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Critical fluctuations at the untilted-tilted phase transition in chiral smectic liquid crystals

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The layer compression modulus B was measured near the Sm-A–Sm-C^* and Sm-A–Sm-C_A^* transitions of chiral smectic liquid crystals. B shows a marked pretransitional softening due to the order parameter fluctuations above the phase transition. The width of the critical region of the Sm-A–Sm-C^* and Sm-A–Sm-C_A^* transitions is smaller than that of the Sm-A–Sm-C_α^* transition. The critical exponents of B are in agreement with the theoretical description based on renormalization-group method. These results reveal that these transitions are not of the Landau mean-field type.

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de Gennes has proposed a simple model where the smectic-A (Sm-A)–smectic-C (Sm-C) and Sm-A–chiral smectic-C (Sm-C^*) phase transitions should be in the three-dimensional (3D) XY universality class ($d=3$, $n=2$) [1]. Contrary to the de Gennes proposal, a large amount of experimental results on the Sm-A–Sm-C^* (or C) transition show mean-field behavior and can be described by extended mean-field model including up to sixth-order terms in the tilt order parameters [2–6]. However, small deviations from a mean-field behavior have been generally observed in the close vicinity of the phase transition. There is room for argument on this point [7]. Actually, there are several examples in which the heat capacity shows Landau behavior [6,8], while the ultrasonic velocity shows non-Landau behavior [9,10]. Benguigui and Martinoty [11] tried to solve this issue using the Ginzburg criterion. They claimed that the critical region of the Sm-A–Sm-C transition is dependent on the physical properties studied, and they concluded that the ultrasonic velocity measurements, i.e., elastic constants, are more sensitive to fluctuation effects than the other measurements. Therefore, measurements of the layer compression modulus are appropriate for studying the pretransitional effect as a direct probe of the elastic constants. These measurements supply the key for clarifying whether or not the phase transition is of the Landau mean-field type. As mentioned above, a large number of investigations on the Sm-A–Sm-C^* transition have been perfomed, and have often suggested the mean-field behavior. However, little attention has been paid to study the direct transition from Sm-A to antiferroelectric chiral smectic-C_A^* (Sm-C_A^*) [12,13], which is characterized by an alternation of the direction of the average molecular orientation in the neighboring layers [14].

In this Rapid Communication, we present the results of layer compression modulus measurements near the Sm-A–Sm-C^* and Sm-A–Sm-C_A^* transitions. The experiments were performed on ferroelectric liquid crystals p-decyloxybenzylidene -p'-amino-2-methylbutyl cinnamate (DOBAMBC), S-4-O-(2-methyl) butyl-resorcylidene-4′-octylaniline (MBRA8) [15], and an antiferroelectric liquid crystal 4-(1-trifluoromethyl heptyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate (TFMHPOBC) [16]. DOBAMBC and MBRA8 are typical ferroelectric liquid crystal materials for which the results of specific-heat measurements are available [4,5]. The specific-heat measurements of both samples as well as x-ray and tilt angle measurements of DOBAMBC show Landau-type behavior.

For measuring the layer compression modulus B, we prepared homeotropically aligned cells consisting of two glass plates treated with a surfactant, as previously reported [17]. The sample thickness ranged from 50 to 100 μm. Using piezoelectric ceramics, the longituidinal mechanical transfer function $Z(\omega)$ was measured over a frequency range from 2 to 500 Hz. B was almost independent of frequency in this range, as was also observed in other materials [17,18]. $Z(\omega)$ is defined as the ratio of the complex stress experienced by a receiving glass plate to the complex longitudinal strain of a driving glass plate. Based on continuum theory, $Z(\omega)$ can be expressed as $Z(\omega)=B+i\omega(\eta_1-\eta_2+\eta_4+2\eta_5)$ [19], where η_1, η_2, η_4, and η_5 are the Martin-Parodi-Pershan viscosity coefficients [20].

