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### Synchrotron X-Ray Study of Novel Crystalline-*B* Phases in Heptyloxybenzylidene-Heptylaniline (7O.7)

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This paper reports an x-ray diffraction study of structures and restacking transitions within the *B* phases of heptyloxybenzylidene-heptylaniline. The system evolves from a hexagonal close-packed structure, through intermediate orthorhombic and monoclinic phases, to a simple hexagonal structure. The monoclinic phase has a temperature-dependent shear which transforms the system from orthorhombic to hexagonal. The latter three phases exhibit a single- $\vec{q}$  sinusoidal modulation of the molecular layers.

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The realization that an infinitesimally weak interlayer coupling will induce three-dimensional (3D) long-range order in a stack of two-dimensional (2D) crystals has altered our view of the phases previously identified as ordered smectics.<sup>1</sup> Many phases classified as smectic *B* actually are layered molecular crystals (crystalline *B*) with unusual features which are as yet both poorly characterized and barely understood. X-ray diffraction experiments show strong diffuse scattering due to modes polarized in the plane of the layers. This scattering has intralayer correlation lengths greater than 3000 Å but has little interlayer correlation.<sup>2,3</sup> This indicates that layers slide rigidly over one another with relative ease. A second feature is the presence of restacking transitions in which there are dra-

matic shifts in the relative positions of adjacent layers.<sup>2, 4-7</sup> No latent heat or other thermal anomaly has been associated with these transitions, leaving their detailed nature a mystery. It is also not known whether the restacking transition is driven by the interlayer coupling or if it arises from a transition occurring within the individual 2D layers. These crystalline-*B* solids thus represent prototypes of 3D systems with unusually large directional anisotropy. We expect that elucidation of their properties will enhance generally our understanding of crossover from 2D to 3D collective behavior.

High-resolution x-ray diffraction studies of freely suspended thick films of heptyloxybenzylidene-heptylaniline (7O.7) were carried out by using synchrotron radiation and the triple-axis

spectrometer installed by one of us (J. A.-N.) at HASYLAB in Hamburg, Germany. Single crystals of Ge(111) were used as monochromator and analyzer. Lower-resolution studies were performed on similar spectrometers at Harvard and the Massachusetts Institute of Technology, using pyrolytic graphite crystals and Cu  $K\alpha$  radiation from rotating-anode sources. Freely suspended films 600 to 3000 layers thick were prepared in a manner similar to others.<sup>2</sup> We were thus able to examine samples with a few single-crystal domains. The samples were oriented with the normal to the molecular layers always in the scattering plane. Scans along  $\vec{q}_x, \vec{q}_y$ , in the plane of the layers, or along  $\vec{q}_z$ , normal to the layers, were done. A third rotation about the normal to the layers allowed us to choose the direction of  $\vec{q}_x, \vec{q}_y$  within the layer.

We find that 7O.7 exhibits rich structural behavior between 63° and 59°C with a series of three transitions involving restacking and subtle changes in the intralayer packing.<sup>3</sup> In order of decreasing temperature, the structures are hexagonal close-packed (69–63°C), orthorhombic  $F$  (63–60.1°C), monoclinic  $C$  (60.1–59.75°C), and hexagonal (59.75–55°C). In the last three phases there is also a long-wavelength modulation in which the smectic layers are displaced along their normals. The relative stacking of adjacent layers is shown in Fig. 1. The real and reciprocal lattices for the three lower-temperature phases are also given in the figure.

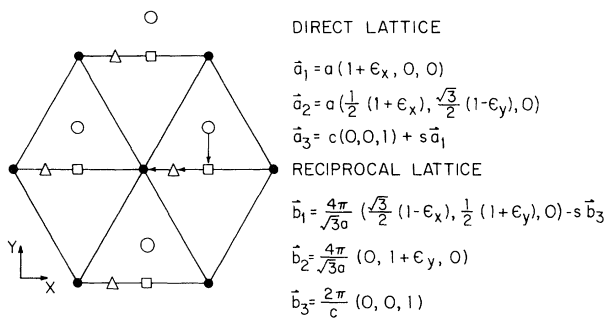


FIG. 1. Relative displacements of adjacent layers in the various phases: closed circles, reference layer position; open circles, hexagonal closed packed; squares, orthorhombic  $F$ ; and triangles, monoclinic  $C$ . In the hexagonal AAA phase the adjacent layer positions coincide with the reference layer. At the right are the primitive unit cells for the real and reciprocal lattices of the orthorhombic- $F$ , monoclinic- $C$ , and hexagonal AAA structures.

