X-Ray Study of the Hexatic-*B*-to-Smectic-*A* Phase Transition in Liquid-Crystal Films

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X-ray studies of thick, free-standing films of the liquid-crystal compound *n*-butyl 4′-*n*-hexyloxybiphenyl-4-carboxylate (46OBC) have determined the critical behavior at the three-dimensional hexatic-*B*-to-smectic-*A* phase transition. The position and width of the scattering peaks exhibited $1-\alpha$ singularities in agreement with theory and heat-capacity results. Measurements on two-layer films of 46OBC provided evidence for a continuous, two-dimensional, hexatic-to-liquid transition.

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The layered hexatic-*B* liquid-crystal phase is the only three-dimensional (3D) physical system in which "hexatic" order has been observed.[1,2] This ordering involves a long-range sixfold symmetric, orientational alignment of the "bonds" connecting neighboring in-plane molecules even though their in-plane positional correlations remain short ranged and is characterized by a local order parameter $\psi(\vec{r})=e^{6i\theta(\vec{r})}$ where $\theta(\vec{r})$ is the angle between the "bonds" and some reference axis.[3] The loss of bond-orientational order upon heating the hexatic-*B* phase results in a layered phase with liquidlike in-plane order—the smectic-*A* phase. Heat-capacity studies[4] of the hexatic to smectic-*A* (hex-*A*) transition in the liquid-crystal compound 65OBC found the transition to be continuous with a large, nearly symmetric heat-capacity peak and critical exponent $\alpha \sim 0.6$. This heat-capacity behavior implies large hexatic fluctuations which couple to the density fluctuations, causing sixfold symmetric x-ray scattering with a singular critical temperature dependence for both the position and width of the scattering peaks. In this Letter we present measurements of this singular behavior at the 3D hex-*A* transition and evidence for a continuous (2D) hexatic-liquid transition. The 3D measurements involved thick films (several hundred molecular layers) while the 2D measurements were on two-layer films. The films were free standing and thus substrate-free.

The liquid-crystal compound studied was *n*-butyl 4′-*n*-hexyloxybiphenyl-4-carboxylate (46OBC). In comparison to 65OBC, this compound exhibited the hexatic and smectic-*A* phases over wider temperature ranges. Furthermore, the range of stability for two-layer films was enhanced, and this material showed no crystalline surface-ordering transition as observed in 65OBC.[1] Heat-capacity measurements[5] on 46OBC indicated that the hex-*A* transition was first order, but only weakly so. The heat capacity, C_p, could be fitted by a power-law divergence up to 30 mK of T_c. Explicitly $C_p \sim A^{\pm} t^{-\alpha^{\pm}}$, where $t=|(T-T_c)/T_c|$, the upper and lower signs refer to $T>T_c$ and $T<T_c$, respectively, and the fitted parameters were $A^+/A^- = 0.75 \pm 0.03$ and $\alpha^+ = \alpha^- = 0.49 \pm 0.02$. Unfortunately, 46OBC films rupture when cooled from the hexatic phase into a monoclinic crystalline phase, and so the hexatic-crystal transition could not be studied.

For our structural studies, the layers of the liquid-crystalline phase were aligned by drawing free-standing films across a $6\times6\text{-mm}^2$ hole in a glass cover slide.[1] The films were kept at a pressure of 0.7 Torr in a two-stage oven whose temperature was regulated to better than 0.01 K. Thick films were studied using a 50-kW rotating-anode x-ray source. A vertically bent pyrolytic graphite (002) crystal was used to monochromate and focus the x rays to a 2-mm^2 spot. Scattered radiation was analyzed using a flat pyrolytic graphite (002) crystal. With the film oriented in a transmission geometry, the in-plane order was probed by scanning the momentum transfer parallel to the layers ($Q_\parallel$ scans) and by rotating the film about its layer normal (χ scans), as shown in the inset to Fig. 1(a). The resolution parameters were $\Delta Q_\parallel = 0.05$ Å^{-1} and $\Delta\chi = 2°$ full width at half maximum (FWHM).

