

Induced hexatic phase in a free-standing two-layer N -(4- n -butoxybenzylidene)-4- n -octylaniline film

C. F. Chou,^{1,*} A. J. Jin,^{2,†} C. Y. Chao,¹ S. W. Hui,³ C. C. Huang,² and J. T. Ho¹
¹*Department of Physics, State University of New York at Buffalo, Buffalo, New York 14260*
²*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455*
³*Department of Biophysics, Roswell Park Cancer Institute, Buffalo, New York 14263*

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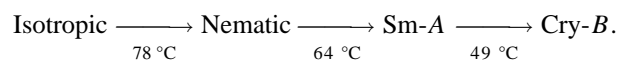
Electron diffraction shows that a free-standing two-layer film of N -(4- n -butoxybenzylidene)-4- n -octylaniline exhibits smectic- A , hexatic- B , and crystal- B phases upon cooling. The hexatic- B is preceded by a phase, called hexatic- B_1 , with hexatic-like positional correlations but no sixfold symmetric arcs in its diffraction pattern. The smectic- A –hexatic- B_1 transition is accompanied by a strong heat-capacity and optical-reflectivity anomaly. [S1063-651X(97)50406-5]

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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, including the nematic, the smectic- A (Sm- A) and the crystal- B (Cry- B) in the bulk. However, it is generally not expected to be a relevant system in which to study possible two-dimensional (2D) melting behavior via the intermediate hexatic phase that has been predicted by the theory of defect-mediated melting [1,2]. An earlier suggestion that the Cry- B phase in bulk 4O.8 might actually be hexatic was invalidated when it was demonstrated that this phase possesses true long-range positional order [3,4]. On the other hand, recent electron-diffraction experiments have indicated that free-standing films of 4O.8 between six and 12 molecular layers thick do display an unexpected two-step freezing phenomenon in which the outermost layers undergo phase transitions from the Sm- A , through an intermediate hexatic- B (Hex- B) phase, to the Cry- B phase [5]. This two-step phase sequence then propagates into at least two additional interior layers in a layer-by-layer manner upon further cooling. This result suggests that a two-layer film of 4O.8 should be an ideal physical system that exhibits the Sm- A –Hex- B –Cry- B phase transitions despite the absence of any hexatic phase in the bulk. Two-layer films are of particular interest because they have been shown to be effectively 2D systems [6] suitable for comparison with the theory of 2D melting. Here, we report the results of structural and thermal measurements on a two-layer free-standing 4O.8 film using electron diffraction, heat capacity and optical reflectivity aimed at investigating this possibility.

Our experimental techniques for making electron-diffraction [7,8], heat-capacity [9], and optical-reflectivity

[10] measurements in free-standing liquid-crystal thin films have been described elsewhere. Bulk 4O.8 samples show the following phase transitions:



Free-standing films were spread across a hole in a sample holder, with a diameter of 1 mm for electron-diffraction measurements and 1 cm for simultaneous heat-capacity and optical-reflectivity measurements.

The electron-diffraction patterns obtained with a two-layer film, shown in Fig. 1, suggest the following phase sequence:

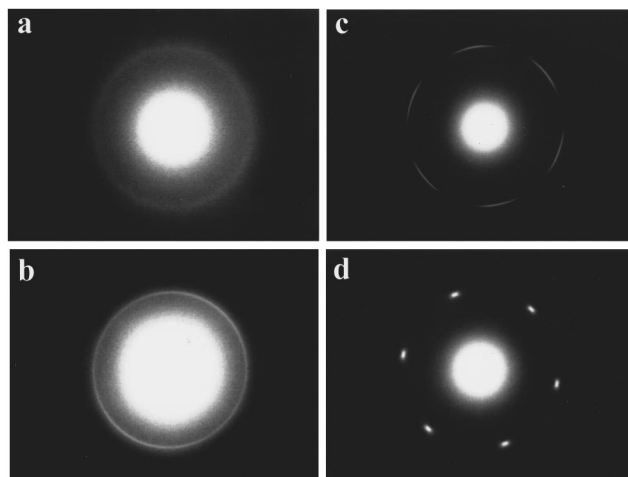
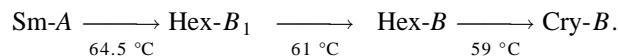


FIG. 1. Electron-diffraction patterns from a two-layer 4O.8 film: (a) Sm- A phase at 64.9 °C, (b) Hex- B_1 phase at 62.2 °C, (c) Hex- B phase at 60.2 °C, and (d) Cry- B phase at 58.0 °C.

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

†Present address: Department of Physics, Case Western Reserve University, Cleveland, OH 44106.

The labels Hex- B_1 and Hex- B do not necessarily imply two distinct phases, but rather refer to the appearance of different features of hexaticlike diffraction as described below. Above 64.5 °C, the film was in the Sm- A phase. Its diffraction pattern, typified by Fig. 1(a), shows a diffuse ring of constant intensity that one expects from a 2D liquid. At about 64.5 °C, the diffuse ring of the Sm- A phase sharpened in the radial direction, but the intensity remained uniform around the ring, as shown in Fig. 1(b). This diffraction pattern, which we characterize as Hex- B_1 , suggests that the positional correlation length is larger than that in an ordinary liquid, and similar to that found in a hexatic phase, but there is no long-range bond-orientational order within our electron beam of diameter 50 μm . Upon further cooling, some modulated patterns began to coexist with the sharp ring, indicating the formation of larger Hex- B domains. At around 61 °C, a single-domain Hex- B phase with long-range bond-orientational order appeared as in Fig. 1(c), which features six symmetric arcs. The azimuthal width of the arcs diminished gradually with decreasing temperature. The film was transformed into the Cry- B phase at 59 °C, with a diffraction pattern consisting of six sharp Bragg spots, as exemplified by Fig. 1(d), which is indicative of long-range positional order.

