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Smectic-A–hexatic-B transition of various compounds in the homologous series of n-alkyl-4′-n-alkoxybiphenyl-4-carboxylate

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Extensive high-resolution heat-capacity measurements have been carried out near the smectic-A–hexatic-B transition of various compounds in the homologous series of n-alkyl-4′-n-alkoxybiphenyl-4-carboxylate. In contrast with the nematic–smectic-A and smectic-A–smectic-C (or chiral-smectic-C) transitions, the critical exponent α characterizing the smectic-A–hexatic-B heat-capacity anomaly is found to be large and does not vary systematically with the size of the disordered-phase (i.e., smectic-A) temperature range.

Between the crystalline and the isotropic-liquid phase many liquid-crystal compounds exhibit two or more distinct mesophases with various degrees of translational and orientational order. These materials are excellent systems for studying melting processes, phase transitions, and critical phenomena. As far as the phase transitions are concerned, liquid crystals have one unique property. Unlike most other materials which have well-separated phase transitions, liquid crystals can have a series of phase transitions in a relatively small temperature range. In other words, the disordered phase, associated with a given continuous phase transition at T_c, may undergo another transition at a higher temperature T_1 to an even more disordered phase. In most of the materials, the ratio T_c/T_1 is significantly smaller than one. In these situations, the order parameter associated with the phase transition at T_1 is almost saturated at T_c and will not dramatically affect the additional order parameter which set in near the transition at T_c. However, in liquid-crystal compounds the ratio T_c/T_1 is very close to one for most of the transitions. Consequently, fluctuations of the order parameter associated with the transition at T_1 may still be large enough to influence the nature of the transition occurring at T_c. In the framework of molecular mean-field theories, McMillan[1] and de Gennes[2] have addressed the importance of the nematic temperature range in determining the nature of the nematic (N)–smectic-A (Sm A) transition. Since then no new theoretical insight into this problem relating, in particular, to critical phenomena has been reported, to our knowledge. Results of careful experiments on the Sm A–smectic-C (Sm C) [or chiral-smectic-C (Sm C^*)] and the N-Sm A transitions indicate the existence of a systematic relationship between the size of the disordered-phase temperature range and the behavior of the given transition.

Among various possible phase transitions between liquid-crystal mesophases, it has been found that at least the N-Sm A, Sm A-Sm C (or Sm C^*) and Sm A–hexatic-B transitions can be continuous. Considerable theoretical and experimental effort has been put into understanding these transitions. While both the N-Sm A and Sm A–hexatic-B transitions are fluctuation dominated, the Sm A-Sm C (or Sm C^*) transition can be well described by an extended mean-field theory.[3] Recently, Huang and Lien[4] have demonstrated that the extended mean-field expression is sufficient to describe the nature of the Sm A-Sm C (or Sm C^*) transition and there exist approximately linear relations between the mean-field coefficients associated with the Sm A-Sm C (or Sm C^*) transition and the Sm A temperature range. For the N-Sm A transition, other research groups[5–9] have found systematic trends between the measured critical exponents and the parameter r_{NA} $(=1-T_{NA}/T_{IN})$ which indicates the size of the nematic temperature range. Here T_{NA} and T_{IN} are the N-Sm A and isotropic (I)–N transition temperatures, respectively. In particular, the critical exponent α characterizing the heat-capacity anomaly of the N-Sm A transition decreases approximately monotonically as r_{NA} increases.

Since our first high-resolution heat-capacity work near the Sm A–hexatic-B transition of n-hexyl-4′-n-pentyloxybiphenyl-4-carboxylate (65OBC),[10] we have carried out similar measurements on seven other different liquid-crystal compounds of the homologous series of n-alkyl-4′-n-alkoxybiphenyl-4-carboxylate. In contrast to the systematic variations being revealed in the N-Sm A and Sm A-Sm C (or Sm C^*) transitions, we have found that the critical exponent (α) associated with the heat-capacity anomaly near the Sm A–hexatic-B transition has a large value (about 0.5–0.6) which seems to be unrelated to the size of the temperature range of the disordered phase (i.e., Sm A phase).

The details of our high-resolution calorimetry technique and data reduction have been published.[11] Thus far, the continuous Sm A–hexatic-B transition has only been found in the homogolous series of n-alkyl-4′-n-alkoxybiphenyl-4-carboxylate. In this homogolous series we have carried out heat-capacity measurements of the following eight compounds with various Sm A temperature ranges. They are n-butyl (45OBC), n-hexyl (65OBC), and n-heptyl (75OBC) of the n-pentyloxy series, n-propyl (36OBC), and n-butyl (46OBC) of the n-hexyloxy series, n-propyl (37OBC) of the heptyloxy series, and n-ethyl [2(10)OBC] and n-propyl [3(10)OBC] of the decyloxy series. All of these compounds have an I–Sm A–hexatic-B transition sequence as well as pronounced and approximately symmetric heat-capacity anomalies associated with the Sm A–hexatic-B transition. Figure 1 shows one typical heat-capacity anomaly near the Sm A–hexatic-B transition of 37OBC. The addendum contribution from the sample cell has been subtracted.

