

High-resolution heat-capacity studies of the hexatic-*B*–smectic-*F* phase transition in liquid-crystal compounds

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High-resolution calorimetric data for several compounds exhibiting the hexatic-*B*–smectic-*F* transition have been obtained. This transition involves the formation of tilt in the presence of bond orientational order. Like most of the smectic-*A*–smectic-*C* transitions, which show no bond orientational order, the heat-capacity anomaly of the hexatic-*B*–smectic-*F* transition exhibits mean-field-like behavior and can be well described by an extended mean-field model. [S1063-651X(98)52108-3]

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Many liquid crystals that show a layered (smectic) phase display a phase transition in which the long axis of each molecule changes its orientation with respect to the layer normal [1]. This transition has now been observed with three different types of in-plane order. Within each layer the molecules may possess liquidlike, long-range bond-orientational, and long-range positional ordering respectively for the following three classes of transitions: (i) smectic-*A* (Sm-*A*)–smectic-*C* (Sm-*C*) [2], (ii) hexatic-*B* (Hex-*B*)-tilted hexatic phase [smectic-*F* (Sm-*F*) or smectic-*I* (Sm-*I*)], and (iii) crystal-*B* (Cry-*B*)-tilted crystal phase [crystal-*G* (Cry-*G*) or crystal-*J* (Cry-*J*)]. Table I gives the relevant molecular order within and between the layers for each of these transitions. Assuming that the molecular tilt from the layer normal is the primary order parameter [$\Psi = \theta \exp(i\phi)$, θ being the molecular tilt angle from the layer normal and ϕ the azimuthal angle], that Ψ does not couple to other degrees of freedom, and the relevant interactions are short range, all three types of transitions are predicted, due to the symmetry of the order parameter, to be continuous and to belong to the *XY* universality class. To date, experimental results have contested this picture. During the past 15 years, extensive experimental data have been obtained near the Sm-*A*–Sm-*C* transition of various liquid-crystal compounds [3–6]. Most of these studies yield mean-field-like static behavior for this transition [3–5]. A long-range interaction would explain this absence of measurable critical fluctuations, a phenomenon that is commonly displayed in conventional superconductors. Yet there exists no experimental evidence of a long-range interaction responsible for the formation of molecular tilt in this liquid crystal transition [3]. Thus, it remains incompletely understood as to why a majority of the Sm-*A*–Sm-*C* transitions can be well characterized by a mean-field free-energy expansion [4]. To the best of our knowledge, only one experiment has been conducted related to the Cry-*B*-tilted crystal phase transition.

The Cry-*B*–Cry-*G* transition of two liquid-crystal compounds is found to be strongly first order [7]. Thus, the ordering of the structure in which the tilt transition takes place may affect the nature of the transition. Because very different results have been obtained when the transition occurs with liquidlike and crystalline in-plane ordering, it is important to investigate the effect of hexatic ordering on the tilt transition. The Hex-*B*–Sm-*F* transition was first discovered recently in two enaminketone derivative homologous series of compounds [8]. We report here our detailed calorimetric investigations of this transition in these compounds. Even with in-plane bond-orientational ordering, we find that the Hex-*B*–Sm-*F* transition is well characterized by the extended mean-field model [4], similar to the ordinary Sm-*A*–Sm-*C* transition. We also show that the mean-field tricritical behavior observed in one mixture of these compounds [9] is consistent with our heat-capacity results.

The sixfold symmetry of hexatic ordering subdivides the tilted hexatic phases into three types. In the Sm-*F* phase each molecule tilts toward one of its next nearest neighbors. This structure may be contrasted with the Sm-*I* phase in which molecules tilt toward next nearest neighbors and the Sm-*N* phase in which molecules tilt in a direction in between those defined by the Sm-*I* and Sm-*F* phases.

Below the Hex-*B*–Sm-*F* transition temperature, a molecular tilt develops within the hexatic structure while long-range positional ordering remains absent. Like the Sm-*A*–Sm-*C* transition, this transition involves a molecular tilt with respect to the layer normal. The results of our calo-

TABLE I. Inter- and intralayer order associated with each transition. BOO, bond-orientational order; SR, short-range order; LR, long-range order; QLR, quasi-long-range order.

