E-type samples (JW 1, 14, 15, 26, 28, 37, and 48) (*36*). Finally, precipitation of diamonds from volatile-rich fluids is also substantiated by diamonds themselves and their impurities. For example, in addition to carbon, diamonds contain nitrogen, hydrogen, boron, and sulfur, all behaving as volatiles. In our model, the resulting oxidation state of mantle rocks and the stability of the diamond and carbonate are imposed by the amount of the oxidized infiltrating fluids or melts relative to that of reduced host rocks.

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Multiple-Step Melting in Two-Dimensional Hexatic Liquid-Crystal Films

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An unexpected three-stage melting transition has been observed in two-dimensional (2D) free-standing liquid-crystal films by in situ electron-diffraction and optical-reflectivity measurements. These data suggest the existence of two phases between the 2D solid and liquid: a hexatic phase and, at a higher temperature, an intermediate liquid phase with hexatic-like positional correlations ($\sim$40 angstroms) but no long-range orientational order. Previous high-resolution heat-capacity measurements have revealed a divergent-like anomaly at the hexatic-liquid transition that sharply contradicts the predictions of 2D melting theories. The observation of an intermediate isotropic phase may alter our understanding of 2D melting and lead to reconciliation between current experiments and theories.

What processes are involved when 2D systems melt? Theories of 2D melting (*1–3*) suggest a mechanism in which a 2D solid could melt through the dissociation of topological defect pairs (*4*). In particular, Halperin and Nelson (*2*) proposed a two-stage melting process involving an intermediate hexatic phase between the 2D crystalline phase and the isotropic liquid. The hexatic phase exhibits short-range positional but quasi long-range bond-orientational order characterized by sixfold symmetry (*5*). The 3D analog of the hexatic phase was first identified in a liquid-crystal (LC) compound (*6*). Subsequently, hexatic order has been reported in free-standing LC films (*7, 8*) and various 2D systems such as colloidal crystals (*9*), high-temperature superconductors (*10*), magnetic-bubble lattices (*11*), charge-density waves (*12*), and Langmuir-Blodgett films (*13*). Among those 2D systems, thin free-standing LC films, without the complication of any substrate, have offered unique opportunities to test the melting theories. To date, apparent discrepancies have persisted between experimental observations and theoretical predictions, including an inexplicably strong thermal anomaly at the hexatic-liquid transition instead of the expected continuous Kosterlitz-Thouless (KT)–type behavior (*14*). To investigate these phenomena, we report in situ electron diffraction (ED), high-resolution heat capacity (C_P) (signal to noise ratio $\sim 3 \times 10^4$), and optical reflectivity (signal/noise $\sim 2 \times 10^4$) measurements on 2D LC films of *n*-pentyl-4′-*n*-pentanoyloxy-biphenyl-4-carboxylate (54COOBC).

Our experimental techniques for making ED (*15*), C_p (*16*), and optical reflectivity (*17*) measurements have been described elsewhere. The free-standing LC films are soaplike films suspended across an aperture (*18*), with a diameter of 1 mm for ED measurements and 1 cm for C_p and optical-reflectivity measurements. The 54COOBC molecules are rodlike with a size of 25 Å by 5 Å (diameter). This compound exhibits orthogonal layered mesophases, namely, the smectic-A (Sm-A), hexatic-B (Hex-B), and crystal-B (Cry-B) phases, where Sm-A is composed of liquid layers, Hex-B is a stacked hexatic phase, and Cry-B is a hexagonal crystalline phase (*19*). The phase sequence for bulk 54COOBC is:

Sm-A (55°C) Hex-B (53°C) Cry-B.

We studied two-layer films of thickness $\sim$50 Å, which display 2D scaling behavior in the hexatic regime and hence are effectively 2D systems (*20*). The ED patterns obtained from two-layer films (Fig. 1) suggest the following phase sequence:

Sm-A (66.3°C) Sm-A′ (63.0°C)
Hex-B (60.1°C) Cry-B.

Above 66.3°C, the film was in the Sm-A phase. Its ED pattern was typified by a diffuse ring of constant intensity that one expects from a 2D liquid (Fig. 1A). At about 66.3°C, the diffuse ring of the Sm-A phase sharpened in the radial direction, but the intensity remained uniform around the ring (Fig. 1B). This unexpected ED pattern, which we characterize as smectic-A′ (Sm-A′), suggests a higher degree of in-plane positional correlations than that in an ordinary liquid and similar to that found in a hexatic phase. However, the lack of sixfold modulation of the diffraction intensity around the ring indicates the absence of long-range bond-orientational order within our probing electron beam of diameter 50 μm. At around 63.0°C, a single-domain Hex-B phase with long-range bond-orientational order appeared, which features six symmetric arcs (Fig. 1C). The azimuthal width of the arcs diminished gradually with decreasing temperature, suggesting an increase in bond-orientational order. The film made another transition at about 60.1°C to the hexagonal Cry-B phase, with an ED pattern consisting of six sharp Bragg spots indicative of long-range positional order (Fig. 1D).

