S5 plays a key role in its somewhat unique layer-by-layer freezing behavior.

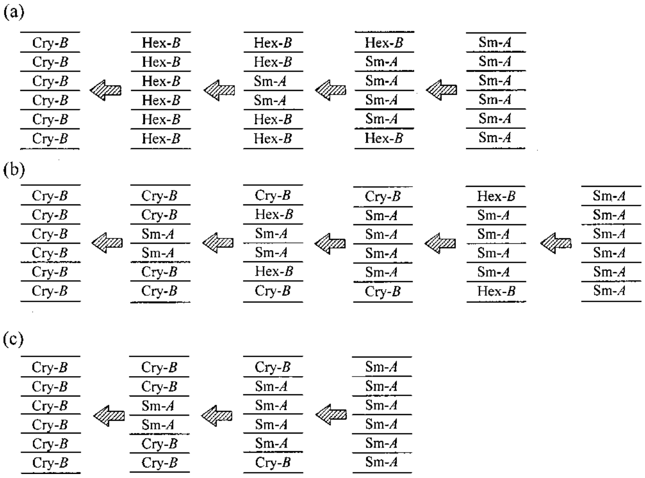

FIG. 3. Schematic representation of the three possible scenarios for the transformation of a six-layer Sm-*A* film into a Cry-*B* film through layer-by-layer surface freezing.

We can suggest possible reasons for the difference between our results and those reported earlier. In the optical experiment describing the transition in 14S5 as Sm-*A*–Sm-*I* [7], the transition temperature reported was significantly different from that seen in this and previous experiments [10,11], signifying that sample purity might have led to the discrepancy. In the x-ray experiment suggesting a possible hexatic three-layer film [11], the diffraction data were taken from a multidomain sample, making the identification of hexatic behavior more difficult than the single-domain data from electron diffraction.

In summary, we have provided an experimental confirmation that the surface freezing in 14S5 films consists of direct Sm-*A*–Cry-*B* layer-by-layer transitions. Contrary to published results [7,10,11], we find no evidence for the involvement of a hexatic phase. Our results suggest the existence of alternative pathways for low-dimensional melting not predicted by the defect-mediated theory.

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[19] We cannot totally rule out the presence of short-range exponential forces in 14S5, since our data can also be fitted to $T-T_c \propto \exp(-L/\xi)$, with a penetration depth ξ of 0.39, albeit with a larger χ^2 than the power-law expression.