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Tim Stoebe [a] & C. C. Huang [a]

[a] School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota, USA

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CALORIMETRIC INVESTIGATION OF THIN FREE-STANDING LIQUID-CRYSTAL FILMS

TIM STOEBE and C.C. HUANG
School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota, USA

Abstract Heat capacity data near the smectic-A-hexatic-B transition in thin free-standing liquid-crystal films has been obtained. Films greater than two molecular layers in thickness display multiple anomalies associated with the smectic-A-hexatic-B transition. The anomalies are sharply peaked and are therefore inconsistent with recent defect mediated melting theory. Moreover, the separate surface and interior transition data can be successfully fit to a simple power law. The fitting results indicate that these films exhibit similar, continuous transitions at significantly different temperatures localized to regions only 30Å apart.

INTRODUCTION

The existence of characteristic defects and their ability to mediate phase transitions has been generally acknowledged but a complete theoretical picture has proven elusive. Significant progress has been made for two-dimensional (2D) systems, however. Kosterlitz and Thouless introduced the concept of topological order and demonstrated that the 2D XY model could form topological defects which could mediate a new type of phase transition.[1] This theory was soon extended by Halperin and Nelson,[2] and Young,[3] to describe the melting of a 2D crystal. One of the most interesting predictions of this analysis was the proposed existence of a novel phase of matter intermediate between the 2D liquid and crystalline phases. Unlike the crystalline state, this phase is predicted to exhibit only short-ranged positional order. However, because the orientations of the local lattices are not distributed randomly, this phase exhibits bond-orientational-order (B.O.O.) and can be distinguished from the isotropic liquid phase. In systems with an underlying six-fold symmetry, there are six nearest neighbors and B.O.O. is equivalent to the preservation of the angles between imaginary bonds coupling nearest neighbors. Such a phase has been termed hexatic and its identification in experimental systems has been the focus of numerous studies.[4]

Subsequent to the introduction of these important ideas, Birgeneau and Litster suggested that certain smectic liquid-crystal phases may be three-dimensional (3D) manifestations of the predicted 2D hexatic phase.[5] One of the most intriguing aspects of many smectic liquid-crystals is that, under the appropriate conditions, they can be spread across an opening to form freely suspended films (much like soap films on a ring).[6] The free-standing film geometry has proven to be particularly well suited to the study of smectic phases and, in 1981, Pindak, et. al, first observed scattering consistent with the predicted hexatic phase in an x-ray diffraction experiment on free standing 46OBC (a member of the *n*-alkyl-4'-*n*-alkyloxybiphenyl-4-carboxylate, nmOBC, homologous series) films.[7] This phase has since been termed the hexatic-B (HexB). Upon increasing temperature, the HexB phase of 46OBC melts into the smectic-A (SmA) phase. Since the SmA phase exhibits purely liquid-like intralayer order, the SmA-HexB transition should represent a liquid-hexatic transition. Observation of a continuous SmA-HexB transition in a sufficiently thin free-standing film (so that it is effectively 2D) could therefore constitute an important test of the 2D KTHNY defect mediated melting theory.

A KTHNY transition is expected to exhibit a rather unique thermal signature. Solla and Reidel predicted the heat capacity anomaly to be a broad hump, reflecting the nature of the essential singularity at the transition temperature (which is located on the low temperature side of the broad hump).[8] While the predicted anomaly is not universal, a sharply peaked, divergent anomaly is not consistent with the theory. Using our recently developed quasi-adiabatic ac calorimeter,[9] we have recently resolved the heat capacity anomaly associated with the continuous SmA-HexB transition in effectively 2D two-layer 3(10)OBC free-standing films.[10] The data are not consistent with KTHNY theory as the heat capacity anomaly is well described by a simple power law: $C_p = A^{\pm}t^{-\alpha} + B$. Here $t = |T - T_c|/T_c$ is the reduced temperature. Fitting yields a value $\alpha = 0.31 \pm 0.04$ for the critical exponent. To the best of our knowledge there is no present theory that can adequately account for these results.

