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Critical fluctuations near the smectic-hexatic phase transition with anticlinic structure

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Layer compression modulus B measurements have been conducted near the transitions between smectic and hexatic phases with synclinic and anticlinic structures. In the synclinic structure, B shows no pretransitional softening near the phase transition. However, in the anticlinic structure, we observed evident critical softening of B near the smectic-hexatic phase transition. These results clearly reveal that the introduction of the in-plane hexatic order in the anticlinic structure is different from the usual smectic-hexatic phase transition.

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Liquid crystals are known as mesophases between solid and liquid. Among liquid crystals consisting of rodlike molecules, most simple nematic liquid crystals possess only long-range orientational order. Another type of liquid crystal is smectic liquid crystals that have a layer structure. Furthermore, there exist a variety of phases with different symmetries in smectic liquid crystals according to the interlayer and intralayer structures. Therefore, the smectic liquid crystal is a treasure house for research on phase transitions. Many physical phenomena appearing in liquid crystals have attracted much attention, particularly because of important analogies to other solid and liquid systems [1].

Layered liquid crystal systems often exhibit hexatic phases, which have at least quasi-long-range bond orientational order, but only short-range positional order. The bond order was first discussed in the film formation process due to evaporation by Landau and Lifshitz [2], and then in the melting process of two-dimensional systems by Halperin and Nelson [3]. Since Birgeneau and Litster [4] suggested the existence of the hexatic phase in liquid crystals, many phases have been assigned to be hexatic [5]. The molecules can be either perpendicular to the layers as in the smectic-hexatic-B (Hex-B) phase, or tilted with respect to the layer normal as in the smectic-hexatic-I (Sm-I) and smectic-hexatic-F (Sm-F) phases. The difference between the Sm-I and Sm-F phases is that the tilt direction is toward a nearest neighbor molecule in the Sm-I phase, and between two nearest neighbor molecules in the Sm-F phase [6]. Some liquid crystal materials exhibit a tilted hexatic Sm-I phase below the tilted smectic-C (Sm-C) phase. The difference between Sm-C and Sm-I is the magnitude of the bond order. At the phase transition from Sm-C to Sm-I, there is no change in the point group symmetry. As a result, the situation is qualitatively analogous to that of a liquid-gas transition in a simple fluid. In the case of phase transitions with no accompanying symmetry change there can be either a first-order transition or no transition, i.e., a continuous evolution from the Sm-C to the Sm-I phase. This implies that there should exist a critical point in the phase diagram [7–10]. The theory predicts that the Sm-C–Sm-I critical point belongs to a new universality class that includes the Sm-A_2 (bilayer phase)–Sm-A_d (partial bilayer phase) critical point [10]. The Sm-C–Sm-I critical point has, in fact, been discovered [11,12], attracting significant attention. However, the mechanical property of the Sm-C–Sm-I transition is a challenging problem that is still not well understood.

In 1989, Chandani *et al.* found antiferroelectricity in a tilted chiral smectic liquid crystal phase and designated this phase as Sm-C_A^*, where the tilting occurs in the same plane but in the opposite sense in adjacent layers [13]. The antiferroelecric hexatic smectic-I_A^* (Sm-I_A^*) phase can also occur below the Sm-C_A^* phase on cooling in some chiral liquid crystal materials [14–16]. Although the Sm-C–Sm-I (or Sm-C^*–Sm-I^*) transition has been intensively studied, less is known about the Sm-C_A^*–Sm-I_A^* transition. Of course, the layer compression modulus near the Sm-C_A^*–Sm-I_A^* transition has never been studied. X-ray diffraction and nuclear magnetic resonance measurements near the Sm-C_A^*–Sm-I_A^* transition indicate different behavior from that near the Sm-C^*–Sm-I^* phase transition, i.e., the layer thickness behavior and the magnitude of the bond orientational order [16]. Elastic constants are known to be more sensitive to fluctuations near the phase transition than other properties [17,18]. Therefore, measurements of the layer compression modulus are appropriate for studying the nature of the smectic-hexatic phase transition. In this paper we report that the phase transition behavior of the layer compression modulus near the Sm-C_A^*–Sm-I_A^* and Sm-C^*–Sm-I^* transitions is distinctly different between these two phase transitions.

