

do not exhibit alloy clustering. Two possible reasons may account for the difference between the LPE and MBE growth. First, the LPE growth rates are 10 to 100 times more rapid than the MBE growth rates. Second, the LPE growth is essentially an equilibrium growth situation while in the MBE growth, the Al partial pressure is far above the equilibrium pressure value at the growth temperature. The difference may in fact provide an additional driving force for the exchange reaction and the phase separation.

The exchange-reaction-induced miscibility gap in the MBE-grown $\text{Ga}_{1-x}\text{Al}_x\text{As}$ films could well result in a spinodal-type reaction which is characterized by a periodic variation in the solid solution composition.¹⁸ This type of surface spinodal reaction which is of course controlled by diffusion at the surface could well be present in other semiconductor systems.¹⁹

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Mechanical Measurements on Free-Standing Films of Smectic Liquid-Crystal Phases

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Shear mechanical properties have been measured for free-standing films of the liquid crystal *n*-hexyl 4'-*n*-pentyloxybiphenyl-4-carboxylate (65OBC) in its stacked-hexatic *B* phase. The smectic-*I* phases of (+)-4-(2'-methylbutyl)phenyl 4'-*n*-nonyloxybiphenyl-4-carboxylate and (-)-2-methylbutyl 4-(4'-*n*-decyloxybenzylideneamino) cinnamate (DOBAMBC) were also studied. Unlike the crystal *B* phase, none of these phases exhibited an in-plane shear modulus. Enhanced crystalline surface ordering was observed in 65OBC.

PAC numbers: 61.30.Eb, 62.20.Dc

Several techniques have been developed to study the shear mechanical properties of free-standing smectic liquid-crystal films.¹⁻⁴ These films, which can be varied in thickness from two to

hundreds of molecular layers, provide good model systems for observing the evolution from two to three dimensions. The mechanical techniques were first used to study the *B* phase in free-

standing films of the liquid crystal *N*-(4-*n*-butyloxybenzylidene)-4'-*n*-octylaniline (4O.8). The *B* phase is a layered phase in which the molecular long axes are oriented perpendicular to the layer planes and are hexagonally ordered within each layer. X-ray measurements⁵ demonstrated that the *B* phase in 4O.8 had long-range, three-dimensional (3D) positional order. The mechanical measurements¹⁻⁴ confirmed the crystalline nature of the 4O.8 *B* phase by showing that it exhibited an in-plane shear modulus. They also revealed that free-standing films of 4O.8 melt in two steps. First, the interior layers melt; then, at a temperature approximately 10° higher, the surface layers melt. This enhancement in the surface melting temperature has made it difficult to study the melting process in two-layer films of 4O.8 since, before the two-layer film melts, the bulk material which wets the film's support frame undergoes a transition into a phase without a layered structure and the film ruptures.

Although a complete study of the 2D melting process has not yet been achieved using free-standing films, these films have provided support for at least one aspect of 2D melting. It was proposed⁶ that, if 2D melting was a dislocation-mediated transition, then an intermediate "hexatic" phase having algebraically decaying bond-orientational order would occur between the 2D solid and liquid phases. X-ray measurements⁷ on the *B* phase in thick, free-standing films of the liquid crystal *n*-hexyl 4'-*n*-pentyloxybiphenyl-4-carboxylate (65OBC) demonstrated that this phase had precisely the structural properties expected for a 3D stack of 2D hexatic layers.⁸ It was referred to as a hexatic *B* phase. Unlike the crystal *B* phase in 4O.8, the hexatic *B* phase had only short-range, in-plane positional order but long-range, 3D, sixfold bond-orientational order. Furthermore, unlike the first-order crystal-*B* to *A* transition in 4O.8, heat-capacity measurements⁹ showed that the hexatic-*B* to *A* transition in 65OBC was second order. In this Letter, we report on the first mechanical measurements on free-standing films of the hexatic *B* phase in 65OBC. We also report mechanical measurements on the *I* phase in (±)-4-(2'-methylbutyl) phenyl 4'-*n*-nonyloxybiphenyl-4-carboxylate (2M4P9OBC) and the ferroelectric, chiral *I* (*I**) phase in (-)-2-methylbutyl 4-(4'-*n*-decyloxybenzylideneamino) cinnamate (DOBAMBC). X-ray studies¹⁰ indicate that these phases are analogs of the hexatic *B* phase except that the molecular long axes are tilted with respect to the layer

planes. The *I* and *I** phases melt respectively into the smectic *C* and chiral smectic *C* (*C**) phases which are tilted analogs of the smectic *A* phase. Our principal result is that the hexatic *B* and its tilted analog phases do *not* exhibit an in-plane shear modulus. Furthermore, we find that the surface layers of 65OBC films stay crystalline several degrees above the crystal-*E* to hexatic-*B* transition temperature. We believe that these solid surface layers are responsible for the enhanced bond-orientational order observed in thick 65OBC films several degrees below the *A* to hexatic-*B* transition.⁷