It is interesting to note that, because of the highly elevated transition temperatures of the film compared to those of the bulk, when the system is heated to sufficiently high temperatures for the two-layer film to exist in the Sm- A phase suitable for spreading, the bulk material surrounding the hole in the sample holder is typically already in the nematic phase, with much less viscosity than the film. This accounts for the difficulty in forming stable two-layer films of 4O.8.

Our observation that the single-domain Hex- B phase is preceded by a phase which we call Hex- B_1 , with hexaticlike positional correlations but no long-range bond-orientational order, has also been seen in other materials including *n*-pentyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate (54COBC) [6]. At this point, we are unable to ascertain whether the Hex- B_1 phase is simply a multidomain Hex- B spatially averaged by the electron beam of diameter 50 μm , or a distinct 2D isotropic phase with longer-range positional correlations than an ordinary 2D liquid.

The results of simultaneous heat-capacity and optical-reflectivity measurements on a two-layer film of 4O.8 are shown in Fig. 2. The film was typically prepared at around 58 °C, and then the temperature was ramped up to above 66 °C to begin a data run. Both heat capacity and optical reflectivity show pronounced changes near the Sm- A –Hex- B_1 transition at 64.8 °C. Although the heat-capacity data display pretransitional contributions, the optical reflectivity exhibits an abrupt jump in the vicinity of the heat-capacity peak. Such a jump indicates that the transition may be first order. However, due to the tendency of two-layer films to spontaneously rupture during thermal cycling, we were unable to determine the thermal hysteresis despite several experimental attempts. The slight difference between the Sm- A –Hex- B_1 transition temperature observed in electron diffraction and that observed in heat capacity and optical reflectivity could be attributed to the different thermometry used in our two laboratories, and to the transition temperature drifts that are common in chemically unstable Schiff's

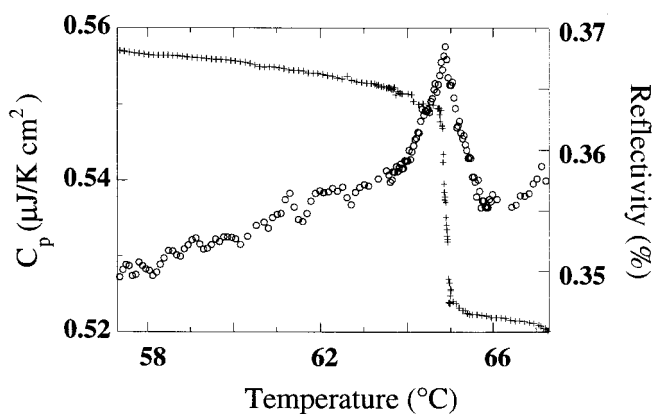


FIG. 2. Temperature dependence of heat capacity (circles) and optical reflectivity (crosses) in a two-layer 4O.8 film.

base compounds like 4O.8. However, neither the heat capacity nor optical reflectivity display any measurable signature at or near the Hex- B –Cry- B transition at 59 °C. On the other hand, the Hex- B –Cry- B transition temperature observed by electron diffraction is consistent with an earlier shear mechanical measurement in a two-layer 4O.8 film [11], where the onset of solidlike shear response was observed at around 59 °C.

According to the prediction of the two-dimensional melting theory [12,13], the behavior of the heat capacity near the Sm- A –Hex- B and the Hex- B –Cry- B transitions should both be of the Kosterlitz-Thouless (KT) type [14], involving only an essential singularity at the transition which is not expected to be observable, as well as a broad hump above the transition due to the dissociation of defect pairs. The strong heat-capacity anomaly we have observed near the Sm- A –Hex- B_1 transition in the two-layer 4O.8 film, which appears not to be in accordance to the theory, is nevertheless similar to that observed in other materials [10,15]. There are several possible explanations for the apparent discrepancy. The fact that the Sm- A first transforms to the Hex- B_1 and not directly to the Hex- B could fundamentally alter the nature of the pretransitional behavior. In fact, it could be argued that the Hex- B_1 –Hex- B and Hex- B –Cry- B transitions are more appropriate candidates to look for KT-type behavior. Interestingly, there is no heat-capacity change observed at or near either transition. Alternatively, it is possible that the character of the Sm- A –Hex- B_1 transition is dominated by the presence of another order parameter, such as herringbone order [16]. We have obtained a preliminary overexposed electron-diffraction pattern which did show weak satellite spots which are suggestive of some discernible herringbone order in the Hex- B phase of 4O.8. Finally, because of the slight difference in transition temperatures among different measurements, we cannot totally rule out the possibility that the heat-capacity peak in the two-layer 4O.8 film actually occurs above the Sm- A –Hex- B_1 transition temperature. Although layer-dependent hexatic order has been observed previously in thicker films of materials that do not possess hexatic phases in the bulk [5,17], this represents an example of a stable surface-induced Hex- B phase in a 2D liquid-crystal system.

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