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Observation of Two-Dimensional Hexatic Behavior in Free-Standing Liquid-Crystal Thin Films

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Bond-orientational ordering in the hexatic-B phase of free-standing liquid-crystal films of two to six molecular layers has been studied quantitatively with electron diffraction. By examination of the scaling relation among the $6n$-fold bond-orientational order parameters, it is demonstrated that the two-layer film exhibits truly two-dimensional hexatic behavior. A departure from two-dimensional behavior is observed in the thicker films.

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The theory of defect-mediated melting in two dimensions predicts the existence of an intermediate "hexatic" phase exhibiting short-range translational order but quasi-long-range bond-orientational order.[1,2] This phase is characterized by a local order parameter $\psi_6(\mathbf{r}) = \exp[i6\theta(\mathbf{r})]$, where θ is the angle between the physical "bond" connecting neighboring molecules and a reference axis. In the laboratory, liquid crystals have been recognized as a promising system in which to look for hexatic behavior.[3] Earlier x-ray measurements confirmed the existence of a three-dimensional or "stacked" hexatic phase in thick films[4] and demonstrated that the behavior of the in-plane positional correlation length was consistent with hexatic behavior in thin films[5,6] or possibly, in some cases, at the surface of films with liquidlike interior layers.[7] Although the positional correlations were quantitatively measured in these experiments, detailed quantitative measurements on the bond-orientational order parameter were only recently achieved for thick films in which a magnetic field was used to obtain a single-domain, tilted, stacked hexatic.[8] However, since these thick films were three dimensional, there has as yet been no quantitative experimental evidence for the existence of truly two-dimensional hexatic behavior in liquid-crystal thin films. The obstacles have included the difficulty of the accurate measurement of the extent of single-domain bond-orientational order in thin films and the lack of a convenient criterion for the determination of the effective spatial dimension of a given laboratory system.

Two recent developments have paved the way for a detailed investigation of the nature and extent of the hexatic ordering in liquid crystals in the two-dimensional limit. The first is the experimental demonstration that it is possible to use electron diffraction to measure the bond-orientational ordering with single domains of free-standing liquid-crystal films, especially those composed of just a few molecular layers.[9] The second is the realization that an excellent way to deduce the spatial dimensionality of a hexatic system is to examine the scaling behavior among its higher-harmonic $6n$-fold bond-orientational order parameters

$$C_{6n} = \mathrm{Re}\langle \psi_6^n \rangle = \mathrm{Re}\langle \exp(i6n\theta) \rangle.$$

It has been shown that these order parameters, at least in the critical region, should follow the relation[10]

$$C_{6n} = C_6^{\sigma_n}, \tag{1}$$

where the exponents σ_n are related to the crossover exponents from the XY to other universality classes. In three dimensions, they are predicted to have the values

$$\sigma_n = n + \lambda n(n-1) \tag{2}$$

with $\lambda = 0.3$. This behavior has been confirmed quantitatively in thick smectic-I films by x-ray scattering.[8,10] It has been further pointed out that, from the spin-wave description of the low-temperature phase of the two-dimensional XY model, Eq. (2) is expected to hold also in two dimensions, but with $\lambda = 1$ (or $\sigma_n = n^2$).[11] These predictions suggest that the value of λ governing the scaling behavior of the higher-harmonic bond-orientational order parameters is a useful indicator of the effective dimensionality of an experimental hexatic system.[12] In this Letter, we describe the results of a measurement of the bond-orientational order parameters using electron diffraction in free-standing liquid-crystal films of various thicknesses and report the first confirmation of two-dimensional hexatic behavior in a two-layer film.