Initially, we studied the Sm-A–Sm-C^* transition. Figures 1 and 2 show the temperature dependence of B in DOBAMBC and MBRA8, respectively. B shows critical softening near the phase transition from Sm-A to Sm-C^*. This substantial pretransitional effect appears from about 6–8 K above the phase transition. These observations can be explained by considering the model proposed by Andereck and Swift (AS). They introduced terms to the free energy that couple the order parameter fluctuations with density variation and layer spacing gradient [21]. From this, AS predicted that the critical behaviors of velocity and attenuation could be extremely anisotropic. Collin *et al.* [9] measured the angular dependence of the ultrasonic velocity and attenuation in the MHz range near the Sm-A–Sm-C transition and found that the anomaly in sound velocity and attenuation coefficient near the Sm-A–Sm-C transition is strongly anisotropic. From this, they inferred a sharp decrease of B toward the phase transition. They also concluded from the fluctuation theory of AS that the Sm-A–Sm-C transition is not of the mean-field type [9]. Our results directly show this sharp critical softening of B and are accounted for by the AS theory, which implies that the critical softening of B is caused by the order parameter fluctuations. In this way, we have observed significant pretransitional fluctuations above the phase transition, which suggests that the Sm-A–Sm-C^*

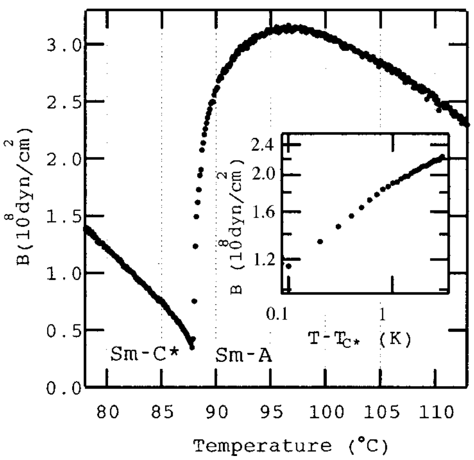

FIG. 1. Temperature dependence of B in DOBAMBC. The inset shows the log-log plot of B in the Sm-*A* phase of DOMAMBC against $\Delta T = T\text{-}T_C^*$.

transition is not of the Landau type. We shall discuss the critical exponents near the phase transition later.

Next we studied the Sm-*A*–Sm-C_A^* transition. The tilt angle measurements of the Sm-*A*–Sm-C_A^* transition can be interpreted by a mean-field behavior [12], as is usually observed for the Sm-*A*–Sm-C^* transition [5]. On the other hand, our result suggests the opposite case. Figure 3 shows the temperature dependence of B in TFMHPOBC. Critical softening of B is evident near the Sm-*A*–Sm-C_A^* transition, as observed at the Sm-*A*–Sm-C^* in DOBAMBC and MBRA8. This substantial pretransitional effect reflects the order parameter fluctuations. These results suggest that the Sm-*A*–Sm-C_A^* transition is not of the Landau type.

In order to evaluate the width of the critical region associated with the phase transition into the tilted phase, the temperature dependences of normalized layer compression modulus B' at the Sm-*A*–Sm-C^* in DOBAMBC (circles), at the Sm-*A*–Sm-C_A^* in TFMHPOBC (squares), and at the Sm-*A*–Sm-C_α^* in 4-(1-methylheptyloxycarbonyl) phenyl 4L-octylbiphenyl-4-carboxylate (MHPBC) [22](solid line) are presented in Fig. 4. The Sm-C_α^* phase is a tilted smectic phase just below the Sm-*A* phase and the tilt angle is small [14]. The normalized B' is determined by dividing B by B_{Max}, i.e., $B' = B/B_{Max}$, where B_{Max} is the maximum value of B in the Sm-*A* phase. The width of the critical region of B' is observed to increase in the order of TFMHPOBC, DOBAMBC, and MHPBC.

Recently, Skarabot *et al.* presented the results of high-resolution birefringence measurements on chiral tilted smectic liquid crystals [13]. They observed critical pretransitional suppression of birefringence due to order parameter fluctuation near the phase transition. The magnitude of the fluctuation is small in the vicinity of the Sm-*A*–Sm-C^* transition. In contrast, near the Sm-*A*–Sm-C_α^* transition, the fluctuation is significant. These results are consistent with our observations that Sm-*A*–Sm-C^* , Sm-*A*–Sm-C_α^* transitions are not of the mean-field behavior and the width of the critical region of the Sm-*A*–Sm-C_α^* transition is larger than that of the Sm-*A*–Sm-C^* transition.

The recent observation by Ema and Yao of the heat capacity anomaly of MHPBC at the Sm-*A*–Sm-C_α^* transition shows a clear deviation from Landau behavior [23]. Their specific-heat results also support our elastic constant result. They observed excess heat capacity from about 2 K above the phase transition. In contrast, we observed substantial pre-

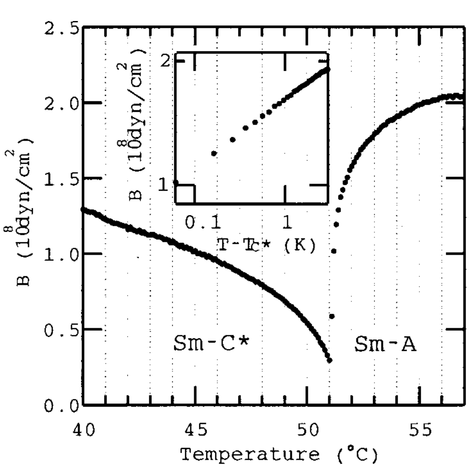

FIG. 2. Temperature dependence of B in MBRA8. The inset shows the log-log plot of B in the Sm-*A* phase of MBRA8 against $\Delta T = T\text{-}T_C^*$.