	Intralayer		Interlayer
	BOO	Positional order	Positional order
Sm- <i>A</i> –Sm- <i>C</i>	SR	SR	QLR
Hex- <i>B</i> -tilted hexatic	LR	SR	QLR
Cry- <i>B</i> -tilted crystal	LR	LR	LR

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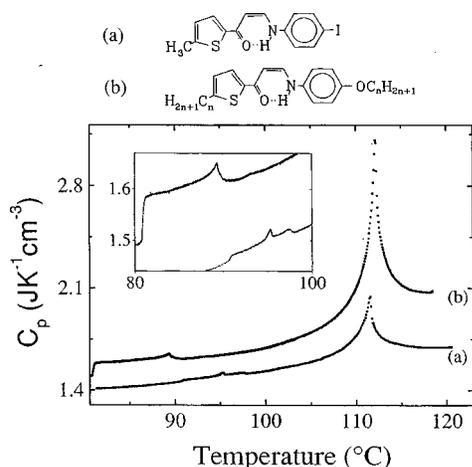


FIG. 1. Temperature variation of heat capacity of (a) 6TEPI and (b) (MTEP7)_{0.7}(MTEP8)_{0.3} compound. The data show anomalies near the Sm-A–Hex-B, Hex-B–Sm-F, and Sm-F–Cry-G transitions. The inset highlights the Hex-B–Sm-F and Sm-F–Cry-G transitions.

rimetric studies of this transition allow us to test the effect of long-range bond orientational ordering without long-range positional order on the formation of a tilted phase.

We focus on the compounds 6TEPI and the homologue mixture (MTEP7)_x(MTEP8)_{1-x} with $x=0.7$ in molar fraction. The molecular structures are diagrammed in Fig. 1. These compounds show the following phase behavior:

(1) 6TEPI:

Isotropic (162 °C) Sm-A (111 °C) Hex-B (97 °C)
Sm-F (94 °C) Cry-G.

(2) (MTEP7)_{0.7}(MTEP8)_{0.3}:

Isotropic (165 °C) Sm-A (112 °C) Hex-B (89 °C)
Sm-F (82 °C) Cry-G.

Compound (1) was selected from the series for the presence of the Hex-B–Sm-F transition while (2) was selected to test the reported tricritical behavior of this mixture [9]. The molecules are somewhat atypical for the presence of a hydrogen bond in the central ring. The melting temperature of the crystalline phase is over 100 °C for all three compounds. Thus, the temperature range of the two hexatic phases is supercooled with respect to the crystalline phase. This fact limits the temperature ramping rates in our studies. Crystallization sometimes occurs during runs at rates below 50 mK/min. We obtain consistent results when operating at rates of 50 mK/min or above.

Details of our bulk ac calorimeter have been described elsewhere [4,10]. Figure 1 displays the results of bulk heat-capacity data for both compounds over a sufficiently large temperature window to cover three relevant phase transitions. To minimize sample deterioration rate, a cooling rate of 500 mK/min in the high temperature range (above 100 °C) and 75 mK/min below that temperature was used. The Sm-A–Hex-B transitions occur at the highest transition temperature of the displayed transitions. Due to a larger sample

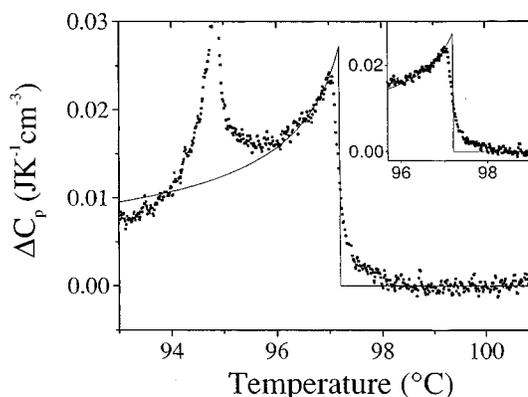


FIG. 2. Heat capacity vs temperature near the Hex-B–Sm-F transition for 6TEPI. The cooling rate is 50 mK/min. As described in the text, the solid line is the best fit to the extended mean-field model [Eq. (1)].

deterioration rate at elevated temperature, we decided not to study the Sm-A–Hex-B transition in detail. This figure clearly elucidates the relative size of the heat-capacity anomalies associated with each transition. The anomaly associated with the Sm-A–Hex-B transition is about 30 times larger than that of the Hex-B–Sm-F transition in both of the samples studied. The Hex-B–Sm-F transition occurs in both samples upon cooling from the Hex-B phase. The Hex-B–Sm-F anomaly is more steplike and smaller in the pure compound than the mixture, as seen in the inset of Fig. 1. Optical polarization transmission microscopy verifies that these anomalies are the result of the formation of tilt in the hexatic phase. The schlieren pattern characteristic of multi-domain tilt structures appears below T_c . This agrees with the onset of tilt reported in Ref. [9]. The Sm-F–Cry-G transition is highly hysteretic both in the location of transition temperature and the shape of the anomaly. Thus, we can clearly distinguish between the tilt transition and the crystallization transition in both samples. In the MTEP n mixture the Sm-F temperature window is seen to be larger (8 °C) than that of either 6TEPI or the pure compounds MTEP7 and MTEP8. We attribute this to the suppression of the crystallization due to the increased entropy inherent in a mixture.