Thicker films ($N > 2$) are also very interesting as they exhibit surface enhanced ordering transitions. For example, three layer thick films exhibit a transition associated with the creation of hexatic order in the two surface layers well above (≈ 10 K) the bulk SmA-HexB transition temperature. The single interior layer becomes hexatic only at a significantly lower temperature (≈ 2 K above the bulk T_c). Because no thermal hysteresis could be detected (down to the 10 mK temperature resolution of our calorimeter), these transitions appear to be continuous. The observation of distinct continuous transitions localized to adjacent smectic layers (average separation ≈ 30 Å) is quite surprising. The divergent correlation length associated with the hexatic ordering of the surface layers would be expected to penetrate into adjacent layers, causing them to order also. The

surface ordering should therefore have a dramatic effect on the ordering of the interior layers. Heat capacity data obtained on three and four-layer thick 3(10)OBC films near the SmA-HexB transition demonstrate that this is not the case. The separate surface and interior heat capacity anomalies can again be well described by a simple power law. Furthermore, the fitting results obtained indicate that these localized transitions are virtually identical to the transition exhibited by the two layer film.

EXPERIMENT

The quasi-adiabatic ac calorimeter and experimental procedure used to observe the SmA-HexB transition in free-standing liquid-crystal films has been described previously and is briefly recounted here.[9,11] The films are created inside a sealed two-stage oven by scraping a spring loaded spreader across an opening (≈ 1 cm^2) in a stainless steel film plate (see Fig. 1). Free-standing films can remain stable for weeks. The film thickness (of sufficiently thin films, $N < 15$) can be determined using a simple optical reflectivity technique.[12] Many films can be created per sample loading and new films are created until one of the desired thickness is obtained. The oven temperature is computer controlled to provide a slow, uniform ramp (typically $\approx$ 15 mK/min) through the transition region. The heat capacity of the film is probed using a chopped (42.5 Hz) IR HeNe laser beam ($\lambda = 3.4$ μm) as an ac heat source. The chopped IR laser beam induces a temperature oscillation in the film and the magnitude of this temperature oscillation can be related to the heat capacity of the film. The temperature oscillation is transmitted through 1/2 atm Ar exchange gas and is sensed by a small thermocouple positioned $\approx$ 30 μm below the film and directly in the path of the laser. The emf induced by this thermocouple is detected using standard lock-in amplification techniques. Physical contact between the film and the thermocouple was avoided by mounting the entire apparatus on a vibration isolation optical table. Because thin films ($N < 15$) transmit over 98% of the incident laser intensity, direct laser heating of the thermocouple results in a significant background contribution. In fact, only 10% of the signal from a two layer thick film is actually due to the film itself. This added background signal can be removed by the introduction of another thermocouple into the system. This thermocouple is termed the lower thermocouple as opposed to the upper (or film) thermocouple discussed above. Since the thermal diffusion length of the 1/2 atm argon exchange gas is $l_g \approx 0.7$ mm at 42 Hz, mounting the lower thermocouple more than 5 mm below the film but directly under the IR beam allows it to detect the direct laser heating while being completely insensitive to the temperature oscillation of the film. The differential mode of the lock-in amplifier could therefore be used to eliminate the unwanted direct laser heating background and the subtraction ratio was generally greater than 95%. Moreover, this

differential circuit also effectively removed most of the addendum signal due to the exchange gas and temperature sensor, greatly facilitating the study of very thin films.

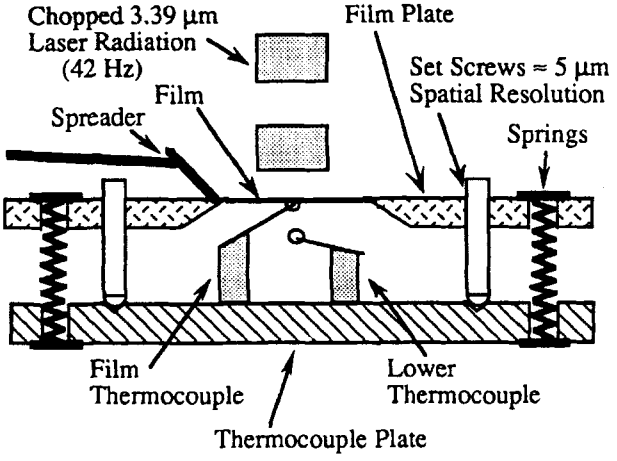

FIGURE 1 Calorimeter Detail. The thermocouple plate is spring loaded so that it is constantly pulled toward the film plate. Three very fine set screws are used to maintain the film plate-thermocouple plate separation when taking data. One edge of the thermocouple plate can be lowered so it pivots on the kinematic mount to allow for cleaning and spreading new films. The lower thermocouple is mounted in the path of the IR laser, but many thermal diffusion lengths (illustrated by circles at ends of the thermocouples) away from the film.