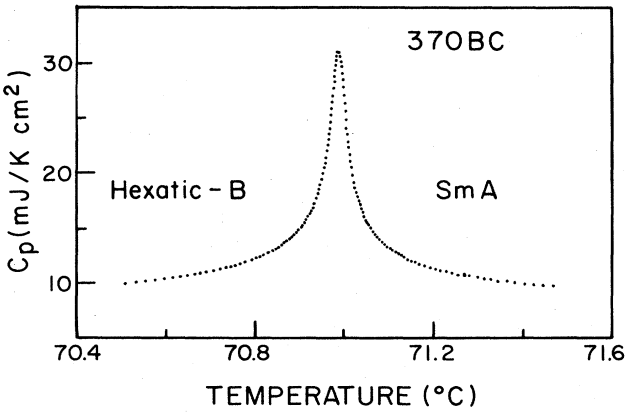

FIG. 1. Heat capacity near the Sm A-hexatic-B transition of 37OBC. Thickness of the sample is about 60 ±5 μm.

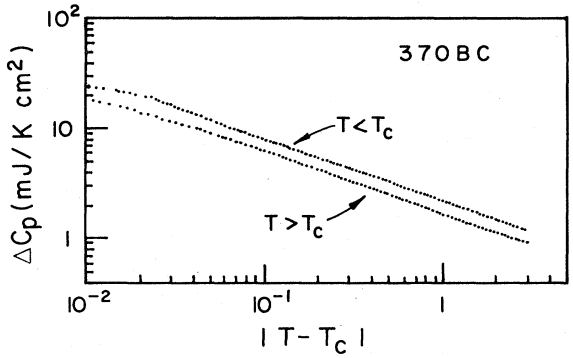

FIG. 2. Anomalous part of the heat capacity $\Delta C_p = C_p - B - Dt - A^{\pm}E^{\pm}|t|^{x-\alpha}$ vs $|T-T_c|$ for 37OBC near the Sm A-hexatic-B transition.

We have performed nonlinear least-squares fittings of our data to the following power-law expression with scaling correction terms:[12]

$$C_p = \begin{cases} A^+|t|^{-\alpha}(1+E^+|t|^x)+B+Dt, & T>T_{AB} \\ A^-|t|^{-\alpha}(1+E^-|t|^x)+B+Dt, & T<T_{AB} \end{cases} .$$

Here $t=(T-T_{AB})/T_{AB}$ and $B+Dt$ is the background term. Nonlinear least-squares fittings of our data to the above expression without the scaling correction terms (i.e., $E^+ = E^- = 0$) consistently gave us better-fitting results for the case with a different constant-background term (i.e., B) for $T>T_{AB}$ and $T<T_{AB}$. This indicates that the scaling correction terms are necessary. Our fitting results indicate that the SmA-hexatic-B transition is categorized by large values of α (about 0.5–0.6). We still do not understand the origin of this large critical exponent α and we do not know which universality class the Sm A-hexatic-B transition belongs to. Although some theoretical predictions have yielded a value of 0.5 for the exponent x in the case of the Ising, XY, and Heisenberg models,[13] we do not know the proper value of x for the Sm A-hexatic-B transition. In one case (i.e., 46OBC), we varied x from 0.5 to 1.0 and found that the variations of the important parameters (α, T_{AB}, and A^+/A^-) were within their standard deviations determined in the fitting (see Table I). This is due to the fact that the scaling correction term, while not negligible, is relatively small. If E^+ and E^- have different signs and the exponent x is less than α, then the scaling correction term will have a discontinuous jump at T_{AB}. To avoid this discontinuous jump in heat capacity,[14] we have chosen a value of x ($\simeq 0.75$) which is larger than all the α's we have obtained near the Sm A-hexatic-B transition. In Fig. 2, the fitted result of sample 37OBC is shown. Here the leading anomalous part of the heat capacity $\Delta C_p = C_p - B - Dt - A^{\pm}E^{\pm}|t|^{x-\alpha}$ is plotted as a function of $|T-T_c|$ for both $T>T_c$ and $T<T_c$. Here $T_c = T_{AB}$.