We examine the Hex-B–Sm-F transition in detail, as we are interested in analyzing the critical onset of molecular tilt in the hexatic phase. Because of the close proximity of the Sm-A–Hex-B transition for all of these compounds, it is necessary to subtract off a small quadratic background term from the data when analyzing the anomaly. Our method of subtraction is to include a quadratic expression in fitting expressions being sure that this expression fits smoothly with data on either side of the anomaly. One typical set of data is depicted in Fig. 2 with the quadratic background subtracted. A total of eight passes were made through this transition for the compound 6TEPI. The T_c -shift rate is about (-8 ± 3) mK/hr. Within this resolution, the Hex-B–Sm-F transition is continuous. The structure of the anomaly was found to be highly reproducible and independent of the temperature ramping direction and rate within our resolution. The heat-capacity anomaly is similar to those found near the conventional Sm-A–Sm-C transition.

The heat-capacity data of this transition is fit to the extended mean-field model first proposed for the Sm-A–Sm-C

transition [4]. In this approach one must retain the sixth order term in a Landau free-energy expansion. The resulting expression for the heat capacity near T_c is given in Eq. (1),

$$\Delta C_p = \begin{cases} 0 & T > T_c \\ AT|T - T_m|^{-1/2} & T < T_c \end{cases} \quad (1)$$

A nonlinear least-squares-fitting program is used to fit the heat-capacity data to Eq. (1). The fit yields the following parameters: $A = (5.0 \pm 0.1) \times 10^{-5} \text{ JK}^{-3/2} \text{ cm}^{-3}$ and $T_m = (97.6 \pm 0.1)^\circ\text{C}$. The error bars on A and T_m are determined by the quality of the fit under independent variance of these parameters. The location of T_c is approximated as at the midpoint of the sharply sloped side of the anomaly with the error bar on T_c determined by the 10%–90% width of the slope. This yields the value $T_c = (97.2 \pm 0.1)^\circ\text{C}$. The close proximity of T_c to T_m is characteristic of the conventional Sm-A–Sm-C transition and suggests that the tilt transition occurs near a mean-field tricritical point.

We faced several limiting factors in acquiring high quality data near this transition. The small size of the anomaly and the relatively large ramping rate cause the fairly large scatter in the data. The large ramping rate may also broaden the region over which the mean-field-like jump in heat capacity takes place. This forces us to exclude from the fitting expression (1) data over a range of approximately 200 mK on the low side of the T_c and 700 mK on the high side. With this exclusion and using a standard deviation determined away from the transition, the χ^2 value of the fit was 1.6. Increasing the range of the excluded region does not substantially alter χ^2 or the value of the parameters. The region of data from $T = 92.4^\circ\text{C}$ to 92.9°C on the high temperature side of T_c can be seen in Fig. 1 to slowly deviate from the model. The value of χ^2 slowly increases with the inclusion of data in this region. For example, including data within a range of 200 mK on the high side of the transition temperature increases χ^2 to 2.6. However, the value of the parameters does not change substantially with this inclusion. Further reduction of the excluded region to below 200 mK on either side of T_c dramatically increases χ^2 . Another limiting factor is the close proximity of the Sm-F–Cry-G transition. Thus, our fitting procedure excludes data below 96°C . The shape of the anomaly within this temperature window and values of the fitting parameters (including T_c) are unaffected by the temperature ramping direction, despite the fact that the Sm-F–Cry-G anomaly is highly hysteretic in both location and shape. This suggests that the Sm-F–Cry-G transition does not noticeably affect the shape of the Hex-B–Sm-F anomaly within our region of analysis. The reproducible qualitative features of the Hex-B–Sm-F anomaly along with the very reasonable fitting results justify our application of the extended mean-field model.