RESULTS

Two-Layer 3(10)OBC Films

The high resolution heat capacity data from a two-layer 3(10)OBC film near the SmA-HexB transition are shown in Figure 2. The two-layer film transition is observed to occur well above the bulk transition temperature (≈ 75°C vs ≈ 66°C). This temperature difference illustrates the strong surface enhanced ordering effects demonstrated by these free-standing films. No thermal hysteresis could be detected (to within ± 10mK) and this transition therefore appears continuous. Because a two-layer film is effectively two dimensional, this transition is expected to exhibit a thermal signature consistent with the prediction of Solla and Reidel. However, unlike the broad asymmetric hump expected, the heat capacity anomaly appears sharply peaked and roughly symmetric. In fact, it is

well described by a simple power-law $C_p = A^{\pm}t^{-\alpha} + B$, over 1.5 decades in reduced temperature, t. The fit yields $A^+/A^- \approx 1$ and $\alpha = 0.28 \pm 0.04$ as the critical exponent. The success of this fitting further supports the identification of this transition as continuous. These results are clearly inconsistent with the theoretical prediction. At present we know of no theory predicting the behavior exhibited by these two-layer films. Recent computer simulation work has suggested that the hexatic order may be created along with some other type of order (e.g. herringbone) through a single continuous transition yielding a heat capacity anomaly that is sharply peaked.[13] However, the theory associated with this observation remains to be fully developed. Since less than 30 nanograms of sample actually contribute to the measured heat capacity signal from a two-layer film, detection of this transition demonstrates the technical achievement of this calorimetric system.

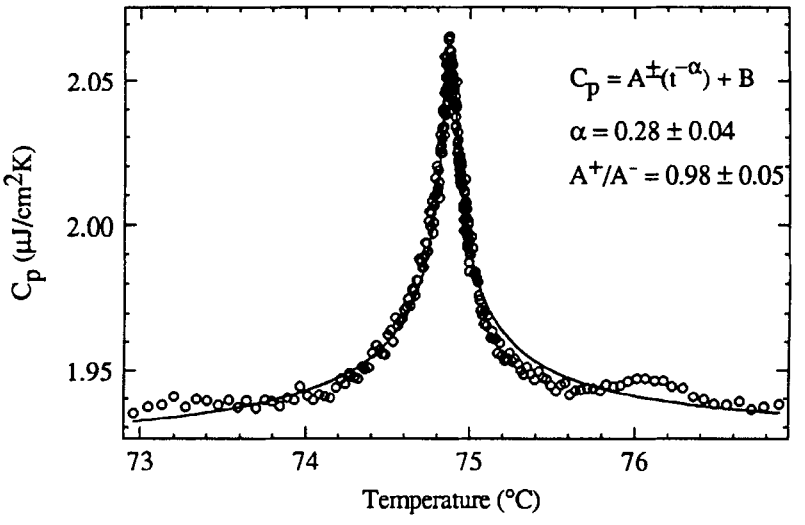

FIGURE 2 Heat -capacity data (circles) and fitting result (line) near the SmA-HexB transition of a two-layer 3(10)OBC film.

Three-Layer 3(10)OBC Films

Three-layer 3(10)OBC films exhibit two anomalies associated with the SmA-HexB transition, both occuring well above the bulk transition temperature (see Fig. 3). The larger of the two anomalies occurs near 74°C, just slightly below the transition temperature exhibited by the two-layer film and is similar in size and shape to the two-layer film anomaly. The smaller of the two anomalies occurs at a significantly lower

temperature (near 68.5°C) and is more difficult to resolve. Neither of these anomalies was observed to exhibit thermal hysteresis and therefore both appear to be continuous. The data suggest that the larger, higher temperature, anomaly corresponds to the ordering of the two external (surface) layers and that the smaller anomaly is due to the ordering of the single interior layer. Based on this identification, the film is heterogeneous between 74°C and 68.5°C since the two outer layers are HexB while the interior layer is SmA through this temperature region.