Direct structural confirmation of hexatic order for a system with short-range positional correlations is the observation of structure in a χ scan.[1] Figure

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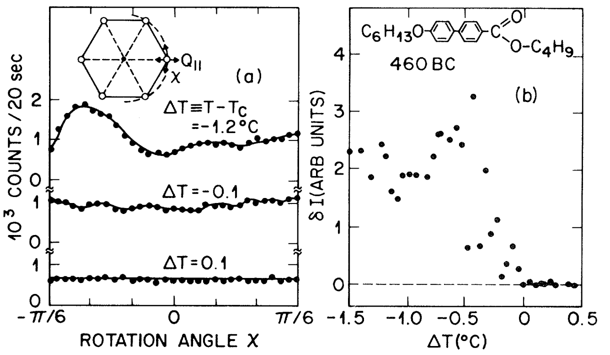

FIG. 1. (a) 60° χ scans in a thick film at temperatures below, near, and above T_c. The inset describes the scan directions. (b) The amplitude of the intensity modulation in χ scans as a function of temperature. $\delta I=0$ implies liquidlike order.

1(a) shows the results of such 60° χ scans for thick films of 46OBC confirming the presence of a hexatic phase and showing the evolution in χ structure as the hex-*A* transition is approached. Figure 1(b) shows the temperature dependence of the amplitude, δI, of the intensity modulation in a χ scan which is a measure of the hexatic order parameter,[3] $|\langle\psi\rangle|$. When $\delta I=0$, the order is liquidlike. At a given temperature, δI varied significantly with time due to a change in the number or size of hexatic domains within the sample area probed; hence, measurements of δI could not be used to determine the critical behavior of $|\langle\psi\rangle|$. Nevertheless, the monotonic decrease of δI to zero in the smectic-*A* phase accurately established T_c for the transition ($T_c=67.63\pm0.03\,°\mathrm{C}$). This independent measurement of T_c is crucial to extract quantitative information from the temperature dependence of the positional correlations. Typical $Q_{\parallel}$ scans near T_c and well away from T_c are shown in Fig. 2. The line shape which has been found to describe scattering data from various liquids with substantial bond-orientational order is well approximated by a square-root Lorentzian (SRL); namely, $S(Q_{\parallel},T)=\{[Q_{\parallel}-Q_0(T)]^2+\kappa^2(T)\}^{-1/2}$, where $Q_0(T)$ is the peak position and $\kappa(T)$ its width.[1,6] The dashed lines in Fig. 2 are the result of convoluting $S(Q_{\parallel},T)$ with the resolution including a linear background which well approximates the tail of a small additional scattering peak[1] at $Q_{\parallel}=1.32Q_0$ [for 46OBC, $I(1.32Q_0)/I(Q_0)\sim0.02$]. The SRL structure factor provides a good fit to the data over the entire temperature range and yields the temperature dependence of Q_0 and κ shown, respectively, in Figs. 3 and 4. It is clear that the onset of hexatic order ($T_c=67.63\,°\mathrm{C}$) causes a substantial increase in both the in-plane density (Q_0) and the in-plane positional correlations which are proportional to κ^{-1}.