The experiments were performed using the liquid cryst alline materials 4-(1-methylheptyloxycarbonyl) phenyl 4′-octylcarbonyloxybiphenyl-4-carboxylate (MHPOCBC) [6,19], 4-(1-trifluoromethylheptyloxycarbonyl) phe-nyl 4′ -nonylcarbonyloxybiphenyl-4-carboxylate (TFMHPNCBC) [16], and P-decyloxybenzylidene-P'-amino-2-methylbutyl cinnamate (DOBAMBC) [20]. For measuring the layer compression modulus B, we prepared homeotropically aligned cells. Using piezoelectric ceramics, the longitudinal mechanical transfer function was measured over a frequency range from 2 to 500 Hz. B was determined by extraporationg $B(\omega)$ to the value at $\omega=0$. Since there is essentially no frequency dependence of B (see the inset in Fig. 1), B is equivalent to the average B in the frequency range used. Our experimental setup is a modified version [18] of the original system developed by Cagnon and Durand [21].

Initially, we studied the Sm-C^*–Sm-I^* transition. Figure 1 shows the temperature dependence of B in DOBAMBC. It

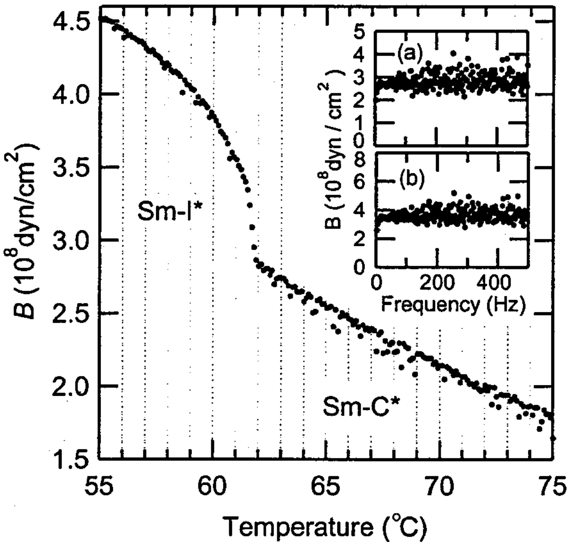

FIG. 1. Temperature dependence of *B* in DOBAMBC. The insets show the frequency dependence of *B* (a) in the Sm-C^* phase (63 °C) and (b) in the Sm-I^* phase (61 °C).

can be seen that *B* shows no pretransitional softening near the Sm-C^*–Sm-I^* transition. This result can be inferred from measurements of the angular dependence of the ultrasonic velocity and damping near the Sm-*A*–Hex-*B* and Sm-*C*–Sm-*F* transitions [22–24]. Our result directly confirms that *B* shows no pretransitional effect above the Sm-C^*-Sm-I^* transition. As shown in the insets of Fig. 1, no frequency dependence of *B* was observed over the range measured in every phase of every material used even in the close vicinity of the phase transition.

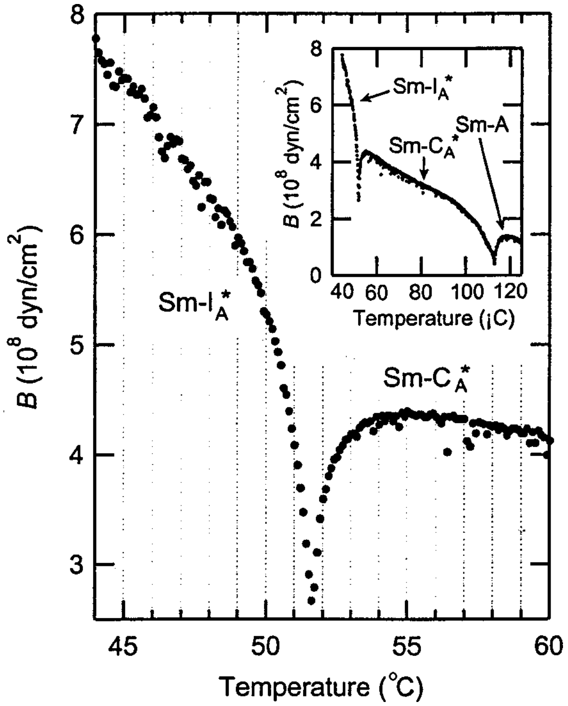

FIG. 2. Temperature dependence of *B* in TFMHPNCBC. The inset shows the temperature dependence of *B* over a much wider range.