The first technique used to measure the shear mechanical properties of hexatic *B* films was a 520-Hz torsional oscillator. Details of the technique have been previously published.^{1,2} An annular free-standing film is introduced between the oscillator and a support ring. The dissipation, Q^{-1} , and period shift, ΔP , of the oscillator-film system are measured. ΔP is measured relative to the unloaded oscillator and is proportional to a sum over the shear elastic response contributed by each layer of the film. In Fig. 1 the temperature dependence of ΔP and Q^{-1} are shown for three 65OBC films with a different number of molecular layers. These measurements were taken while cooling. The range of the crystal *E*,¹¹ hexatic *B*, and *A* phases in 65OBC as determined by heat capacity,⁹ x-ray,⁷ and polarized light microscopy¹² measurements are illustrated. Also illustrated is the smallest period shift, ΔP_D , expected per layer at a dislocation-mediated, 2D melting transition due to a discontinuous jump in the 2D shear modulus.⁶ Several features are evident: (a) There is no period shift (shear modulus) at the *A* to hexatic-*B* transition. (b) At a lower temperature $T_0 = 65.0^\circ\text{C}$ there is a jump in the period which is essentially independent of the number of layers. (c) The period shift at T_0 is comparable to that expected for 2D melting. The absence of an in-plane shear modulus for the hexatic *B* phase is consistent with the x-ray observation⁷ that the hexatic *B* phase has only short-range, in-plane positional correlations. The jump in period shift at T_0 is similar to what occurred above the crystal *B* phase in free-standing films of 4O.8 where the surface layers stayed crystalline to temperatures higher than the bulk crystal-*B* to *A* transition temperature.¹⁻⁴ In the case of 65OBC it is the surface layers remaining in the crystal *E* phase to a higher temperature than the bulk crystal-*E* to hexatic-*B* transition temperature. If the interior layers were involved in the

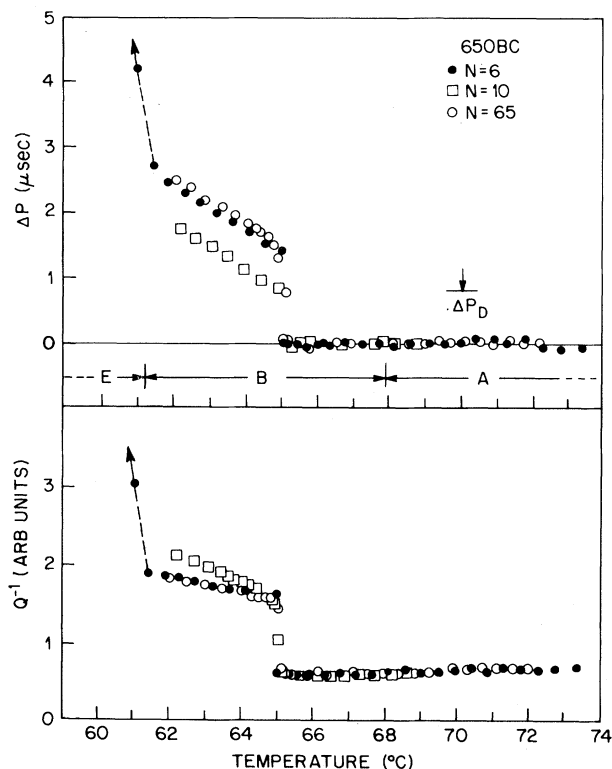


FIG. 1. The period shift (top) and dissipation (bottom) are shown as a function of temperature for 65OBC films consisting of different numbers of molecular layers (N).

transition, then the jump in ΔP should scale with the number of layers. There is some variation in the magnitude of the jump, but this variation is at most a factor of 2 and is not correlated to the number of layers (note the 10-layer data in Fig. 1 which is lower than both the 6- and 65-layer data). There is a correlation between the magnitude of the jump and the sample history. If a sample is kept at a temperature below T_0 for several days the measured ΔP will increase. This is presumably due to defects being annealed. Finally, the onset of a thickness-dependent shear modulus *does* occur as the temperature is further lowered into the crystal E phase (note the onset of this shear modulus in the six-layer film in Fig. 1).