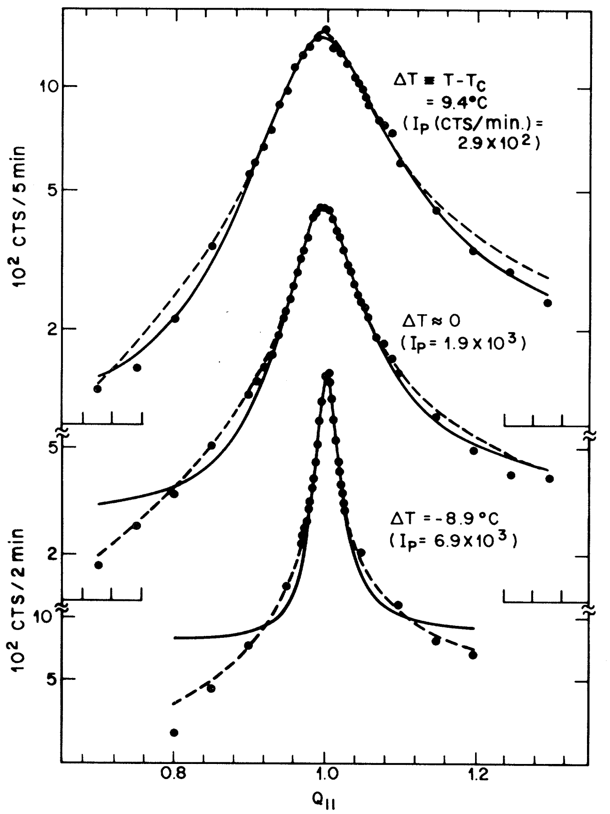

FIG. 2. Logarithm of the intensity for $Q_{\parallel}$ scans in a thick film at temperatures below, near, and above T_c. Each data point was integrated over 60° in χ. The solid and dashed lines are, respectively, fits to a Lorentzian and square-root Lorentzian line shape. The in-plane momentum transfer $Q_{\parallel}$ is in units of 1.410 Å^{-1}. I_p is the peak intensity.

Motivated by these measurements, Aeppli and Bruinsma constructed a theory[7] which takes into account the coupling of hexatic to density fluctuations and shows the critical behavior of the hexatic structure factor. In particular, they explicitly calculate that unless $T\gg T_c$ a SRL structure factor should describe our data. Furthermore, they show that the critical behavior of Q_0 and κ is determined by the singular behavior of $\langle|\psi|^2\rangle$, which is proportional to an integral of the heat capacity. Taking $\langle|\psi|^2\rangle=C[1\mp A^{\pm}t^{1-\alpha}]$, we can write

$$Q_0(T)=C_0[1\mp A^{\pm}t^{1-\alpha}], \tag{1}$$

$$\kappa^2(T)=\kappa_0^2-|C_1|[1\mp A^{\pm}t^{1-\alpha}]^{1/2}+C_2[1\mp A^{\pm}t^{1-\alpha}], \tag{2}$$

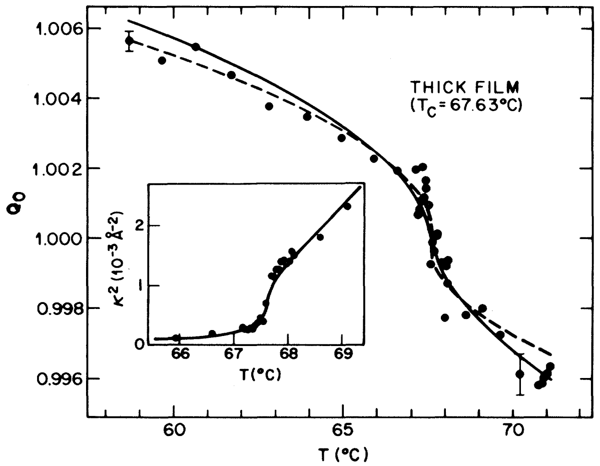

FIG. 3. Temperature dependence of the peak position Q_0 (in units of 1.410 Å^{-1}). The lines are fits to Eq. (1). The inset is the temperature dependence of κ^2 near T_c. The line in the inset is a fit to Eq. (2).

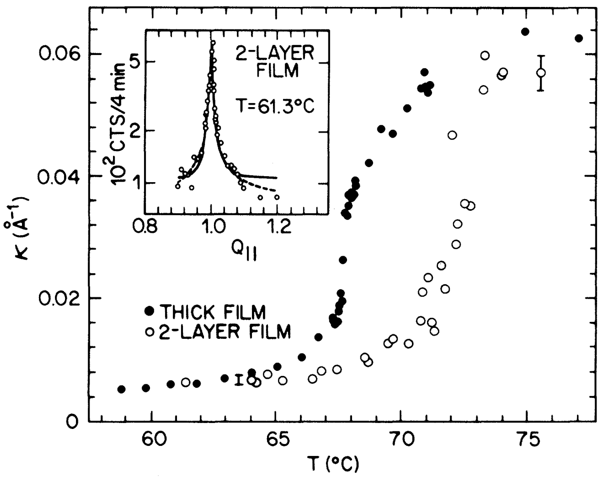

FIG. 4. Temperature dependence of κ for a thick film (closed circles) and two-layer films (open circles). The inset is the log of the intensity for a $Q_{\parallel}$ scan in the hexatic phase of a two-layer film taken at the synchrotron. The solid and dashed lines are respectively fits to a Lorentzian and square-root Lorentzian line shape.

