X-Ray Observation of a Stacked Hexatic Liquid-Crystal *B* Phase

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X-ray studies have been performed on a new liquid-crystal material which exhibits a noncrystalline *B* phase. Using free-standing liquid-crystal film techniques, we find that this *B* phase has short-range in-plane positional correlations but long-range, three-dimensional, sixfold bond-orientational order. We interpret our results in terms of a system of interacting two-dimensional hexatic layers.

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The liquid-crystal *B* phase is a layered phase with the molecules oriented perpendicular to the layer planes and hexagonally ordered within each layer. X-ray structural studies[1,2] recently demonstrated that this hexagonal order in the prototypical *B*-phase liquid crystal N-(4-*n*-butyloxybenzylidene)-4-*n*-octylaniline (4O.8) involves positional correlations which are three dimensional (3D) and long range. This *B* phase is, therefore, crystalline. It supports a shear both within and between its layers[3,4] and melts into the smectic-*A* phase, a higher-temperature phase with fluidlike layers, by a first-order transition.[5] Crystalline *B* phases have also been observed by us in N-(4-*n*-butyloxybenzylidene)-4-*n*-butylaniline (4O.4) and *trans*-1,4-cyclohexane-*di*-4-*n*-octyloxybenzoate (TCOB).[6] Although many *B* phases appear to be crystals, Leadbetter, Frost, and Mazid[7] claimed that some materials exhibited *B* phases which lacked interlayer correlations. In this paper we report x-ray studies on a similar material using free-standing liquid-crystal film techniques. This approach enables us to ascertain the novel structural nature of this new *B* phase. Unlike previous crystalline *B* phases, this new phase has short-range in-plane positional correlations, but it differs from the *A* phase in having long-range, sixfold bond-orientational order. Halperin and Nelson first proposed the possibility of bond-orientational ordering in their treatment of two-dimensional (2D) melting.[8] They found that a 2D phase having algebraically decaying bond-orientational order (a hexatic phase) would occur between the 2D solid and liquid phases if 2D melting was a dislocation-mediated second-order phase transition. Subsequently, Birgeneau and Litster[9] suggested a 3D liquid-crystal phase consisting of 2D hexatic layers which interact to produce long-range, 3D bond-orientational order. As we will discuss below, this stacked hexatic phase has the structural properties which we have observed in the *B* phase of a new liquid-crystal material. We refer to this phase as a hexatic *B*. The discovery of this phase has already motivated experiments which show that this hexatic *B* phase does not support an in-plane shear[10] and that it melts by a second-order transition.[5]

In the present experiments we have used the same rotating-anode x-ray techniques as in our previous study of the crystalline *B* phase in 4O.8.[1] Samples were free-standing films at least 100 molecular layers thick. Our work on 4O.8 demonstrated that these films are single-crystal-quality samples with in-plane domains ~ 1 mm^2 and with layer alignment better than 0.01°. These qualities offer considerable technical advantages over the conventional field-aligned bulk samples. For this experiment, field-aligned samples would not permit a study of the bond-orientation structure within the layers since such samples are completely disordered with respect to rotation about the layer normal.

We chose to examine the liquid-crystal material *n*-hexyl-4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC),[11] which exhibits the following sequence of phase transitions on cooling:

$$\text{Isotropic} \xrightarrow{85^\circ} \text{smectic-}A \xrightarrow{68^\circ} B \xrightarrow{60^\circ} E\ (\text{crystal}).$$

Three different types of scans are necessary to establish the structural properties of 65OBC (see inset to Fig. 1). These scans are referred to in hexagonal reciprocal-lattice coordinates with $a^* = 4\pi/(3^{1/2}a) = 1.420$ Å^{-1} and $c^* = 2\pi/c = 0.242$ Å^{-1}. Scans with $Q = Q_\parallel$ (momentum transfer in the plane of the layers) probe the extent of in-plane positional correlations. Scans which rotate the film about the layer normal (χ scans) probe bond-orientational order. Finally, scans along $Q_\perp$ at $Q_\parallel = 1$ probe the extent of interlayer correlations.