To yield additional information about both the bond-orientational order and the positional order in the two-layer 54COOBC film, we analyzed the ED data by fitting the circular intensity of the hexatic arcs (χ-scan) as a function of the azimuthal angle (*7*) to obtain the sixfold

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bond-orientational order parameter C_6 (Fig. 2A) (*21*), and by fitting the intensity of the ED pattern as a function of the wave vector along the radial direction ($q_{\parallel}$-scan) to obtain the in-plane positional correlation length (Fig. 2B). The radial line shape used in the fitting for the positional correlation length is Lorentzian in the Sm-A phase, but is square-root Lorentzian (SRL) in the Hex-B phase because of the coupling of hexatic order to liquid density fluctuations; in the Sm-A′ phase, the SRL-fit gives a much better result than the Lorentzian-fit (Fig. 3) (*22*). We did not apply any deconvolution to correct for instrumental resolution, which resulted in the apparent saturation of the positional correlation length near the Hex-B–Cry-B transition (Fig. 2B). In addition, we also performed simultaneous high-resolution C_p and optical-reflectivity measurements of a two-layer 54COOBC film (Fig. 2C).

Taken together, the experimental data establish the existence of an unusual sequence of phase transitions (*23*). The behavior of the order parameter C_6 (Fig. 2A) suggests no long-range bond-orientational order above 63.0°C, and a monotonic increase in the bond-orientational order in the Hex-B phase with decreasing temperature from 63.0° to 60.1°C. The film underwent an apparently continuous transition at about 60.1°C to the Cry-B phase. However, the temperature dependence of the in-plane positional correlation length between 69° and 60.1°C (Fig. 2B) reveals three distinct phase regions, corresponding to the Sm-A (above 66.3°C), Sm-A′ (66.3° to 63.0°C), and Hex-B (63.0° to 60.1°C) phases. This conclusion is further reinforced by the optical-reflectivity data (Fig. 2C), which also exhibit three distinct phase transitions at 66.3°, 63.0°, and 60.1°C, in excellent agreement with the behavior of the positional correlation length. The most important observation here is the existence of the Sm-A′ phase. On the basis of ED (Fig. 1B) alone, one could argue that the Sm-A′ signal could be the result of powder diffraction from a multidomain Hex-B sample spatially averaged by the electron beam of diameter 50 μm. However, our data indicate that (i)

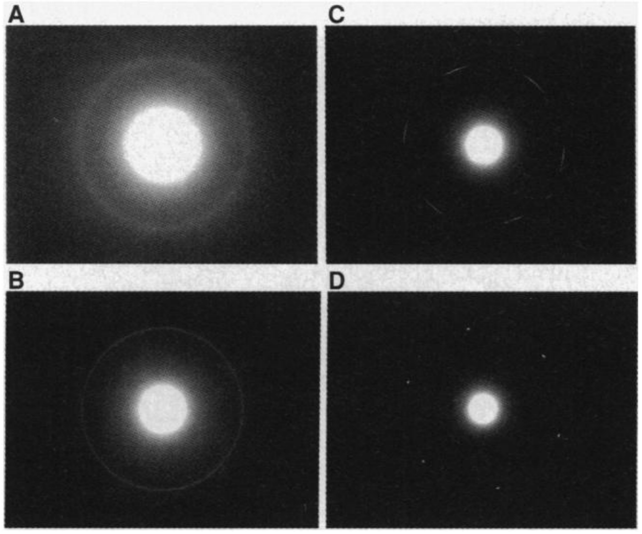

Fig. 1. Typical ED patterns from two-layer 54COOBC films. (**A**) Sm-A phase at 68.4°C, (**B**) Sm-A′ phase at 66.3°C, (**C**) Hex-B at 61.2°C, and (**D**) Cry-B phase at 59.1°C. The exposure time was typically a few seconds with electron beam current of ~0.1 e/Å²·s. A diffuse ring of constant intensity in (A) is a typical ED pattern from an ordinary 2D liquid. In (B), the diffuse ring in (A) sharpens in the radial direction, indicating higher positional correlations in Sm-A′, but the film is still in an isotropic phase. The sixfold modulation in (C) but not in (B) signifies the existence of long-range bond-orientational order in Hex-B but not in Sm-A′. The six symmetric Bragg spots in (D) indicate the crystalline nature of the Cry-B phase. The radius of the diffraction circle, q_o, is 1.4 Å^{-1}, corresponding to an average in-plane distance of 5.3 Å between the nearest-neighbor molecules.