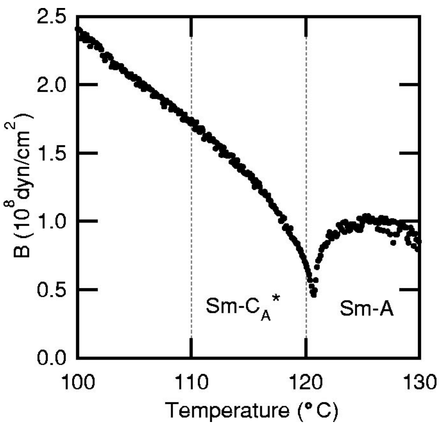

FIG. 3. Temperature dependence of B in TFMHPOBC.

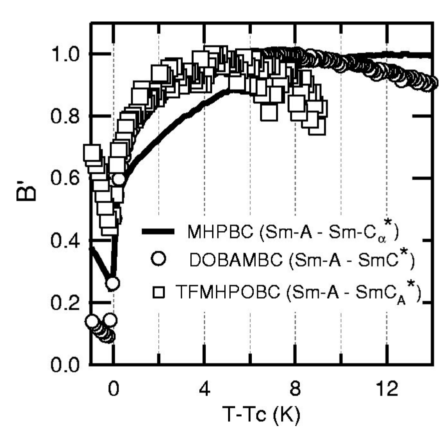

FIG. 4. Temperature dependence of the normalized layer compression modulus B' at the Sm-*A*–Sm-C^* transition in DOBAMBC (circles), at the Sm-*A*–Sm-C_A^* transition in TFMHPOBC (squares), and at the Sm-*A*–Sm-C_α^* transition in MHPBC (solid line).

TABLE I. Critical exponent ν and other adjustable parameters obtained by least-squares fitting in reduced temperature range of t above T_C^*.

System	t	B_0 (10^8 dyn/cm^2)	T_C^*	ν
DOBAMBC	0.003	1.91	91.91	0.208
	0.01	1.89	91.96	0.156
MBRA8	0.003	1.62	51.14	0.166
	0.01	1.62	51.15	0.158
MBOBB* (Ref. [17])	≃0.01			0.15
6OBPy8 (Ref. [17])	≃0.01			0.16
MHPBC (Ref. [18])	0.003	1.49	75.70	0.124
	0.01	1.43	75.48	0.189

transitional effects from about 10 K above the phase transition. Using the Ginzburg criterion, Benguigui and Martinoty demonstrated that the width of the critical region of the Sm-*A*–Sm-*C* transition is dependent on the physical quantity considered, i.e., the deviation from the Landau model, which occurs in the close vicinity of the Sm-*A*–Sm-*C* transition when specific heat is concerned, may be observable far from the phase transition temperature in elastic measurements. The comparison of the results of the specific heat and the layer compression modulus measurements of MHPBC clearly shows that the critical region of the Sm-*A*–Sm-C_α^* transition is dependent on the observable properties studied. These results provide clear evidence in support of the claim that the elastic constants are very sensitive to the pretransitional fluctuations in tilted smectics [11].

From the consideration of these results one may say that, in the case of the Sm-*A*–Sm-C_α^* transition, the width of the critical region is so large and fluctuations are so significant that layer compression modulus and high-resolution birefringence measurements show stronger deviation from Landau behavior than those observed for the Sm-*A*–Sm-*C**, and Sm-*A*–Sm-C_A^* transitions. A deviation from Landau behavior can also be observed in specific-heat measurements. In the case of the Sm-*A*–Sm-*C** and Sm-*A*–Sm-C_A^* transitions, the width of the critical region is relatively small and fluctuations are not significant, so that layer compression modulus and high-resolution birefringence measurements indicate a deviation from Landau behavior in the smaller temperature range than that in the Sm-*A*–Sm-C_α^* transition, and specific-heat measurements cannot detect the critical flctuations and show the Landau mean-field behavior. It seems reasonable to conclude that all the Sm-*A*–Sm-*C**, Sm-*A*–Sm-C_A^*, and Sm-*A*–Sm-C_α^* transitions are not of the Landau mean-field type.