where C, κ_0, C_1, and C_2 are constants. Note that the heat-capacity amplitude ratio A^+/A^- and exponent α appear explicitly. For $Q_0(T)$ the solid line in Fig. 3 is a fit to Eq. (1) with T_c fixed to 67.63 °C and the amplitude ratio A^+/A^- and exponent α fixed to their measured heat-capacity values. The best-fit values for the parameters ($A^+/A^- = 1.3 \pm 0.5$ and $\alpha = 0.49 \pm 0.04$) resulted in the dashed line. Hence, the temperature dependence of Q_0 is in good agreement with theory and heat-capacity results. For $\kappa(T)$ we fitted the measured values of κ^2 within 1.5 K of T_c to Eq. (2) with T_c, A^+/A^-, and α fixed as above for the solid line. Again there is good agreement between theory and experiment. Finally, for $T >> T_c$, Aeppli and Bruinsma show that the structure factor could evolve into a Lorentzian. In Fig. 2 we show the results of fitting our data to a Lorentzian (solid lines). Only for $T >> T_c$ does it fit the data as well as a SRL, showing consistency with a SRL → Lorentzian crossover.

Having determined the 3D hex-A critical behavior of the structure factor in thick films of 46OBC, we next studied hexatic ordering and 2D critical behavior in two-layer films of 46OBC. Measurements on the two-layer films were carried out on the wiggler beam line VII-2 at the Stanford Synchrotron Radiation Laboratory. We had previously succeeded in observing the scattering from a two-layer *crystalline* film using an all Si(111) spectrometer.[8] However, the scattering from hexatic order is broader and the peak intensity correspondingly weaker (by $> 10^3$); therefore, a pair of asymmetrically cut Ge(111) crystals were used in the monochromator and a LiF(200) crystal in the analyzer to improve signal rates a factor of 20 at the expense of resolution [$\Delta Q_{\parallel} = 0.004$ Å^{-1} (FWHM)]. A typical $Q_{\parallel}$ scan in the two-layer hexatic phase is shown in the inset to Fig. 4.

Just as for thick films of 46OBC, the two-layer film $Q_{\parallel}$ data could be fitted by a SRL line shape, yielding a temperature dependence for κ shown in Fig. 4. With decreasing temperature κ sharply but continuously decreased from a value $\kappa \simeq 0.058$ to $\kappa \simeq 0.0065$ Å^{-1}. Thus, the in-plane positional correlations evolved from 17 to 160 Å. The latter value is comparable to the correlation length in the thick-film hexatic phase and is strong evidence for a liquid-hexatic transition in the two-layer films. Furthermore, there was no observed thermal hysteresis in κ, which is consistent with the transition being second order. In spite of this order-of-magnitude change in the positional correlations we did not observe any χ structure for the two-layer films. We expect that this is due to the occurrence of multiple domains over the area probed (3×4 mm^2) as well as a 2D enhancement of the hexatic bond-angle fluctuations whose rms magnitude is given by $\delta\theta = [(k_B T / 2\pi K_A)\ln(L/a)]^{1/2}$, where K_A is the bond-angle stiffness constant, L is the sample size probed, and a is the molecular spacing (~ 5 Å).[9] Since thermodynamic stability requires $K_A / k_B T \gtrsim 72/\pi$, the 2D fluctuations can be as large as $\delta\theta \sim 19°$ and thus cause significant broadening.

Finally, it is also evident that the decrease in κ occurred at a higher temperature in the two-layer film than that in the thick film. A free-surface-induced increase in T_c has been observed for other phase transitions[8] in two-layer films and is probably the reason for the higher-temperature κ decrease. We note, however, that the decrease in κ signals a heat-capacity peak which should occur at a temperature higher than T_c in two dimensions.[10]

In summary, a complete quantitative characterization of the critical behavior of the 3D hexatic-liquid transition has been obtained in 46OBC. Taking advantage of the variable dimensionality of liquid-crystal films, measurements were extended to the 2D limit using two-layer films. The characteristic thick-film hexatic signature of a sharp evolution in κ was also clearly evident for two-layer films, confirming the presence of a 2D liquid-hexatic transition. Since heat-capacity measurements on two-layer films are feasible,[5] the quantitative analysis of the critical behavior demonstrated for the thick-film measurements should also be possible in the future for the very important 2D case.

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