Table I lists our fitting results along with the I-Sm A transition temperature (T_{IA}) measured in the course of our experiment. We also list the parameter $r_{AB} = 1 - T_{AB}/T_{IA}$, which measures the relative size of the Sm A temperature range. The results indicate that while r_{AB} varies from 0.041 to 0.086, the critical exponent α stays fairly constant except for the compounds 46 and 45OBC, which have slightly smaller values of α ($\simeq 0.49$). In Fig. 3, we have plotted the critical parameters A^+/A^- and α vs r_{AB}. As the Sm A temperature range increases from 17 to 32 K, the ratio A^+/A^- remains reasonably constant within experimental error, and the critical exponent α seems to be unrelated to this increase. We do not know why the compounds 46 and 45OBC have slightly smaller values of α.

Guided by x-ray diffraction results[15] and the large value of the critical exponent α from our heat-capacity measurements[10] on the continuous Sm A-hexatic-B transition of 65OBC, Bruinsma and Aeppli[16] proposed a plausible explanation for the nature of the Sm A-hexatic-B transition in 65OBC. Based on the coupling between the bond-

TABLE I. The parameters obtained from heat-capacity measurements near the Sm A-hexatic-B transitions of various compounds.

Compound	T_{IA} (K)	T_{AB} (K)	$1-\frac{T_{AB}}{T_{IA}}$	α	A^+/A^-
45OBC	366.7	345.426 ±0.03	0.058	0.48 ±0.03	1.00 ±0.08
65OBC	358.2	340.441 ±0.03	0.050	0.60 ±0.03	0.85 ±0.08
75OBC	354.2	337.525 ±0.03	0.047	0.62 ±0.03	0.91 ±0.08
36OBC	380.2	348.540 ±0.03	0.083	0.58 ±0.03	0.93 ±0.08
46OBC	365.0	340.408 ±0.03	0.067	0.49 ±0.03	0.77 ±0.08
37OBC	375.4	344.141 ±0.03	0.083	0.56 ±0.03	0.78 ±0.08
2(10)OBC	381.6	367.414 ±0.03	0.037	0.67 ±0.03	0.90 ±0.08
3(10)OBC	372.3	340.387 ±0.03	0.086	0.59 ±0.03	0.71 ±0.08

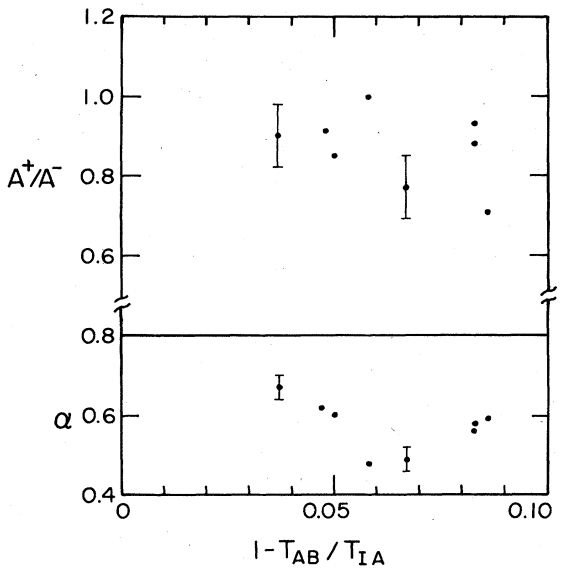

FIG. 3. Amplitude ratio A^+/A^- and critical exponent α vs $1-T_{AB}/T_{IA}$.

orientional order and the local herringbone order, their theory suggests that the Sm A–hexatic-B transition of 65OBC is near a fluctuation-induced tricritical point. In the case of 65OBC, the measured critical parameters are inconsistent with a Gaussian tricritical point. For 46 and 45OBC, although the exponents α^+ and α^- agree with those for a Gaussian tricritical point ($\alpha^+=\alpha^-=0.5$), the amplitude ratio (A^+/A^-) is still at variance with both a theoretical calculation[17] and experimental results on ^{3}He-^{4}He mixtures.[18] Nevertheless, a tricritical-point hypothesis could still be correct. For example, a tricritical point induced by fluctuations with cubic lattice symmetry has a different fixed point from the Gaussian tricritical point in renormalization-group parameter space.[19] Such a tricritical point may have different criticality (i.e., critical exponents and amplitude ratios) from that of the Gaussian tricritical point.

In summary, in contrast to the N–Sm A and Sm A-Sm C (or Sm C^*) transition, we have found that the critical exponent associated the heat-capacity anomaly of the Sm A–hexatic-B transition has a large value and remains fairly insensitive to the variation of the disordered-phase temperature range from 16 to 32 K. This result suggests two possible and different scenarios for this Sm A–hexatic-B transition. First, the ordering of the Sm A phase is well established above the Sm A–hexatic-B transition and the large critical exponent α is the intrinsic property of this kind of Sm A–hexatic-B transition. Further studies on compounds or mixtures with a small Sm A temperature range will shed some light on this conjecture. Second, even with a temperature range as wide as 32 K, the Sm A ordering is still not well established. If this is the case, one should study compounds or mixtures with a much wider Sm A temperature range.

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