Scans in the *B* phase of 65OBC are shown in Fig. 1. There is no evidence for any Bragg peaks such as seen in the crystalline *B* phase of 4O.8. Rather we find a rod of scattering along $Q_\perp$ which

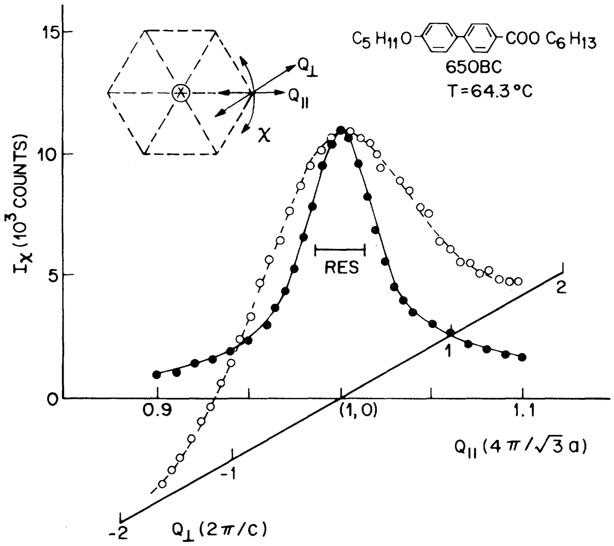

FIG. 1. χ-averaged intensity for a $Q_\parallel$ scan (closed circles) and a $Q_\perp$ scan (open circles) in the B phase of 65OBC. Note that the $Q_\parallel$ scale has been expanded relative to the $Q_\perp$ scale. The scattering along $Q_\perp$ is a diffuse rod. The resolution width for the $Q_\perp$ scan ($\Delta Q_\perp = 0.006$ Å^{-1} full width at half maximum) was too small to illustrate. The inset describes the three scan directions.

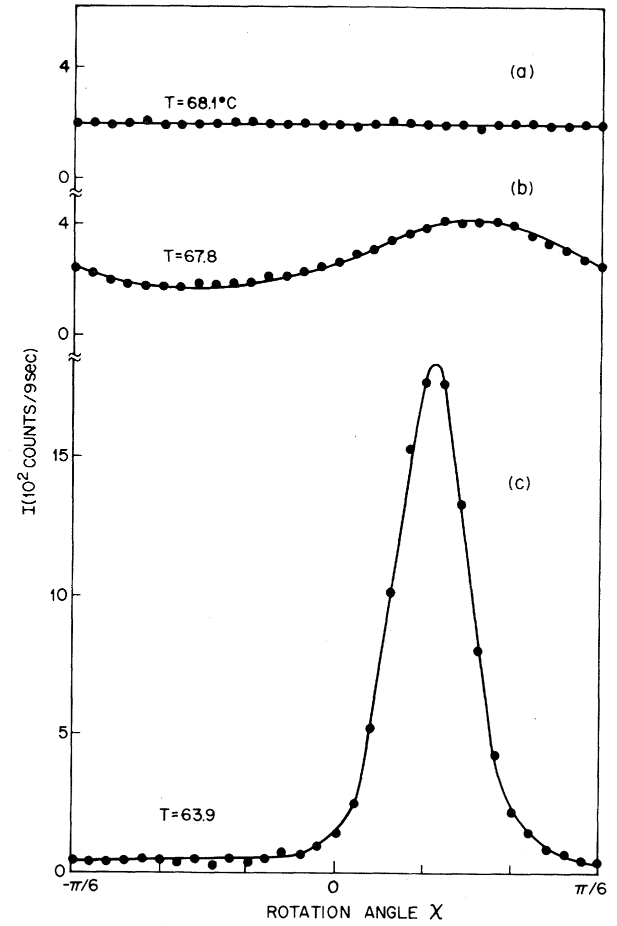

FIG. 2. χ scans for three different temperatures: (a) In the smectic-A phase; (b) just below the smectic-$A \rightarrow B$ transition; (c) well into the B phase (below T_0).

indicates the complete absence of interlayer correlations. Furthermore, the peak is not resolution limited in $Q_\parallel$. The solid line through the data points is the result of a least-squares fit of the χ-averaged 2D Lorentzian structure factor $S(Q_\parallel) = 1/[(Q_\parallel - Q_0)^2 + \kappa^2]$ convoluted with the Gaussian instrumental resolution function of width $\Delta Q_\parallel = 0.038$ Å^{-1} full width at half maximum. This scan demonstrates that the in-plane positional correlations decay exponentially with a correlation length $\xi_\parallel = 1/\kappa \simeq 100$ Å.