While MTEP7 is reported to have a continuous Hex-B–Sm-F transition, the homologue MTEP8 shows a first order discrete jump in the tilt angle at the transition temperature [9]. The onset of the first order transition may be due to a smaller Hex-B temperature range of MTEP8. A similar correspondence has been discussed in the case of the Sm-A–Sm-C transition [11]. Pocięcha, Gorecka, and Przedmojski have reported tricritical behavior in tilt angle measurements for the 0.7/0.3 mixture of these two compounds

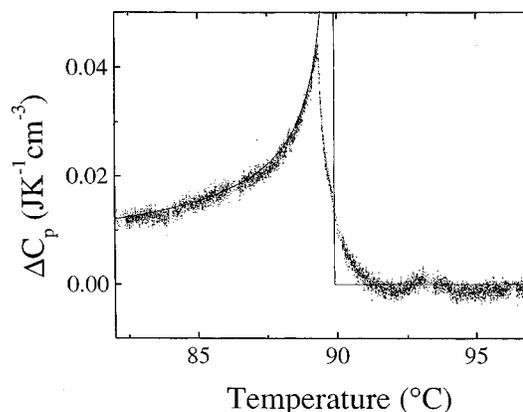


FIG. 3. Temperature variation of heat capacity near the Hex-B–Sm-F transition of $(\text{MTEP7})_{0.7}(\text{MTEP8})_{0.3}$. The cooling rate is 50 mK/min. As described in the text, the solid line is the best fit to the extended mean-field model [Eq. (1)]. In this plot, T_c is set equal to T_m in order to show that the data is consistent with tricritical behavior. The small hump on the high temperature side of the anomaly is irreproducible among the experimental runs.

[9]. We prepared such a mixture by heating the compounds to a temperature of 170°C (just above the Sm-A–isotropic transition temperature) and stirring for 5 min. This mixing procedure was performed in a helium atmosphere in order to minimize sample contamination. Figure 3 shows our heat-capacity data for the Sm-B–Sm-F transition for this mixture with a fit to Eq. (1). The fitting results yield the following values for the parameters: $A = (9.6 \pm 0.1) \times 10^{-5} \text{ JK}^{-3/2} \text{ cm}^{-3}$ and $T_m = (89.9 \pm 0.2)^\circ\text{C}$. The value of T_c is found to be $(89.7 \pm 0.3)^\circ\text{C}$. Tricritical behavior requires $T_c = T_m$. Within the resolution of our T_c and T_m values, the fit is consistent with the tricritical behavior observed by Pocięcha, Gorecka, and Przedmojski [9]. Note also that because the crystallization transition has been suppressed, the fit may be carried out over a wider temperature range on the low temperature side of the transition. We detected a slight hysteresis of (50 ± 25) mK and a transition temperature drift rate of less than 2 mK/h. We could detect no hysteresis in the shape of the anomaly. The mixture is thus very close, on the first order side, to the tricritical point [12].

For this transition we find that we must exclude 900 mK on either side of T_c in order to obtain reasonable values for χ^2 . With this exclusion, we obtain $\chi^2 = 1.77$. The value of χ^2 increases dramatically with reduction of the excluded region. This result is easily seen in Fig. 2 as arising from the inclusion of the rounded region near T_c . The widening of the excluded region for the mixture may be caused by degradation during the high temperature mixing process. Unlike the pure sample, which was never heated beyond 120°C , the mixture was heated into its isotropic phase. Such thermally induced degradation may also explain the presence of the minute feature above the transition. This feature was irreproducible over several experimental runs.

Mean-field behavior in tilt transitions may be explained in part by a sufficiently large heat capacity jump (ΔC_p) and a correlation length on the order of the molecular size [13]. The mean-field to critical fluctuation crossover region is characterized by the Ginzberg parameter [14] t_G

$=k_B^2/[32\pi^2(\Delta C_J)^2\xi_0^6]$, where ΔC_J is the observed heat-capacity jump and ξ_0 is the bare correlation length. By using our measured ΔC_J , provided that $\xi_0=10\text{ \AA}$, t_G is smaller than 10^{-4} for the compounds studied here. This is beyond our experimental resolution for these compounds. Similar to the Sm-A–Sm-C transition, even though the bare correlation length may not be too large, a sufficiently large value in ΔC_J will significantly reduce the critical fluctuation region, in some cases, beyond the experimental resolution. A pertinent question to be addressed concerning the mean-field behavior found near the Sm-A–Sm-C and Hex-B–Sm-F transition may be the following: Why does the molecular tilt produce a large ΔC_J value? Even though the bare correlation ξ_0 is on the order of the molecular size, the Ginzberg parameter t_G becomes sufficiently small to make the critical region experimentally inaccessible in most of cases.

To date, to the best of our knowledge, there exists no theoretical explanation of both the large value of ΔC_J and

closeness of this class of transitions to a mean-field tricritical point. This Rapid Communication addresses the question of possible effects of bond-orientation order on the nature of tilt transition. The question of whether the reasonably good fit of our calorimetric data to the extended mean-field model is intrinsic to the nature of the molecular tilt transition remains to be addressed experimentally and theoretically. So far the Hex-B-tilted hexatic phase transition has only been found in one series of compounds [8]. More compounds are needed to more conclusively determine the nature of the Hex-B-tilted hexatic phase transition.

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