Finally, we have to discuss the critical exponents of *B* near the phase transitions. The insets of Figs. 1 and 2 show the log-log plot of *B* in the Sm-*A* phase of DOBAMBC and MBRA8, respectively, against $\Delta T = T\text{-}T_C^*$, where T_C^* is the transition temperature. The observed pretransitional softening of *B* can be represented by a simple power law $B = B_0(T - T_C^*)^\nu$. Table I shows the critical exponent ν, which was determined by least-squares fitting within the temperature range of $t = (T\text{-}T_C^*)/T_C^*$ from the transition point. Other adjustable parameters are also listed in Table I. To compare these results with other materials, we also present the results of MBOBB* near the Sm-*A*–Sm-*C**, 6OBPy8 near the Sm-*A*–Sm-*C* [17], and MHPBC near the Sm-*A*–Sm-C_α^* phase transitions [18]. These critical exponents ν are extremely small; they are smaller than those of the Sm-*A*–nematic phase transition (0.3-0.6) [24]. According to the theoretical calculation based on renormalization-group approach by Kats and Levedev, this exponent ν should be 1/8 for $K_1 = K_2$, and 1/14 for $K_1 \gg K_2$ or $K_1 \ll K_2$ in the vicinity of T_{AC}, where K_1 and K_2 are the Frank elastic constants [25]. It is useful to comment on the results of the Sm-*A*–Sm-C_α^* transition for discussing the Sm-*A*–Sm-*C** transition. The specific-heat results near the Sm-*A*–Sm-C_α^* transition show a crossover from 3D *XY* critical to tricritical behavior [23]. It is seen in Table I that the critical exponent ν of *B* depends on the fitting range, which may be accounted for by the crossover behavior [18]. In the close vicinity of the the Sm-*A*–Sm-C_α^* transition, ν in MHPBC seems to be in good agreement with the theoretical prediction by Kats and Lebedev [25]. In contrast to this behavior in the Sm-*A*–Sm-C_α^* transition, ν is independent of the fitting range in the Sm-*A*–Sm-*C** transition of MBRA8, as shown in Table I. This behavior is also seen in the inset of Fig. 2, where the inclination of the line has no change in this temperature range. These features have been observed in MBOBB* and 6OBPy8, i.e., the critical exponents ν of *B* are 0.15–0.16 for 0.01 K$<\Delta T<$3 K [17]. As we have seen, ν in many smectic liquid crystals near the Sm-*A*–Sm-*C** is about 0.15–0.16 and slightly larger than that of MHPBC near the Sm-*A*–Sm-C_α^*. The difference between ν of *B* near the Sm-*A*–Sm-*C** and that near the Sm-*A*–Sm-C_α^* could be explained by much larger fluctuation effects near the Sm-*A*–Sm-C_α^* transition.

In the close vicinity of the Sm-*A*–Sm-*C** transition, ν of *B* in DOBAMBC is somewhat larger than those of the MBRA8, MBOBB*, and 6OBPy8. Also, ν in DOBAMBC depends on the fitting range, as shown in Table I. This behavior is clearly seen in the inset of Fig. 1, where an inflection point appears around 1 K above the transition temperature. We cannot say whether this behavior is a characteristic feature of DOBAMBC or not. It may be worth mentioning that the coefficients of Landau free energy obtained by heat-capacity studies between MBRA8 and DOBAMBC show much difference [4].

In this way, we obtain the experimental results that are nearly in accordance with the model by Kats and Lebedev [25]. However, we must draw attention to the problems mentioned below. ν of *B* near the Sm-*A*–Sm-*C** as well as near the Sm-*A*–Sm-C_α^* transitions rather favors the case for $K_1 = K_2$, even though $K_1 \neq K_2$ actually. In addition, Kats and Lebedev claimed that this model is valid for a reduced temperature range *t* of less than 0.001. However, the change has never been observed in the vicinity of this reduced temperature range. We cannot define the applicabile temperature range of this model exactly by our limited results, though we believe that it is possible to apply this model to our results. Moreover, the critical exponent of *B* is expected to be equal to the negative of the specific-heat capacity critical exponent [25]. Contrary to our results, however, the results of the specific-heat on the Sm-*A*–Sm-*C** transition can be described by the extended Landau theory and are incompatible with the prediction by Kats and Lebedev. The modified model to clarify these questions is needed.