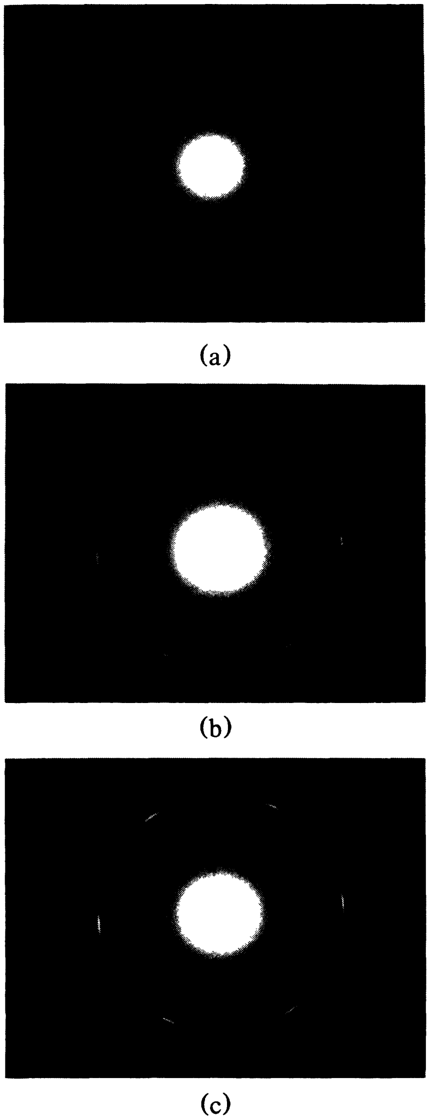

FIG. 1. Electron-diffraction patterns from free-standing films of (a) two, (b) four, and (c) six molecular layers of a 25 wt.% mixture of PP5CC in 65OBC at 45 °C.

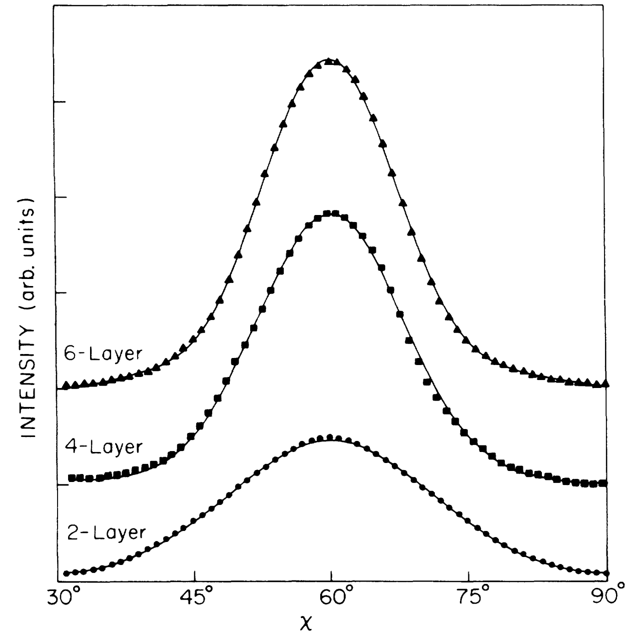

FIG. 2. Angular χ scan of diffraction intensity for films of various thicknesses at 45 °C. The points are experimental and the curves are fits by Eq. (3).

Our experiment was conducted in an electron diffractometer equipped with a pressurized, differentially pumped sample chamber.[13] Free-standing films consisting of two, four, and six molecular layers of a 25 wt.% of 4-proprionylphenyl-*trans*-(4-*n*-pentyl)cyclohexane carboxylate (PP5CC) in *n*-hexyl-4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC), which exhibits hexatic-*B* and smectic-*A* phases in the bulk,[14] were studied. The purpose of our adding PP5CC was to lower the hexatic-*B* temperature range to accommodate the temperature limitations of the apparatus. Films were drawn outside the diffractometer before insertion. Their thickness was measured with the standard optical reflectivity technique.[15] Diffraction within single hexatic domains was made possible by the use of an electron beam of less than 10 μm in diameter. The electron wavelength was 0.03 Å. The beam current was 0.1 $e/\text{Å}^2\text{s}$. The diffraction intensity on a plane perpendicular to the incident beam was recorded on Kodak high-resolution x-ray photographic film with a typical exposure time of a few seconds and analyzed with computerized imaging techniques by digitizing into 720×720 pixels with eight-bit intensity resolution.