In the temperature range  $69^\circ\text{C} > T > 63^\circ\text{C}$ , 7O.7 exhibits the hcp structure with  $ABAB$  stacking common in crystalline- $B$  materials.<sup>2-4</sup> Scans along  $\vec{q}_z$  passing through any of the six Bragg peaks with  $\vec{q}_z = 0$  show peaks at intervals of  $2\pi/c$  ( $c$  is the spacing between smectic layers) as shown in Fig. 2(a). At  $T = 63^\circ\text{C}$  there is an abrupt first-order transition to a phase which can be described either by an orthorhombic- $F$  structure or by a triclinic primitive cell with one 7O.7 molecule per unit cell. Here  $\vec{q}_z$  scans through  $\vec{b}_1$  and  $\vec{b}_2$  are not equivalent [Figs. 2(b) and 2(d)]. High-resolution measurements show that the lattice is compressed along  $\hat{y}$  and extended along  $\hat{x}$  [see Fig. 3(a)]. The relative changes are parametrized by  $\epsilon_x$  and  $\epsilon_y$  in Fig. 1. The distortion is very near to being area conserving with  $\epsilon_x = \epsilon_y = 0.0010 \pm 0.0001$ . The choice  $s = \frac{1}{2}$  in Fig. 1 yields the lattice vector of the triclinic primitive cell.

At 60.1°C the orthorhombic- $F$  structure shears into a monoclinic- $C$  structure. Within the monoclinic- $C$  phase the displacement between adjacent layers is  $s\vec{a}_1$  (Fig. 1) where  $s$  varies approximately linearly with decreasing temperature from 0.45 to 0.05 [Fig. 3(b)]. The lattice vectors given in Fig. 1 are again these of the primitive cell. There are small, weakly first-order jumps in  $s$  at both the upper and lower transitions. Scans along  $\vec{q}_z$  through  $\vec{b}_1$  [Fig. 2(c)] and through  $\vec{b}_2$  [Fig. 2(d)]

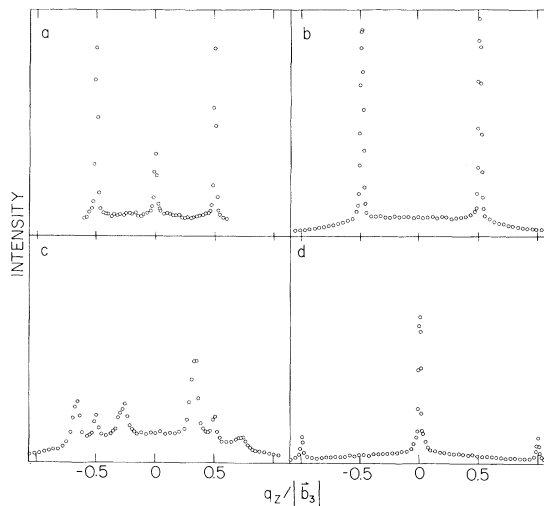


FIG. 2. (a)  $\vec{q}_z$  scan through an in-plane peak for  $T > 63^\circ\text{C}$  ( $T = 65.43^\circ\text{C}$ ). (b)  $\vec{q}_z$  scan through  $\vec{b}_1$  in orthorhombic- $F$  phase at  $T = 60.88^\circ\text{C}$ . (c)  $\vec{q}_z$  scan through  $\vec{b}_1$  in monoclinic- $C$  phase at  $T = 60.02^\circ\text{C}$ . (d)  $\vec{q}_z$  scan through  $\vec{b}_2$  in hexagonal AAA phase at  $T = 59.35^\circ\text{C}$ . Identical scans through  $\vec{b}_2$  are found in both the orthorhombic and monoclinic phases.

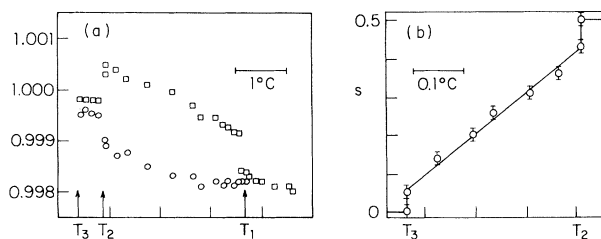


FIG. 3. (a) Measurement of distortion in intralayer packing: Circles,  $|\vec{b}_1 \times \hat{z}|$ ; squares,  $|\vec{b}_2|$ . Data are plotted in units of  $1.434 \text{ \AA}^{-1}$ . Transition temperatures are marked;  $T_1$ , hexagonal close packed to orthorhombic  $F$ ;  $T_2$ , orthorhombic to monoclinic;  $T_3$ , monoclinic to hexagonal  $AAA$ . (b) Adjacent layer displacement vs temperature in the monoclinic- $C$  phase.

show that the layers shear along the  $\vec{a}_1$  direction. The presence of peaks at both  $\pm 0.3|\vec{b}_3|$  at  $T = 60^\circ\text{C}$  indicates that although the shear is along a single direction, there are both  $\pm s\vec{a}_1$  displacements. Although the relative intensities of the  $\pm s\vec{a}_1$  peaks are sample dependent, there is no evidence of hysteresis. There are small residual peaks at  $\pm 0.5\vec{b}_3$  that could arise from strain-induced coexistence. The distortion from hexagonal intralayer packing relaxes in this phase to  $\epsilon_x \approx \epsilon_y \approx 0.0002 \pm 0.0001$ .