Although the positional order is short range in the B phase of 65OBC, the scattering differs distinctly from the smectic-A phase in a χ scan. A 60° segment of a χ scan is shown in Fig. 2 for several temperatures. From heat-capacity measurements[5] the $A \rightarrow B$ transition temperature is $T_{AB} = 67.9$ °C. Above T_{AB} the scattering shown in Fig. 2(a) is a constant, independent of χ. For temperatures below T_{AB} the χ scan develops substantial sine-wave modulation [Fig. 2(b)] indicative of a sixfold periodicity. This scattering is direct evidence for hexagonal bond-orientational correlations which are three-dimensionally ordered over distances of the order of the area illuminated by the x-ray beam (~2 mm^2).

Structure factor calculations[12] for the stacked hexatic phase demonstrate that, in principle, a measurement of the amplitude of the χ-scan modulation provides a method for measuring the temperature dependence of the bond-orientational order parameter. In practice, the situation is complicated by the presence of more than one orientational domain within the scattering volume. If different domains produce sine-modulated scattering with different χ phase shifts, the resulting scattering will still be a single sine wave of reduced amplitude. It is not possible to interpret unambiguously the amplitude of the modulation unless one knows that the film contains only a single domain. Since the amplitude that we measure is not a reproducible function of temperature in the vicinity of T_{AB}, we believe that a small but variable number of domains are probably present within the area probed.

As the hexatic B phase is cooled, the amplitude of the χ-scan modulation abruptly stabilizes at a temperature $T_0 = 66.4\,^\circ\mathrm{C}$. Below T_0, the 60° χ scans can develop a single sharp peak [Fig. 2(c)] indicating a single, well-oriented domain. This behavior is thermally reproducible and there is no anomaly at T_0 in either the positional correlation length (arrow in Fig. 3) or in the heat capacity.[5] Mechanical measurements[10] on 65OCB suggest this enhanced bond-orientational order is possibly due to the crystallization of the surface layers of the film at T_0. Similar surface crystallization has also been observed in films of 40.8 at temperatures above its crystalline B phase.[3]

We next consider whether the bond-orientational order that we have observed in the hexatic B phase of 65OBC is the primary order parameter of this phase or whether it is being induced by coupling to another ordering field. As we have shown above, long-range lattice positional order does not develop at T_{AB}. Figure 3 shows measurements of the positional correlation length over the relevant temperature region. In the vicinity of T_{AB}, there is a rapid increase in $\xi_\parallel$ on cooling (from about 20 to 60 Å) but it does not diverge. Hence, positional ordering is not a relevant order parameter.

Another possible ordering field is associated with the orientation of the molecules about their long axes. The benzene rings of the molecules are approximately coplanar with a lateral van der Waals size $6.7 \times 3.7\ \text{Å}^2$. It is evident that such molecules cannot pack with a spacing $a = 5.11$ Å and still maintain complete rotational freedom about their long axes. A local herringbone packing structure was proposed by Levelut.[13] This structure explains the additional scattering observed at $Q_\parallel = 1.32$, which is shown in Fig. 4. The absence of a peak at $Q_\parallel = 0.5$ implies the presence of a glide-plane symmetry which is contained in the herringbone packing model. The local herringbone order can assume three distinct directions $\vec{x}_1, \vec{x}_2, \vec{x}_3$ each contributing four diffraction spots at $Q_\parallel = 1.32$ (see inset, Fig. 4). Below T_0, even when we observe a single bond-orientation domain, all directions of the herringbone are simultaneously present and contribute equally to the scattering. It is, therefore, clear that the herringbone structure is correlated over distances much smaller than the bond-orientational order. Furthermore, it is known from neutron scattering measurements[14] that the molecular-orientational ordering is dynamic with a molecular orientation time $\sim 10^{-11}$ sec. For these reasons we rule out the possibility that the molecular-orientational order is driving the bond-orientational order, although it is certainly possible that the molecular orientational order enhances the bond-orientational order.

