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Synchrotron X-Ray Study of the Thickness Dependence of the Phase Diagram of Thin Liquid-Crystal Films

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The phase diagram of freely suspended thin films of heptyloxybenzylidene-heptylaniline shows dramatic changes for thicknesses below 22 layers. The most surprising feature of the phase diagram is the inclusion of two phases lacking long-range crystalline order (smectic-F and hexatic-B phases) between two crystalline phases (crystalline smectic B and smectic G). Neither the smectic F nor the hexatic B occurs in bulk samples. Between sixteen and ten layers the width, in temperature, of the hexatic-B phase increases.

Freely suspended liquid-crystal films provide one system for studying the crossover from three to two dimensions.[1] Interest in this problem has been stimulated by suggestions that transitions in three-dimensional (3D) smectic liquid crystals may be related to transitions within individual 2D layers[2,3] and by the development of a detailed theory of 2D melting.[4] The most experimentally accessible prediction of the theory of 2D melting is the existence of an intermediate hexatic phase with short-range positional order but with quasi-long-range bond-angle orientational order. A recent study of melting in variable-thickness films of $\overline{14}S5$ has shown the existence of an intermediate hexatic phase in a three-layer film which is not observed in bulk.[5] In this study we report the existence of a smectic-F phase (hexatic layers with a molecular tilt) in films as thick as 22 layers and the appearance of a hexatic-B phase at sixteen layers in a system which has no such phases in bulk samples.

We have examined freely suspended films of 4-n-heptyloxybenzylidene 4-n-heptylaniline (7O.7) varying in thickness from 5 to 22 layers. Previous work[6] has shown that thick films (>500 layers) of 7O.7 exhibit rich structure with a series of three transitions involving restacking of the layers and subtle changes in the intralayer packing. In order of decreasing temperature, the observed crystal structures are hexagonal-close-packed (hcp), orthorhombic face-centered (ortho-F), monoclinic C-centered (mono-C), and simple hexagonal (hex-AA) structures. The last three of these have a one-dimensional modulation of the smectic layers which has a wavelength of 95 Å, a wave vector in the plane of the molecular layers directed along a reciprocal-lattice direction, and a polarization normal to the plane of the smectic layers. Immediately below the hex-AA structure is a smectic-G phase, a monoclinic structure with the long axes of the molecules

tilted by 24 deg with respect to the layer normal. The projection of the long axes of the molecules onto the 2D triangular in-plane lattice is directed halfway between nearest neighbors.[7] This complex behavior is undoubtedly due to a combination of intralayer and interlayer effects. The present study was undertaken to clarify the origin of the restacking transitions and to look for the effects of reduced dimensionality.

X-ray diffraction studies were carried out on the triple-axis spectrometer installed on beam line VII-2 at the Stanford Synchrotron Radiation Laboratory.[8] A pair of asymmetrically cut Ge[111] crystals were used in the double-crystal monochromator. Low-resolution measurements were made with a pyrolytic graphite [002] analyzer which resulted in a longitudinal resolution of $\Delta Q = 22 \times 10^{-3} \text{ Å}^{-1}$. Higher-resolution measurements were done with a LiF[200] analyzer which provided a longitudinal resolution of $\Delta Q = 3.8 \times 10^{-3} \text{ Å}^{-1}$. In both cases a 5-mrad horizontal divergence of the input beam was accepted by the focusing mirror. The films were oriented with the normal to the smectic layers always in the scattering plane. Scans were done along Q_{xy}, parallel to the planes of the smectic layers, or along Q_z, normal to the layers. A rotation angle χ, about an axis normal to the smectic layers, specified the direction of Q_{xy} within the smectic layers.