In contrast, near the Sm-C_A^*–Sm-I_A^* transition, *B* exhibits unusual behavior. Figure 2 shows the temperature dependence of *B* in TFMHPNCBC for a narrow region in the vicinity of the Sm-C_A^*–Sm-I_A^* transition together with an inset showing *B* over a much wider range in temperature. Critical softening in *B* near the phase transition from Sm-C_A^* to Sm-I_A^* is clearly seen in this figure. This substantial pretransitional effect may reflect the fluctuations of the hexatic order parameter. This kind of pretransitional softening of *B* is usually observed near the Sm-*A*–Sm-C^* and Sm-*A*–Sm-C_A^* transitions [18]. However, critical softening of *B* has never been observed in phase transitions from a smectic phase to a hexatic phase, as already shown in Fig. 1.

Andereck and Swift (AS) introduced the free energy terms that couple the order parameter to the density variations (coupling constant γ_p) and to the layer spacing gradients (coupling constant γ_u). They predicted that the critical effects on velocity and damping can be extremery anisotropic, the degree of anisotropy depending on the γ_u/γ_p ratio [25]. Rogez *et al.* [22] measured the angular dependence of the ultrasonic velocity and damping in the MHz range near the Sm-*C*–Sm-*F* transition. They found that the anomalies in sound velocity and damping coefficient near the Sm-*C*–Sm-*F* transition are isotropic. They concluded from AS theory and experimental results that the absence of anisotropy near the Sm-*C*–Sm-*F* transition indicates that γ_u is null or very small compared to γ_p. Gallani *et al.* and Collin *et al.* [23,24] also measured the sound velocity and damping coefficient near the Sm-*A*–Hex-*B* transition and concluded from AS theory that $\gamma_u < \gamma_p$ in this case. In contrast, we observed critical softening of *B* near the Sm-C_A^*–Sm-I_A^* transition. This result clearly suggests that γ_p is small compared to γ_u. Our result for the Sm-C_A^*–Sm-I_A^* transition is completely different from the behavior of the usual smectic-hexatic phase transition [22–24], and is rather similar to the behavior of the untilted Sm-*A* to tilted smectic phase transition [18].

Figure 3 shows the temperature dependence of *B* in MHPOCBC for a narrow region in the vicinity of the Sm-C_A^*–Sm-I_A^* phase transition together with an inset showing *B* over a much wider range in temperature. Pretransitional behavior in *B* is again observed near the Sm-C_A^*–Sm-I_A^* transition, similar to that in TFMHPNCBC shown in Fig. 2. In the case of MHPOCBC, however, the pretransitional softening of *B* is not as prominent as that in TFMHPNCBC. This may be because the Sm-C_A^*–Sm-I_A^* transition is strongly first order in MHPOCBC, while it is weakly first order in TFMHPNCBC. In MHPOCBC, *B* steeply increases with decreasing temperature in Sm-I_A^*, and suddenly jumps without pretransitional behavior around 70 °C due to the Sm-I_A^*–crystal phase transition.