In conclusion, our x-ray study has established the existence of a 3D stacked hexatic B phase with sixfold bond-orientation as the order parameter. Since the existence of a 2D hexatic phase

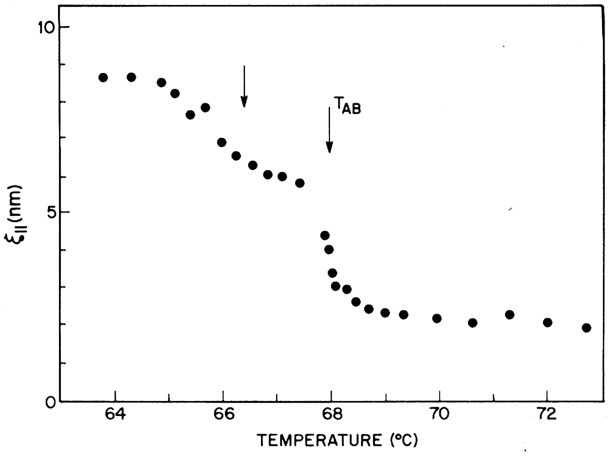

FIG. 3. Temperature dependence of the in-plane positional correlation length $\xi_\parallel$.

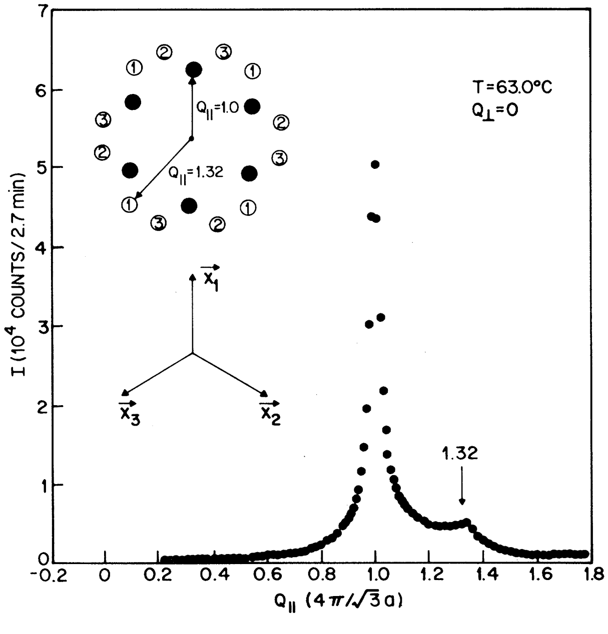

FIG. 4. An expanded $Q_\parallel$ scan showing the additional scattering at $Q_\parallel = 1.32$. The inset describes the scattering that results from a local herringbone packing: A herringbone oriented in the direction $\vec{x}_1$ ($\vec{x}_2, \vec{x}_3$) gives rise to four diffraction spots labeled 1 (2, 3).

has not yet been experimentally confirmed, our study gives important experimental support to the existence of hexatic ordering. Furthermore, there exists the possibility that films of 65OBC will exhibit a 2D hexatic phase when studied in the thin film limit (2 molecular layers). These experiments are currently in progress. We note that the crossover from 3D to 2D crystalline order has already been observed in thin films of 4O.8 in its crystalline *B* phase.[1] Finally, we have also used the free-standing film technique to study smectic phases in which the molecules are tilted with respect to the layer planes. Our results[15] are in agreement with previous studies[16] which indicated a new phase without long-range positional order at temperatures below the smectic-*C* phase (tilted analogue of the smectic-*A* phase). In this case of tilted molecules, the coupling of the tilt direction to sixfold bond-orientational order adds a new and potentially interesting aspect to the physics.

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Inelastic Atom Scattering from a Cu(001) Surface and an Ordered Adsorbed Layer of Xe Atoms at 16°K

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Energy-transfer events have been observed between a He atom and a Cu(001) surface at 16°K. Only phonon creation events were observed which were confined to the subspecular region. Parallel momentum was conserved and bulk and surface modes detected. For an ordered Xe layer, both phonon creation and annihilation events were detected and parallel momentum was not conserved.

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Neutral-atom (e.g., He and Ne) scattering has recently[1,2] been demonstrated as a useful tool in detecting surface modes of vibration by measuring energy changes with use of time-of-flight techniques. Here is described a similar study with use of low-energy (22.6 meV) He atoms scattered from a Cu(001) surface at low temperature (16°K) as well as from an ordered adsorbed layer of Xe atoms deposited under various conditions. This is a desirable region for study but in the