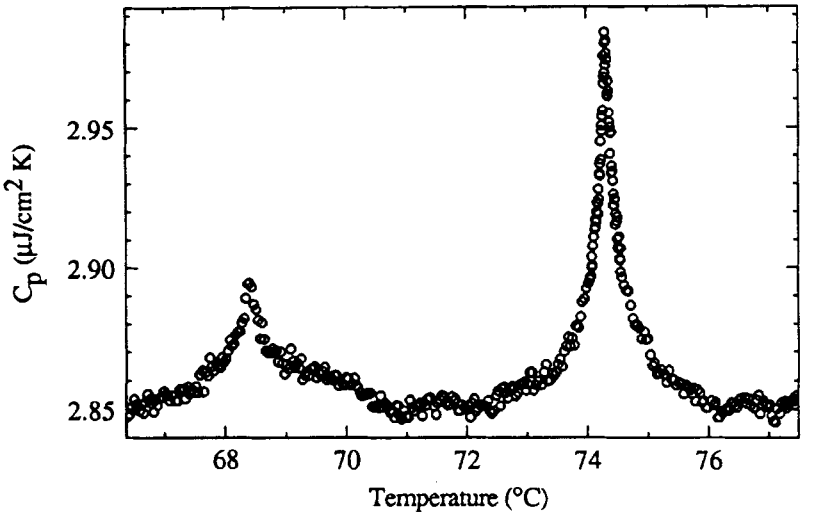

FIGURE 3 Heat -capacity data near the surface and interior layers of a three-layer 3(10)OBC film.

Separate continuous transitions occuring in such close proximity is highly unexpected since the correlation length, ξ, for hexatic fluctuations associated with the ordering of the surface layers is anticipated to diverge at the surface ordering transition temperature. Smectic phases are highly anisotropic and the ratio of the in-plane molecular coupling to the interlayer coupling may be quite large. However, even if these coupling constants differ by orders of magnitude so that the in-plane correlation length, $\xi_{\|}$, is much larger than the interplane correlation length, $\xi_{\perp}$, one would expect the hexatic ordering to penetrate into at least the adjacent layer ($\xi_{\perp} \approx 30$ Å) as hexatic order is created over macroscopic length scales ($\xi_{\|} \approx 1$ mm) in the surface layers. Even if the surface ordering does not preclude a separate interior transition, the hexatic order of the surface layers would be expected to strongly influence the nature of the separate interior transition. Similarly, the presence of an adjacent SmA layer might be expected to alter the

SmA-HexB transition in the surface layers. Unfortunately, the data quality near the smaller anomaly is too poor perform reasonable fitting. However, the simple power law characterizing the two-layer film transition has also been found to adequately describe the surface transition of the three-layer film (see Fig. 4). The fit yields parameter values very similar to those obtained for the two-layer film, $A^+/A^- \approx 1$ and $\alpha = 0.29 \pm 0.04$. The success of this fitting again supports the identification of this transition as continuous. The fitting results also indicate that the surface transition of a three-layer film is basically the same as the transition exhibited by the two-layer film and support the hypothesis that three-layer films exhibit separate SmA-HexB transitions localized to adjacent smectic layers. The scaling of the two-layer film anomaly onto the three-layer film surface surface anomaly further demonstrates this point (Fig. 4). The enthalpy removed by the interior transition (obtained by integrating the area under the heat capacity anomaly) is significantly less than half that of the surface transition, which would have been expected assuming the enthalpy change per layer to be a constant. Even though the hexatic order does not appear to penetrate between the layers above the interior layer transition temperature, center of mass fluctuations in the interior layers may be reduced by increased film stiffness due to the hexatic outer layers, lessening the entropy removal (and size of the heat-capacity anomaly) associated with the interior transition.

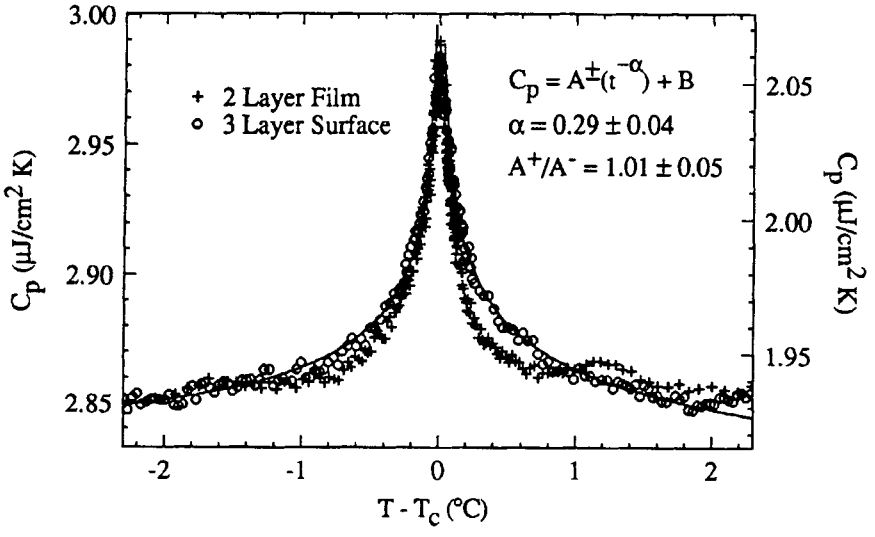

FIGURE 4 Heat -capacity data (circles) and fitting result (line) near the surface SmA-HexB transition of a three-layer 3(10)OBC film. The two-layer film anomaly (crosses) is scaled onto the three-layer film surface anomaly to further demonstrate their similarity.