In summary, we report the critical pretransitional behavior of B in the Sm-A phase of several chiral smectic liquid crystals, which indicates significant order parameter fluctuations. Critical regions associated with the untilted-tilted phase transition are dependent on the type of the phase transition, i.e., critical pretransitional effect in the Sm-A–Sm-C_α^* transition is more significant than that of the Sm-A–Sm-C_A^*, and Sm-A–Sm-C^*. The pretransitional softening of B can be represented by a simple power law. The critical exponent ν of B near the Sm-A–Sm-C^* transition are slightly larger than that of the Sm-A–Sm-C_α^* transition, and are nearly in accordance with the theoretical prediction investigated by the renormalization-group method. These results exhibit that the phase transition from the untilted Sm-A to a tilted smectic phase seems not to belong to a single universality class. Also, critical region is dependent on the physical quantity and elastic constants are more sensitive to fluctuations than the other one.

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[1] P. G. de Gennes, Mol. Cryst. Liq. Cryst. **21**, 49 (1973).
[2] C. C. Huang and J. M. Viner, Phys. Rev. A **25**, 3385 (1982).
[3] R. J. Birgeneau, C. W. Garland, A. R. Kortan, J. D. Litster, M. Meichle, B. M. Ocko, C. Rosenblatt, L. J. Yu, and J. Goodby, Phys. Rev. A **27**, 1251 (1983).
[4] S. C. Lien, C. C. Huang, T. Carlsson, I. Dahl, and S. T. Lagerwall, Mol. Cryst. Liq. Cryst. **108**, 149 (1984).
[5] S. D. Dumrongrattana, C. C. Huang, G. Nounesis, S. C. Lien, and J. M. Viner, Phys. Rev. A **34**, 5010 (1986).
[6] P. Das, K. Ema, and C. W. Garland, Liq. Cryst. **4**, 205 (1989).
[7] Y. Galerne, J. Phys. (Paris) **46**, 733 (1985).
[8] C. A. Schanz and D. L. Johnson, Phys. Rev. A **17**, 1504 (1978).
[9] D. Collin, J. L. Gallani, and P. Martinoty, Phys. Rev. Lett. **61**, 102 (1988).
[10] D. Collin, S. Moyses, M. E. Neubert, and P. Martinoty, Phys. Rev. Lett. **73**, 983 (1994).
[11] L. Benguigui and P. Martinoty, Phys. Rev. Lett. **63**, 774 (1989); J. Phys. II **7**, 225 (1997).
[12] F. Beaubois, V. Faye, J. P. Marcerou, H. T. Nguyen, and J. C. Rouillon, Liq. Cryst. **26**, 1351 (1999).
[13] M. Skarabot, K. Kocevar, R. Blinc, G. Heppke, and I. Musevic, Phys. Rev. E **59**, R1323 (1999).
[14] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, and H. Takezoe, J. Mater. Chem. **4**, 997 (1994).
[15] K. Skarp, K. Flatischler, K. Kondo, Y. Sako, K. Miyasato, H. Takezoe, A. Fukuda, and E. Kuze, Jpn. J. Appl. Phys. **22**, 566 (1983).
[16] Y. Suzuki, T. Hagiwara, I. Kawamura, N. Okamura, T. Kitazume, M. Kakimoto, Y. Imai, Y. Ouchi, H. Takezoe, and A. Fukuda, Liq. Cryst. **6**, 167 (1989).
[17] J. Yamamoto and K. Okano, Jpn. J. Appl. Phys., Part 1 **30**, 754 (1991).
[18] S. Shibahara, J. Yamamoto, Y. Takanishi, K. Ishikawa, H. Takezoe, and H. Tanaka, Phys. Rev. Lett. **85**, 1670 (2000).
[19] K. Okano and J. Yamamoto, Jpn. J. Appl. Phys., Part 1 **29**, 1149 (1990).
[20] P. C. Martin, O. Parodi, and P. S. Pershan, Phys. Rev. A **6**, 2401 (1972).
[21] B. S. Andereck and J. Swift, Phys. Rev. A **25**, 1084 (1982).
[22] N. Okabe, Y. Suzuki, I. Kawamura, T. Isozaki, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys., Part 1 **29**, 131 (1992).
[23] K. Ema and H. Yao, Phys. Rev. E **57**, 6677 (1998).
[24] M. Benzekri, J. P. Marcerou, H. T. Nguyen, and J. C. Rouillon, Phys. Rev. A **41**, 9032 (1990).
[25] E. I. Kats and V. V. Lebedev, Zh. Éksp. Teor. Fiz. **90**, 111 (1986) [Sov. Phys. JETP **63**, 63 (1986)].