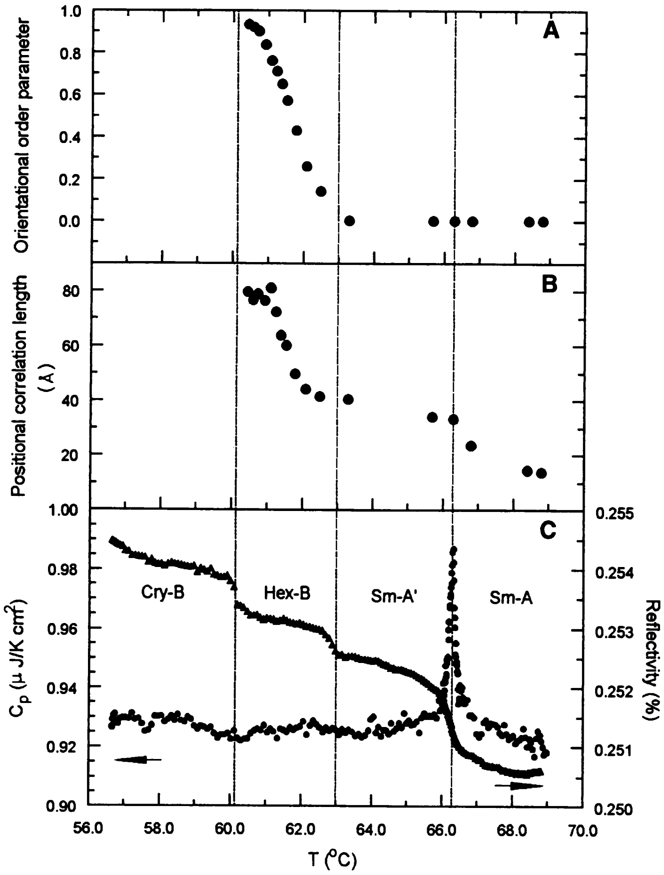

Fig. 2. Temperature dependence of (**A**) the bond-orientational order parameter C_6, (**B**) the in-plane positional correlation length, and (**C**) simultaneously measured heat capacity C_p (●) and optical reflectivity (▲) in two-layer 54COOBC films. The ED patterns in Fig. 1, the structural analysis in (A) and (B), and the optical-reflectivity data in (C) unambiguously point to a distinctive three-stage melting transition sequence. The dashed lines at 66.3°, 63.0°, and 60.1°C signify the Sm-A–Sm-A′, Sm-A′–Hex-B, and Hex-B–Cry-B transitions, respectively.

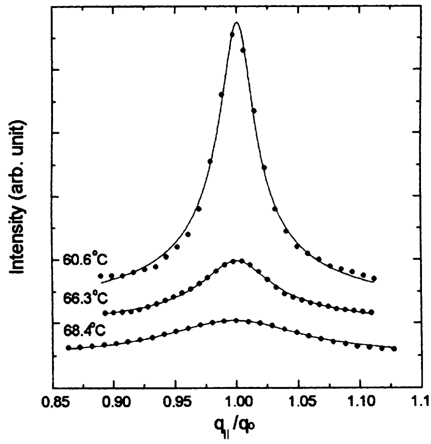

Fig. 3. Radial $q_{\parallel}$ scans from a two-layer 54COOBC film at 68.4°C (Sm-A), 66.3°C (Sm-A′), and 60.6°C (Hex-B phase). The corresponding positional correlation lengths are 14.5 ± 0.6, 33.1 ± 1.3, and 76.5 ± 4.0 Å, respectively. The points are data and the solid lines are Lorentzian fits in the Sm-A and square-root Lorentzian fits in the Sm-A′ and Hex-B phase. The abscissa is normalized to the peak position, q_o, of the radial line shape.

the bond-orientational order parameter vanishes above 63.0°C, (ii) the positional correlation length increases sharply below 63.0°C, and (iii) the optical reflectivity has a distinct anomaly indicating a pronounced in-plane molecular density change (*24*) at 63.0°C. The consistent and reproducible behavior of these results all point to the existence of a Sm-A′–Hex-B transition at 63.0°C and strongly suggests that the Sm-A′ is indeed a distinct 2D isotropic phase with longer range positional correlations than an ordinary 2D liquid. The nature of the Sm-A′ phase is not yet apparent. It could be a disordered phase with closer packing than the Sm-A and stronger orientational fluctuations than the Hex-B phase. The existence of this intermediate phase may be related to the strong anisotropy of the LC molecules, but its possible occurrence in other non-LC 2D systems has yet to be explored.