Four-Layer 3(10)OBC Films

Like the three-layer film results, the heat capacity data associated with the SmA-HexB transition in a four-layer 3(10)OBC film exhibit two distinct anomalies (see Fig. 5). The higher temperature anomaly is due to the ordering of the two surface layers, while the lower temperature anomaly is due to the ordering of the two interior layers. The temperature separation between surface and interior anomalies is increased relative to the three-layer film results. Neither anomaly exhibits detectable thermal hysteresis (down to our 10 mK resolution), and therefore again appear to be continuous. The four-layer film surface and interior anomalies are much more similar in size and shape than the three-layer film results, consistent with the identification of transitions localized to individual smectic layers. Again the observation of separate, continuous transitions associated with the SmA-HexB transition in four-layer films is difficult to reconcile with the expected divergence in hexatic order fluctuations associated the the surface transition.

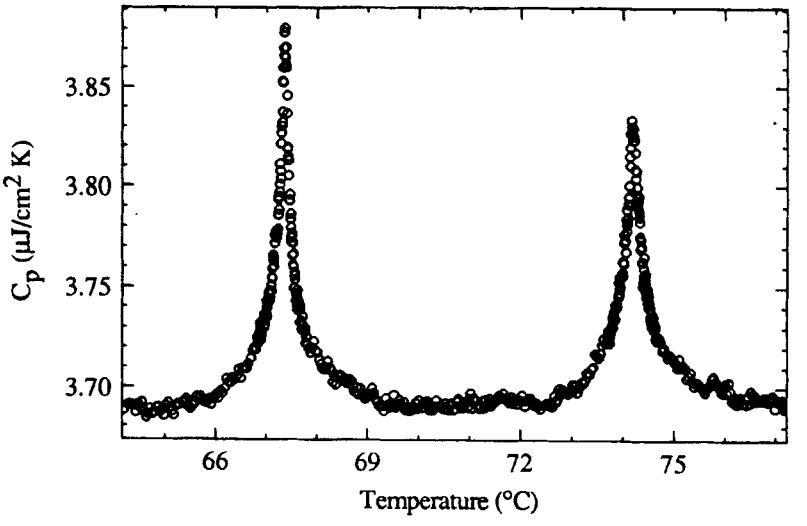

FIGURE 5 Heat -capacity data near the surface and interior layers of a four-layer 3(10)OBC film.

Both the surface and the interior transitions of the four-layer 3(10)OBC film could be successfully fit using the simple power law previously described. The fitting of the surface transition yielded $A^+/A^- \approx 1$ and $\alpha = 0.28 \pm 0.04$ as the critical exponent (Fig. 6), while fitting the transition due to the two interior layers yielded $A^+/A^- \approx 1$ and $\alpha = 0.31 \pm$

0.04 (Fig. 7). The transition due to the interior layer appears somewhat sharper than the surface transition, but the distinction is not great. The enthalpies associated with surface and interior transitions are very similar. The similarity of these results again strongly supports the hypothesis that these anomalies represent similar phase transitions localized to different regions within the film. The surface and interior transition temperatures differ presumably due to ordering effects of the surface tension associated with the free surfaces of the film. The surface tension reduces center of mass fluctuations in the layers nearest the surface and these layers may therefore be expected to order at higher temperatures than the more fluctuating interior layers. The observation of separate, continuous transitions localized to adjacent smectic layers may also indicate that the hexatic order largely resides in the biphenyl molecular cores. The more flexible alkyl tails may act as buffer layers that effectively screen the hexatic order between biphenyl cores in adjacent layers. The hexatic domains of adjacent layers would align only at a sufficiently low temperature (i.e. near the bulk transition temperature). Above this temperature, hexatic order within each smectic layer would be created independently, and the four-layer interior transition would not be expected to differ significantly from the four-layer surface transition.