Figure 1 displays examples of electron-diffraction data taken at 45 °C with films of two, four, and six molecular layers. The existence of six symmetric arcs in all three diffraction patterns suggests the occurrence of hexatic ordering in these films of various thicknesses. Detailed analysis shows that the six arcs have identical intensity, indicating that the hexatic phase existing in these films is that of the untilted hexatic-*B*,[16] just as in the case of the bulk material. It can also be seen that the angular width of the arcs increases with reduced thickness. This is consistent with the expectation that increased fluctuations as the two-dimensional limit is approached will reduce the bond-orientational ordering.[5,17]

The diffraction patterns at various temperatures and for films of different thicknesses were analyzed by our computing the intensity $I(\chi)$ along an arc over an angular range χ of 60°, integrated over a finite range of radial wave vector, and fitting the data with the expression

$$I(\chi)=I_0\left[\tfrac{1}{2}+\sum_{n=1}^{\infty}C_{6n}\cos[6n(90^\circ-\chi)]\right]+I_{\mathrm{BG}}, \tag{3}$$

where I_{BG} is a fitting parameter representing the back-

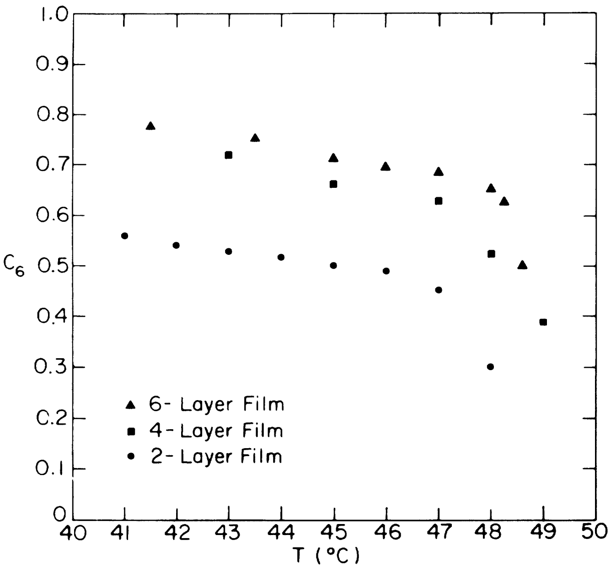

FIG. 3. Temperature dependence of the sixfold bond-orientational order parameter C_6 for films of various thicknesses.

ground intensity. Figure 2 shows examples of the fits of Eq. (3) to data from various films at 45 °C. The maximum usable harmonic generated in the fitting is $n=4$. The excellent degree of fit and the trend of decreasing order with decreasing thickness are apparent. To illustrate this more quantitatively, Fig. 3 shows the temperature dependence of the fundamental six-fold bond-orientational order parameter C_6 for the three different thicknesses. It can be seen that C_6 decreases with increasing temperature in essentially the same manner in all three films, with the overall values of C_6 being the highest for the six-layer film and the lowest for the two-layer film. It also appears that the smectic-*A* to hexatic-*B* transition temperature does not change appreciably with film thickness. However, we are unable to achieve sufficient temperature resolution in the current apparatus to examine in detail the behavior near the transition or to ascertain whether the transition is first or second order.