The existence of the Sm-A′ phase allows us to have a possible explanation for the puzzling behavior of C_p (Fig. 2C), which exhibits a single sharp symmetric peak at 66.3°C that can be fitted by a simple power law (*25*). The thermal hysteresis of this transition is found to be 80 ± 50 mK, and the transition appears to be weakly first order. Because the phase transition at 66.3°C was previously interpreted as a Sm-A–Hex-B transition (*25*), the pronounced pretransitional behavior and divergent character of the C_p anomaly were thought to be inconsistent with the KT-type behavior expected in such a transition (Fig. 4). Until now, it has been unclear why the Halperin-Nelson model (*2*) is so successful in describing the bond-orientational order derived from structural measurements in hexatic LC films (*7, 8, 20*) but fails to give a proper account of the C_p data (*14*). Because our ED data in the two-layer 54COOBC film suggest that the transition at 66.3°C corresponds, not to the Sm-A–Hex-B transition, but to the Sm-A–Sm-A′ transition, which is not expected to be KT-like, the power-law anomaly in the heat capacity is not necessarily surprising. Because there is no symmetry breaking involved, the Sm-A–Sm-A′ transition should be first order, which is consistent with slight thermal hysteresis observed (*26*).

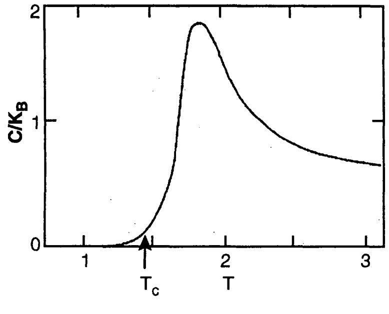

Fig. 4. Theoretical prediction of the C_p profile for a KT-type transition in two dimensions (*27*). The heat capacity should involve only an essential singularity at the transition temperature T_c that is not expected to be observable, as well as a broad hump far above T_c due to the gradual dissociation of defect pairs—for example, dislocation pairs in the crystalline phase and disclination pairs in the hexatic phase.

Our measurements lead to the following important observations. The existence of the Sm-A′ phase as a 2D isotropic liquid with enhanced positional correlations (~40 Å) has not been anticipated. The transformation of the Sm-A phase first to the Sm-A′ phase and not directly to the Hex-B phase could fundamentally alter our understanding of the 2D melting phenomenon. Our ED and optical-reflectivity data have unambiguously revealed the 2D Sm-A–Sm-A′–Hex-B–Cry-B transition sequence in two-layer 54COOBC films. This observation may help to reconcile the discrepancy between the Halperin-Nelson model (*2*) and the C_p data. One possible explanation of these observations is the following: near 60.1°C, the dislocation pairs in the crystalline phase (Cry-B) start melting through a KT-type transition into free dislocations in the hexatic phase (Hex-B); around 63.0°C, the dislocations, which are disclination pairs, start dissociating through another KT-type transition into a 2D liquid with a low density of free disclinations (Sm-A′); and finally at about 66.3°C, all disclination pairs melt into an ordinary liquid with free disclinations (Sm-A). The apparently continuous Sm-A′–Hex-B transition at 63.0°C and Hex-B–Cry-B transition at 60.1°C have not been resolvable in our C_p measurement at the current level of accuracy. Our results suggest, however, that these two transitions are excellent candidates for observing KT-type behavior in an LC system.

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21. C_6 is so defined (*7*) to be in the range $0 \leq C_6 \leq 1$. It is a quantitative measure of the sixfold nature of the scattering function. When C_6 is zero (one), the sample is in the isotropic liquid (crystalline) phase. When $0 < C_6 < 1$, the sample is in the hexatic regime exhibiting long-range bond-orientational order.
22. G. Aeppli and R. Bruinsma [*Phys. Rev. Lett.* **53**, 2133 (1984)] have explicitly shown that a SRL structure factor should describe our data in the hexatic regime. The SRL form used in our fit is

$$I(q_\parallel) = A[(q_\parallel - q_o)^2 + \kappa^2]^{-1/2}$$

where A is the scattering amplitude, κ the inverse of in-plane correlation length, and q_o the peak position. We have subtracted the background contribution from the primary (nondiffracted) electron beam. In the Sm-A phase, the Lorentzian and the SRL fit equally well. The Sm-A′ phase was fitted by SRL because its radial line width is comparable to that of a hexatic and it yields a better χ^2 (by 30%) than a Lorentzian fit. Our analysis on the radial line shape is consistent with those from x-ray measurement on other LC films [S. C. Davey, J. Budai, J. W. Goodby, R. Pindak, D. E. Moncton, *ibid.* **53**, 2129 (1984); E. B. Sirota, P. S. Pershan, S. Amador, L. B. Sorensen, *Phys. Rev. A* **35**, 2283 (1987)].
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