We find that the phase sequence of 7O.7 undergoes dramatic changes as a function of film thickness. Part of the thickness-temperature plane of the phase diagram is shown in Fig. 1. The measured points are shown together with speculative phase boundaries. The most striking feature of this phase diagram is the inclusion of phases lacking long-range crystalline order (smectic-F and hexatic-B phases) between the crystalline-B and smectic-G phases, both of which are crystalline. For thicknesses below 22 layers, we find
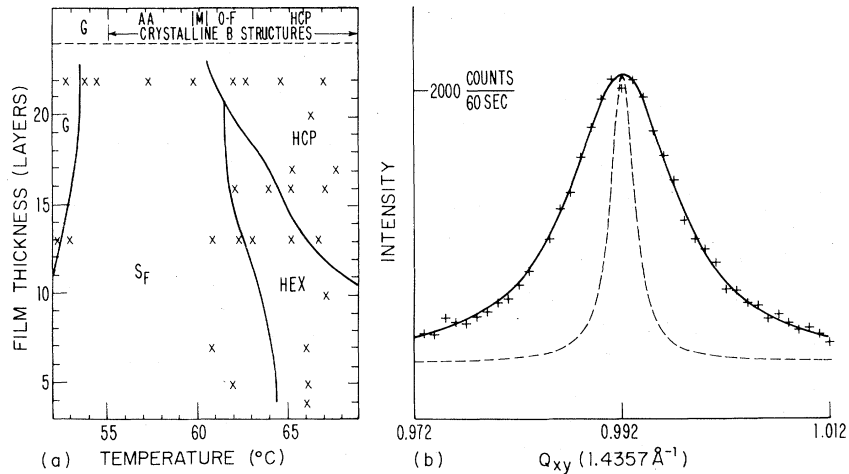
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FIG. 1. (a) Thickness vs temperature phase diagram for 7O.7. The phases are denoted by G, crystalline G; AA, hex-AA crystalline B; M, mono-C crystal; O-F, ortho-F; HCP, hcp; S_F, smectic F; and HEX, hexatic B. Measured points are marked by crosses with speculative phase boundaries shown. (b) Q_{xy} scan in hexatic-B phase of thirteen-layer film at $T = 65.07\,°\mathrm{C}$. The solid line is a fit by the sum of a Lorentzian and a constant background. The dashed line is the spectrometer resolution displayed on the same background.

that a smectic-F phase occupies the temperature region corresponding to the hex-AA and mono-C phases in bulk samples. As the sample thickness is reduced to sixteen layers, a hexatic-B phase appears between the smectic-F and the crystalline-B phases. Between sixteen and ten layers the hexatic-B phase gradually replaces the crystalline-B phase. Below ten layers the crystalline-B phase seems to disappear.

All of the four phases (crystalline B, hexatic B, smectic F, and smectic G) observed in thin films are observed in thirteen-layer films. Figures 1(b) and 2 illustrate the interlayer and intralayer correlations for a thirteen-layer film. Figure 2(a) shows a Q_z scan in the crystalline-B phase at $T = 67.4\,°\mathrm{C}$. There are definite peaks at $Q_z = \pm\frac{1}{2}$ but no peak at $Q_z = 0$. The $Q_z = 0$ peak is more difficult to observe because the theoretical intensity is only $\frac{1}{3}$ that of the $Q_z = \pm\frac{1}{2}$ peaks and stacking faults reduce its relative intensity even further.[9]

At $65.5\,°\mathrm{C}$ there is a transition to a hexatic-B phase. This has the properties theoretically predicted[3] and observed in other smectic materials.[10] These properties include a finite intralayer correlation length, a lack of interlayer correlations, and the presence of bond-angle orientation order. Figure 1(b) shows a Q_{xy} scan at $Q_z = 0$ which has a width corresponding to a correlation length of 130 Å. This is similar to other hexatic-B materials and is much longer than the correlation lengths observed in the smectic-

A and -C phases of 7O.7. Figure 2(b) shows a Q_z scan through the peak of the scan shown in Fig. 1(b). This scan shows a single broad peak with full width at half maximum of $1.7(2\pi/d)$. This width is similar to the width expected from the molecular form factor and indicates that there are no significant interlayer correlations. Finally, χ scans in this phase show considerable struc-
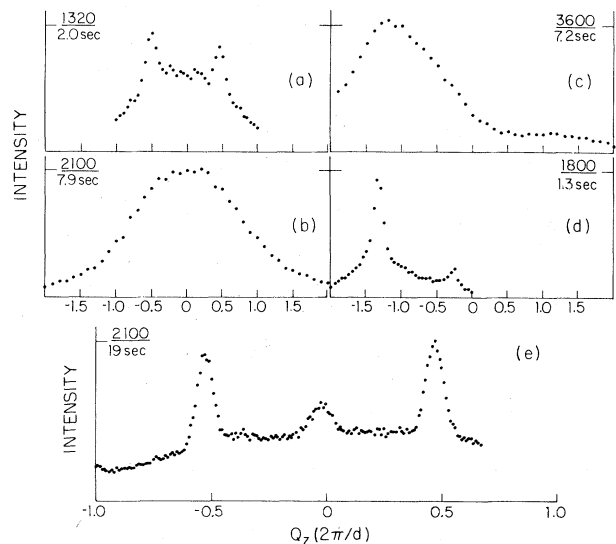

FIG. 2. Q_z scans: (a) thirteen-layer crystalline B at $T = 67.4\,°\mathrm{C}$, (b) thirteen-layer hexatic B at $T = 62.8\,°\mathrm{C}$, (c) thirteen-layer smectic F at $T = 60.8\,°\mathrm{C}$, (d) thirteen-layer crystalline G at $T = 51.2\,°\mathrm{C}$, and (e) seventeen-layer crystalline B at $T = 67.6\,°\mathrm{C}$.