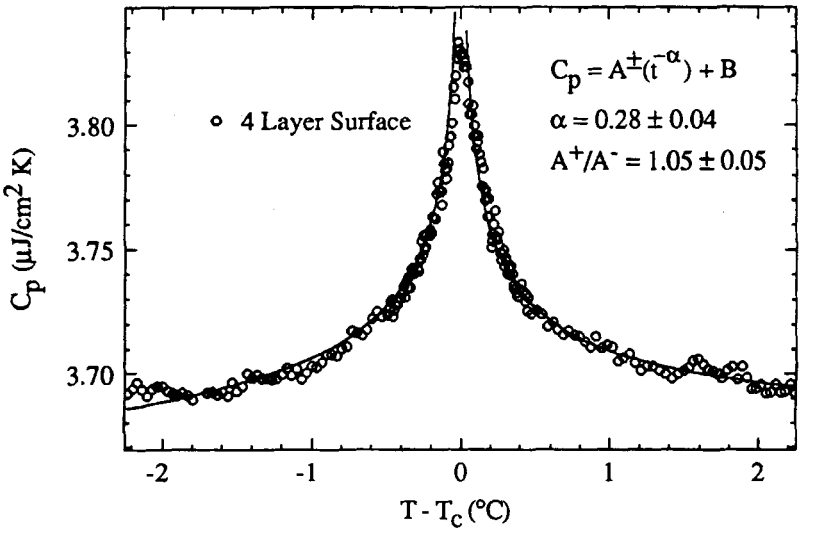

FIGURE 6 Heat -capacity data (circles) and fitting result (line) near the surface SmA-HexB transition of a four-layer 3(10)OBC film.

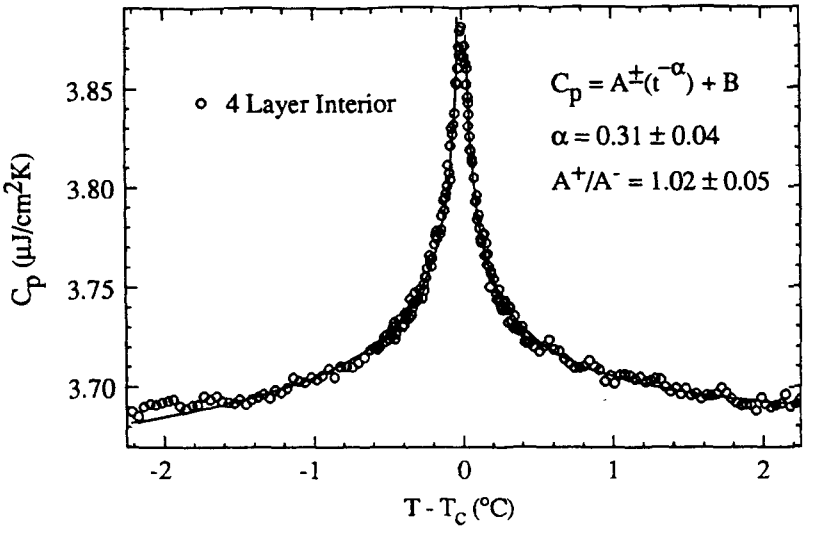

FIGURE 7 Heat -capacity data (circles) and fitting result (line) near the interior SmA-HexB transition of a four-layer 3(10)OBC film.

CONCLUSION

High resolution heat capacity data near the SmA-HexB transition of two-, three-, and four-layer free-standing 3(10)OBC films has been obtained. The three- and four-layer film results exhibit separate anomalies associated with the ordering of surface and interior layers at temperatures well above the bulk sample transition temperature. The elevated transition temperatures of the smectic layers nearest the surfaces are presumably due to ordering effects associated with the surface tension of the free-standing films. The heat capacity anomalies are sharply peaked and can be fit to a simple power law, $C_p = A^{\pm}t^{-\alpha} + B$, and are characterized by very similar fitting parameters ($A^+/A^- \approx 1$ and $\alpha = 0.30 \pm 0.04$). This system is therefore highly unusual in that virtually identical phase transitions are observed in localized regions in very close proximity at significantly different temperatures. The success of these fits and the lack of observed thermal hysteresis indicate that these transitions are continuous. The observation of continuous transitions localized to adjacent smectic layers (≈ 30 Å separates layers) demonstrates the highly anisotropic nature of these phases and suggests that an effective barrier to hexatic fluctuations must exist between the layers. Flexible, disordered alkyl tails may provide

such a barrier, suggesting that the smectic order may be primarily associated with the biphenyl cores of the molecules. The success of the power-law fits also indicates that our experimental results do not support recent 2D defect mediated melting theory that predicts a broad hump associated with the 2D liquid-hexatic transition.

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