In this way, *B* shows unique behavior near the transition between smectic and hexatic phases with anticlinic structure. We shall discuss this in detail. The x-ray Laue patterns of the hexatic phases usually show a sixfold modulated diffuse pattern [6,26]. On the other hand, the anticlinic Sm-I_A^* phase barely shows a sixfold Laue pattern [16]. Neundorf *et al.*

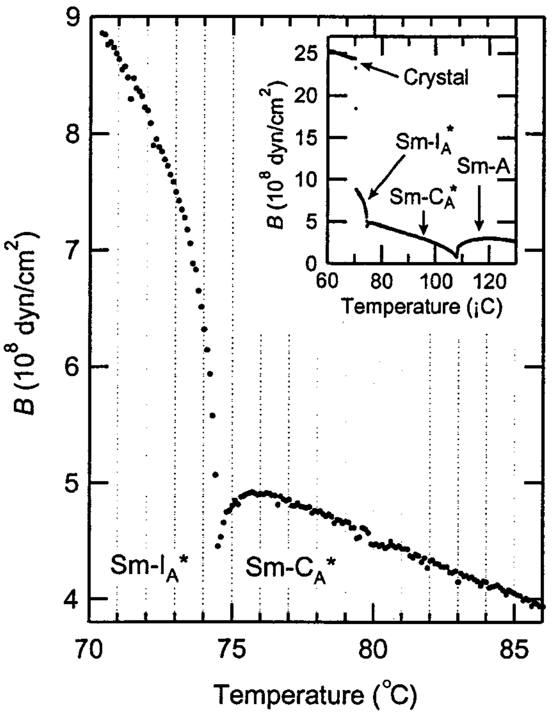

FIG. 3. Temperature dependence of B in MHPOCBC. The inset shows the temperature dependence of B over a much wider range.

reported that the Sm-I^* phase emerges below the Sm-I_A^* phase [15]. Therefore the Sm-I_A^* phase can be considered to be less ordered than the Sm-I^* phase. In the case of the Sm-C–Sm-F and Sm-A–Hex-B transitions, specific-heat measurements carried out in many compounds show unusually high specific-heat exponents [6]. Selinger has shown that these phase transitions occur in strongly fluctuating systems, and these fluctuations could lead to a frustration that is geometrical in origin and introduces a coupling between the hexatic order parameter and layer fluctuations if the hexatic stiffness constants are sufficiently large [27]. This coupling could explain the unusually high specific-heat exponent. As already mentioned, the Sm-I_A^* phase is a less ordered phase than the usual hexatic phases and is expected to be less stiff than typical hexatic phases. Therefore, according to the model by Selinger [27], a significant pretransitional effect should not appear near the transition to the less fluctuating Sm-I_A^* phase.

One plausible reason for the pretransitional softening of B is the anticlinic structure. In the synclinic structure, the hexatic order is introduced without reconstruction of the structure [28]. On the other hand, in the case of anticlinic structure, the introduction of the hexatic order is not the same as in the synclinic structure, but may require reconstruction of the structure. The reconstruction of the structure may induce strong fluctuations, which lead to a pretransitional softening of B. Actually, at the Sm-C to Sm-F or Sm-I transition, the layer thickness increases [28,29], which is explained by an increase in the orientational order of the alkyl chains [28]. On the other hand, at the Sm-C_A^* to Sm-I_A^* transition, the layer thickness increases at the phase transition and becomes even longer than that in the Sm-A phase [14,16]. Takanishi *et al.* [16] concluded from x-ray and NMR results that the main cause of the layer thickness increase is a change in molecular interdigitation, although the conformational change of the achiral chain may influence the pretransitional phenomenon of the appearance of hexatic ordering. This claim is consistent with the polarized Fourier-transform-IR results by Yin *et al.* [30]. In this way, the mechanism of the Sm-C_A^*–Sm-I_A^* transition is clearly different from that of the other smectic-hexatic phase transitions. The increase in hexatic order at the Sm-C_A^*–Sm-I_A^* phase transition is accompanied by a change in molecular interdigitation due to the intralayer molecular reorientation, which may lead to a large γ_u compared with γ_p and pretransitional softening of B above the phase transition.