To further study the surface melting transition in 65OBC we used a second apparatus. This apparatus was designed to measure the strain relaxation in free-standing films.^{2,4} Its advantage over the oscillator apparatus was an improved thermal uniformity (better than 0.01°) achieved

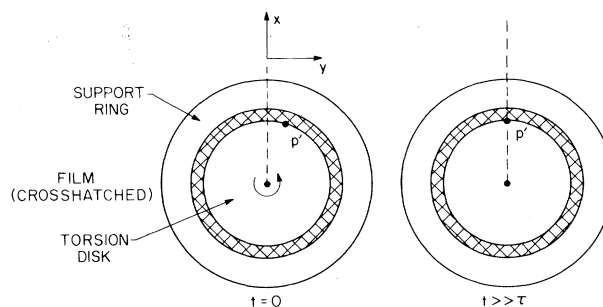


FIG. 2. Experimental geometry for the strain relaxation measurements. τ is the mechanical relaxation time of the film.

by radiation shielding above and below the free-standing films. Films in this apparatus were more stable against rupture. The strain relaxation technique again involved preparing free-standing films in an annular geometry between a disk and support ring. A torsional fiber was attached to the disk and a torque applied to the disk which rotated it about an axis normal to the film resulting in an in-plane shear stress on the film. As illustrated in Fig. 2, a point p' on the disk would rotate from its initial position, (x_0, y_0) , to its zero-torque position, $(x \approx x_0, y = 0)$. This rotation involved an initial elastic response and then strain relaxation in the annular film. The instantaneous stress, σ , and strain angle, ϕ , for the films were related to the disk displacement, y , by $\sigma = K'y$ and $\phi = K'y/\mu$, where K' is the torsional elastic constant of the fiber and μ is the shear modulus of the film. The total displacement, y_0 ($\approx 100 \text{ \AA}$), was within the linear response regime.

For different thicknesses of free-standing 65OBC films we measured the fractional displacement, y/y_0 , of the disk 22.5 msec after the external torque was applied. This quantity was proportional to the shear modulus that would be measured at 45 Hz and was probably a combination of elastic response and dislocation relaxation. Similar measurements^{2,4} on films of 40.8 produced results in agreement with torsional oscillator results.¹ In Fig. 3, data for the thinnest and thickest measured films are presented. The data are indicative of these two observed trends: (a) The surface melting involved hysteresis on heating and cooling indicative of a first-order transition. (b) The amount of hysteresis decreased as the films became thinner. We were not able to study films of 65OBC thinner than four layers. Even

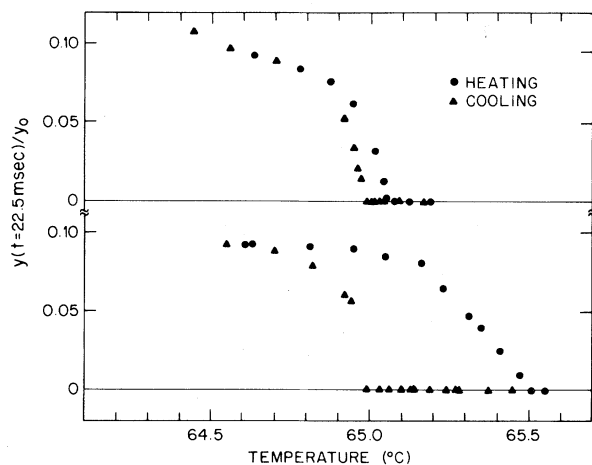


FIG. 3. The temperature dependence on heating and cooling of the relative disk displacement, y/y_0 , 22.5 msec after an applied torque. Data are for the thinnest (top), $N = 4$, and thickest (bottom), $N > 100$, 65OBC films studied.

the four-layer film required very slow cooling (< 0.1 deg/h) so that it would not rupture when cooled through the surface crystallization temperature. The persistence of this surface crystalline order was observed on heating as high as 65.5 °C. An enhanced bond-orientational ordering had been observed in x-ray measurements⁷ on thick, free-standing 65OBC films which continued up to 66.4 °C. This enhancement is probably related to the persistence of the surface crystalline order. The difference in temperatures may be due to mobile dislocations which resulted in a vanishing mechanical response even though the film's surface was still crystalline to higher temperatures. Such fast dislocation relaxation times have been observed in crystal B films of 4O.8 which are only several layers thick.⁴

Finally, using the torsional oscillator technique we also studied materials which exhibit *tilted* stacked-hexatic phases (I and I^*). The temperature range of these phases for the two compounds studied is given in Fig. 4. The G' (or J) phase is a tilted analog of the crystal B phase. The transition temperatures and phase types have been determined by heat capacity,¹³ x-ray,¹⁰ and polarized light microscopy measurements. The main result is that there is no evidence for an in-plane shear modulus in the I or I^* phases. For 2M4P9OBC there is an onset of a shear modulus only at the I to G' transition.