At  $T = 59.75^\circ\text{C}$  the monoclinic- $C$  phase transforms into a simple hexagonal phase with  $AAA$  stacking. Molecules in adjacent layers occupy the reference sites in Fig. 1 and the intralayer distortion vanishes. Scans along  $\vec{q}_z$  through  $\vec{b}_1$  and  $\vec{b}_2$  are identical and are shown in Fig. 2(d). Figure 4 shows a high-resolution  $\vec{q}_y$  scan taken at HASYLAB. The intensity of the Bragg peak relative to the thermal diffuse background is about 500. The full width at half maximum of the primary peak is  $0.0006|\vec{b}_2|$ . The orthorhombic- $F$ , monoclinic- $C$ , and hexagonal  $AAA$  phases all exhibit a 1D modulation of the molecular layers polarized normal to the layers and having a wave vector  $\vec{Q} \approx 0.046 \vec{b}_2$ . These appear as pairs of sidebands in scans along  $\vec{q}_y$  through the  $(0, 1, \pm 1)$  peaks as indicated in Fig. 4. High-resolution data show the sidebands to be only slightly broader than the resolution indicating a correlation length greater than  $4000 \text{ \AA}$ . Leadbetter *et al.*<sup>4</sup> have reported the existence of modulations with this polarization in crystalline- $B$  materials that have  $G$  phases at temperatures immediately below the  $B$ . The high-quality samples we were able to produce allowed us to show that in  $70.7$  the modulation  $\vec{q}$  vector is in the direction of the

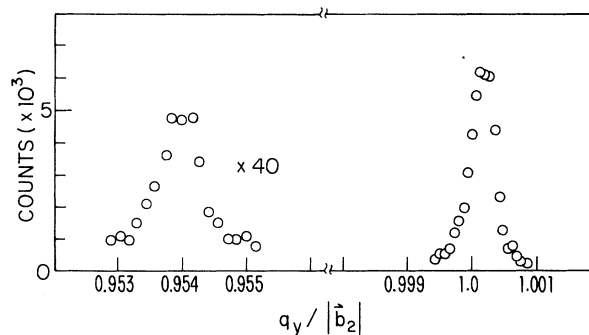


FIG. 4. Synchrotron high-resolution  $\vec{q}_y$  scans through  $\vec{b}_2 + \vec{b}_3$  and through the satellite peak at  $0.954\vec{b}_2 + \vec{b}_3$  in hexagonal  $AAA$  phase.

molecular displacements that occur at the hept-orthorhombic- $F$  restacking transition.

In discussing the above structures in  $70.7$  we should note that an  $AAA$  simple hexagonal structure with one high-symmetry unit per primitive cell does not appear to have been observed previously in nature. However, the very sharp  $\vec{b}_2$  satellite peaks which we observe in these novel crystalline- $B$  phases suggest that the underlying structures must be more complicated. From the intensity of the satellite peak shown in Fig. 4 we infer that the amplitude of the  $\vec{b}_2$  transverse sinusoidal modulation wave is about  $0.05c$  in the direction perpendicular to the planes. Since the period is about 20 molecules this corresponds to a nearest-neighbor vertical displacement of only 1% of the molecular length. In the lower-temperature  $G$  phase of  $70.7$  the corresponding displacement<sup>5</sup> is about 8%. The driving mechanism for the sinusoidal modulation is almost certainly the tilt degree of freedom. From Fig. 1 it is evident that a tilt of the molecule in the  $\vec{b}_2$  direction will facilitate the packing of adjacent layers. We have not, however, succeeded in producing a microscopic model that can account quantitatively for the sinusoidal modulation. Similar modulations observed in lipid-water systems have been modeled as a martensitic transformation by Chan and Webb.<sup>9</sup> However, their inferred displacements are much too large to account for our observed intensities in  $70.7$ . It is possible, however, that their model is relevant to systems such as  $50.7$  where the  $B$ - $G$  transition is more weakly first order.<sup>4</sup> Indeed the temperature variation of the observed intensities in  $50.7$  can be simply understood on the basis of an increasing amplitude of the density wave.

Finally, we should emphasize that the new features which our high-resolution single-domain studies have revealed are by no means unique to 7O.7. Doucet and Levelut<sup>5</sup> have reported lower-resolution x-ray studies of a number of  $nO.m$  compounds. In 7O.7, 7O.5, and 5O.7 they report a  $B$  phase with an extra "ring" of low-angle scattering in powder patterns; this may now be identified as originating from the sinusoidal modulation peaks around  $(0,0,1)$ . Moncton and Pindak<sup>2</sup> reported some single-domain data on the  $B$ -phase restacking transitions in 4O.8. Although their investigation was not extensive enough to make unambiguous identifications, it seems likely that the lowest two phases which they observe correspond to our orthorhombic- $F$  and monoclinic- $C$  phase.

It is evident that these quasi-2D solids exhibit highly unusual structures and structural phase transitions. The continuous shear transformation in the monoclinic phase of 7O.7 is particularly interesting since adjacent layers slide over one another with only minute distortions in the intralayer packing. The sinusoidal corrugation of the layers throughout the  $B$  phases is a novel feature which remains unexplained. In order to disentangle intralayer versus interlayer effects we plan to study these structures as a function of film thickness. Finally, it is clear that there is need for a significant development of theories for the structures of quasi-2D molecular solids.

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