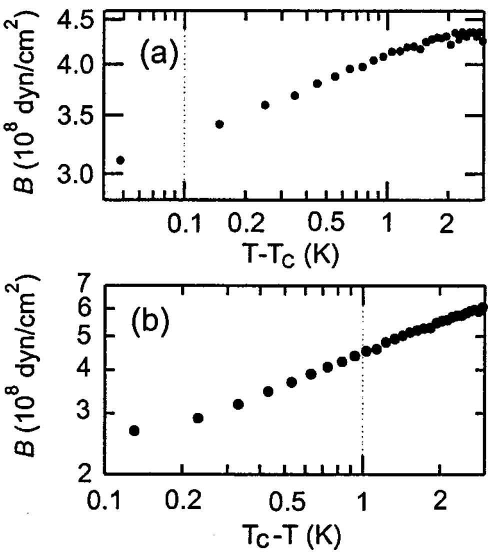

FIG. 4. Log-log plot of B in TFMHPNCBC as a function of $\Delta T = T - T_C$. (a) and (b) are for the high (Sm-C_A^*) and low (Sm-I_A^*) temperature sides, respectively.

Finally, we have to discuss the critical exponent of B near the phase transition. Fitting to a simple power law $B = B_0(T - T_C)^\nu$ or $B = B_0(T_C - T)^\nu$, respectively, for the high or low temperature side of the transition temperature was done by a least-mean-square method for an appropriate $\Delta T = T - T_C$ using T_C, ν, and B_0 as fitting parameters. Figure 4(a) shows log-log plots of B in the Sm-C_A^* phase of TFMHPNCBC as a function of $\Delta T = T\text{-}T_C$. The observed pretransitional softening of B can be represented by a simple power law $B = B_0(T - T_C)^\nu$. To our surprise, the critical exponent ν on the high temperature side has a very small value: $\nu = 0.09 \pm 0.01$ for $0.1 < \Delta T < 2$ K and $T_C = 51.75\,^\circ\text{C}$. There is no theory for the Sm-C_A^*–Sm-I_A^* phase transition. Prost *et al.* [31] measured the compressional modulus in the vicinity of the Sm-A_2–Sm-A_d critical point. They observed a critical vanishing of the elastic modulus with an exponent of about 0.4 ± 0.1. They claimed that the critical exponent appears to disagree with both mean-field and Ising predictions and favors the idea that the Sm-A_2–Sm-A_d critical point belongs to a different universality class, as predicted [10,32]. As already mentioned, theory predicted that the Sm-C–Sm-I critical point belongs to the same universality class as that for Sm-A_2–SmA_d. The critical exponent obtained in the Sm-C_A^*–Sm-I_A^* transition disagrees with any theoretical prediction and is quite different from the critical exponent of the Sm-A_2–Sm-A_d critical point. We also analyzed the data on the low temperature side of the Sm-C_A^*–Sm-I_A^* transition, by a simple power low $B = B_0(T_c - T)^{\nu}$ as shown in Fig. 4(b). The critical exponent obtained is $\nu = 0.31 \pm 0.02$ for $0.1 < \Delta T < 2$ K and $T_C = 51.76\,°\mathrm{C}$. ν is much larger than that of the high temperature side (0.09). These results are also distinctly different from that near the Sm-A_2–Sm-A_d critical point. In the vicinity of the Sm-A_2–Sm-A_d transition, the critical exponents of the low and high temperature sides are only slightly different; 0.42 for the low temperature side and 0.4 for the high temperature one [31]. In this way, the critical behavior of the Sm-C_A^*–Sm-I_A^* transition in TFMHPNCBC is wholly distinct from the former one.

To conclude, we reported B in the vicinity of the smectic-hexatic phase transitions of chiral smectic liquid crystals. We observed critical pretransitional behavior of B near the Sm-C_A^*–Sm-I_A^* transition, suggesting reconstruction of the structure. Thus the pretransitional softening of B was observed near the phase transition from smectic to hexatic phase with anticlinic molecular tilt, although no pretransitional softening occurs near the phase transition from the smectic to hexatic phase with synclinc molecular tilt. The critical softening of B can be represented by a simple power law on both sides of the transition temperature. The critical exponent ν is not in accordance with any theoretical prediction; ν on the high temperature side is very small compared with that of the Sm-A_2–Sm-A_d critical point and is several times smaller than ν on the low temperature side.

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