The fit of each diffraction pattern by Eq. (3) produced not only C_6 but also the higher-harmonic $6n$-fold bond-orientational order parameters C_{6n} up to $n=4$. From these the scaling exponents σ_n were calculated according to Eq. (1). These values of σ_n were then fit with Eq. (2) to obtain the value of λ that best described the data. The results of such an analysis are summarized in Fig. 4, which shows the temperature dependence of λ for various film thicknesses. The most striking observation is that, in the temperature range shown, the results for the two-layer film are consistent with $\lambda=1$, which is what is expected in two dimensions.[11] This represents the first convincing confirmation of the occurrence of two-dimensional hexatic behavior in a liquid-crystal film. For the four-layer film, λ increases with temperature from 0.8 to 0.9 near the transition, while for the six-layer film, λ increases from 0.7 to 0.85. Since λ is expected to be 1 in two dimensions and 0.3 in three dimensions, the general pattern of decreasing values of λ with increasing thickness in these films is suggestive of the departure from two-dimensional behavior even in films only a few molecular layers thicker. The increasing values of λ as the temperature is increased in the four-layer and six-layer films can also be indicative of a trend toward more two-dimensional-like behavior close to the transition to the liquid phase.

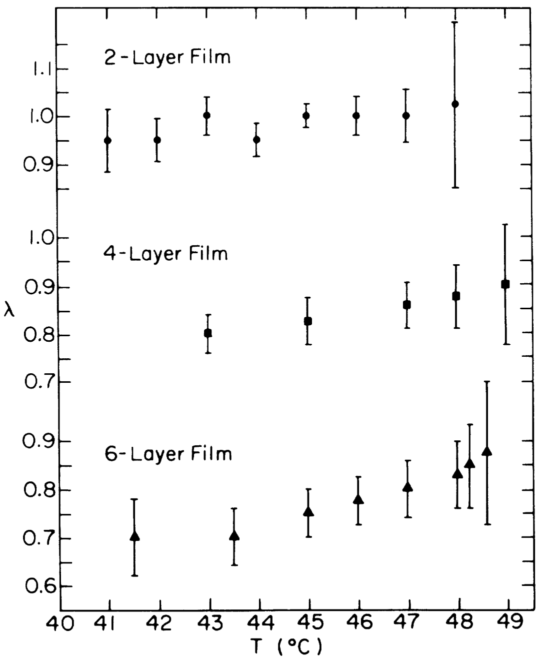

FIG. 4. Temperature dependence of the scaling parameter λ in Eq. (2) for films of various thicknesses.

In summary, we have measured quantitatively the $6n$-fold bond-orientational order parameter in hexatic-*B* liquid-crystal films of two to six molecular layers. The scaling of these order parameters provides the first definitive evidence for the existence of two-dimensional hexatic ordering in a two-layer film, as well as the departure from two-dimensional behavior in thicker films on a few molecular layers.

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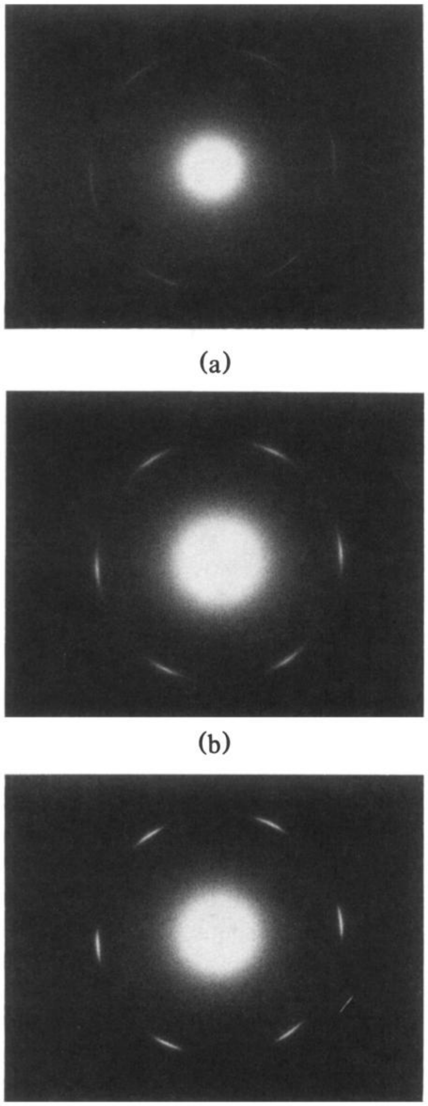

(a)

(b)

(c)

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