In conclusion, we have demonstrated that the

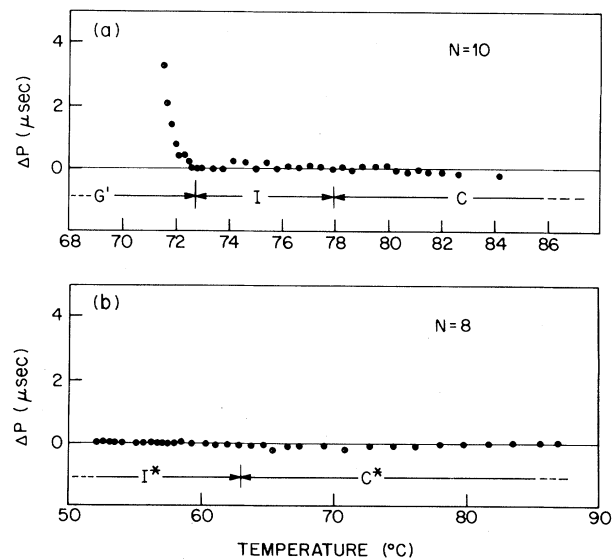


FIG. 4. Temperature dependence of the period shift for films of (a) 2M4P9OBC and (b) DOBAMBC.

hexatic B and its tilted analog phases (I and I^*) do not exhibit an in-plane shear modulus. This is consistent with x-ray structural studies which showed that these phases have only short-range, in-plane positional correlations. We have also demonstrated that in free-standing 65OBC films crystalline surface layers can coexist with hexatic- B interior layers. The solid surface layers melt by a first-order transition with an associated thermal hysteresis in their mechanical properties which decreases as the number of hexatic- B interior layers is reduced. Because two-layer 65OBC films did not last long enough for any significant measurements, it could not be determined whether the solid phase in a two-layer film melts continuously into a hexatic phase. We are currently studying different materials in which the liquid-crystal phases exist over larger temperature ranges. These materials should produce more stable two-layer films in which the 2D limit as well as the bulk properties can be studied in detail.

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Orientational Ordering of Nitrogen Molecular Axes for a Commensurate Monolayer Physisorbed on Graphite

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Low-energy electron diffraction has been used to study the orientational ordering of the molecular axes of nitrogen molecules physisorbed on graphite single crystals. A 2×1 superlattice structure with in-plane orientations is inferred for the monolayer where the molecular centers have the commensurate $(\sqrt{3} \times \sqrt{3}) 30^\circ$ structure. The superlattice intensity decreases significantly near 30 K but persists up to 40 K, consistent with a first-order transition with finite-size effects.

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Previous structural studies of N_2 molecules physisorbed on graphite have shown that at sub-monolayer coverages and $T < 47$ K, N_2 molecules have a commensurate structure in which the centers of mass of the molecules are in a $(\sqrt{3} \times \sqrt{3}) 30^\circ$ array.^{1,2} With neutron scattering, Eckert *et al.* detected a new superlattice peak at $T < 30$ K due to ordering of the N_2 molecular axes, while the centers of mass remained in the $(\sqrt{3} \times \sqrt{3}) 30^\circ$ structure.³ Because of intensity limitations, the neutron study was unable to distinguish between various proposed 2×1 and 2×2 superlattice structures,⁴⁻⁶ nor could it detect any superlattice intensity above 30 K. In this study, low-energy electron diffraction (LEED) is used to show that the commensurate monolayer has a 2×1 superlattice herringbone structure essentially the same as that predicted from an energy-minimization calculation.⁴ In addition, residual superlattice intensity is detected above 30 K, which indicates a persistence of some orienta-

tional order up to at least 40 K.

In this experiment we used a natural graphite single crystal about 5 mm in diameter and 0.2 mm in thickness. It was prepared by cleaving in air with Scotch tape and then baking at 1000 °C in flowing dry nitrogen gas. The crystal was then mounted on a sample holder which was installed in our ultrahigh-vacuum system. The entire system was baked at 110 °C for 24 h, after which the residual gas pressure was about 10^{-10} Torr. Typical beam parameters for these measurements were 5×10^{-10} A current, 25–200 eV energy, and a beam diameter of about 0.3 mm. LEED patterns were measured by taking photographs of the patterns or by measuring the intensity of a particular diffraction feature with the spot photometer described previously.² Spot profiles were measured by scanning the photometer aperture across the spot. The acceptance angle of the photometer when used in this mode was about 0.75° , or roughly the same size as a sharp dif-