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ture although single domains were not observed and the domain structure drifted with time.

At 61 °C there is an abrupt transition to a smectic-F phase, which is a hexatic phase with long axes of the molecules tilted with respect to the normal to the smectic layers. The correlation length is similar to the hexatic-B phase and χ scans also show structure. The Q_z scan in Fig. 2(c) differentiates this phase from the hexatic-B phase; the width of the broad peak is similar to the scan in the hexatic phase [Fig. 2(b)] but the center of the peak is displaced to nonzero Q_z. This is because the molecular form factor has its maximum in the direction normal to the long axis of the molecule. From the position of the peak the molecular tilt is estimated to be 20 deg in the smectic-F phase.

At $T = 51.6$ °C the thirteen-layer film crystallized into a smectic-G phase. Figure 2(d) shows a Q_z scan in this phase which shows sharp peaks characteristic of the monoclinic structure. The Q_{xy} scans in this phase show no excess width with graphite resolution, implying that the intralayer ordering is long ragne.

In films with thicknesses greater than ten molecular layers, the first phase which appears at temperatures below the smectic-C phase is the crystalline-B hcp structure. This phase is characterized by resolution-limited peaks in the Q_z = 0 plane. When Q_{xy} is scanned through one of these in-plane peaks, results similar to the dashed line in Fig. 1(b) are obtained. Peaks appear at integer and half-integer values of Q_z (measured in units $2\pi/d$, where d is the molecular length). Figure 2(e) shows a scan in a seventeen-layer film; here the intensities of the peaks are in the 3:1:3 ratio expected for the hcp structure. As the transition to the hexatic-B phase is approached, the intensity of the peak at $Q_z = 0$ drops relative to the half-order peaks and the intensity of the thermal diffuse background grows relative to the peaks [Fig. 2(a)]. The widths of the peaks in these Q_z scans are greater than the finite size limit. The resolution of the present experiments was not high enough to distinguish an ortho-F structure from a faulted hcp structure.

Films thinner than ten layers appear to have no crystalline-B phase, only the hexatic-B and smectic-F phases. We have not yet measured very thin films in the region of the smectic-F to smectic-G transition, but we expect the G phase to occur below the F. There is one difference between the data taken on five-layer films and those obtained from thirteen-layer films. The

hexatic-B and smectic-F phases in the five-layer films show no structure in χ scans. We identify these phases by the intralayer correlation lengths obtained from Q_{xy} scans and from the interlayer correlations measured with the Q_z scans. The loss of measurable orientational order in very thin films of materials which have bulk hexatic-B phases has been noted in other experiments.[11] This is assumed to be related to both static defects and the quasi-long-range nature of the orientational ordering in the two-dimensional hexatic.[11,12] The interlayer correlations measured in the smectic-F phase for the five-layer film clearly rule out the possibility of a smectic-C phase with unusually long intralayer correlation lengths.

The nature of this transformation of the system from a crystalline solid to a hexatic with short-range positional order is not understood. At present we do not know at what thickness the crystalline phases characteristic of bulk 7O.7 are replaced by the smectic-F phase. The fact that a tilted hexatic phase replaces the crystalline structures supports the suggestion that molecular tilt is involved in the restacking transitions observed in the bulk.[6] The crossover from the crystalline phases to the smectic-F phase is probably due to a competition between bulk and surface energies. As the thickness of the sample is reduced, the contribution of the surface term to the total free energy becomes more important and ultimately results in the instability of the crystalline structures. The free-energy difference between the crystalline structures and the bulk smectic-F structure may be very small, since materials such as 5O.6 have a phase sequence in bulk (crystalline B-smectic F-smectic G) which is identical to the one observed in 22-layer films of 7O.7.[7]

This study reveals an amazing richness of structure which poses a new set of questions to be answered. A systematic study of crystalline-B line shapes as a function of thickness may give further insight into the details of the crystal to hexatic transition. Preliminary data suggest that the smectic-F to smectic-G transition in the thin films may be a second-order transition. An understanding of this system may lead to the understanding of other bulk liquid-crystal systems such as 5O.6 which have a liquidlike phase sandwiched between two crystalline phases.[7] Further studies of these systems promise to enhance our understanding of both three-dimensional layered systems and the role of reduced dimensionality.

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