RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 27, NUMBER 2 FEBRUARY 1983

Smectic-A –smectic-C transition: Mean field or critical

R. J. Birgeneau
Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

C. W. Garland
Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

A. R. Kortan and J. D. Litster
Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

M. Meichle
Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

B. M. Ocko
Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

C. Rosenblatt
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

L. J. Yu
Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

J. Goodby
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 12 August 1982)

We have carried out a detailed study of the smectic-A –smectic-C transition in butyloxybenzylidene heptylaniline (40.7) using high-resolution x-ray, heat-capacity, and light scattering techniques. Although the order-parameter data are consistent with heliumlike critical behavior, the data as a whole are uniquely described by a mean-field Landau model with an anomalously large sixth-order term.

Smectic-A and smectic-C liquid crystals may be simply described as orientationally ordered fluids with one-dimensional mass density waves.[1] The density wave may be either along (smectic-A) or at an angle (smectic-C) to the unique orientational axis. Many liquid crystals exhibit second-order transitions with decreasing temperature between the smectic-A and the smectic-C phases.[2] De Gennes[1] has proposed a simple model which places this transition in the universality class of superfluid helium, that is, $d=3$, $n=2$. Safinya *et al.*,[2] however, using a Landau-Ginzburg model, have argued that the bare length characterizing the tilt fluctuations is generally large so that the true critical region should be unobservably small. Huang and Viner[3] also favor the mean-field model; however, they have made the important additional observation that, in order to understand the heat-capacity anomaly associated with the A-C transition, one must postulate the existence of unusually large higher-order terms in a Landau free-energy expansion.

In a recent paper Galerne[4] has argued quite differently. He has found that over the reduced temperature range $5\times10^{-5} < 1-(T/T_c) < 5\times10^{-3}$, the tilt in the C phase of azoxy-4, 4′-di-undecyl-α-methylcinnamate (AMC-11) is well described by a power-law singularity with $\beta=0.36\pm0.005$; that is, this system apparently exhibits heliumlike critical behavior. Further, he has argued that the bare length is anomalously small. Although the Landau-Ginsburg model of Safinya *et al.*[2] certainly allows for exceptions, one must address carefully the question of uniqueness of power-law fits in particular systems. In some initial measurements of the tilt order parameter in butyloxybenzylidene heptylaniline (40.7), behavior very close to that observed by Galerne[4] in AMC-11 was found. We therefore decided to examine this A-C transition in much more detail using a variety of experimental techniques in order to ascertain if 40.7 also exhibits true critical rather than mean-field behavior over the 10^{-2} to 10^{-5} reduced temperature range. We report the results of this study in this paper. New heat-capacity data on AMC-11 together with a reanalysis of Galerne's order-parameter data are also presented.

Before presenting our experimental results we first review the predictions of the critical behavior and mean-field models. For $d=3$, $n=2$ one expects power-law behavior in reduced temperature $\tau = T/T_c - 1$. In particular, the order parameter $\phi \sim |\tau|^{\beta}$ with $\beta = 0.35$, heat capacity $C \sim |\tau|^{-\alpha}$ with $\alpha = -0.02$, susceptibility $\chi \sim \chi_0 |\tau|^{-\gamma}$ with $\gamma = 1.32$, and correlation length $\xi = \xi_0 |\tau|^{-\nu}$ with $\nu = 0.67$. Further, for these exponents to be observable, the bare length ξ_0 must be of the order of the interparticle spacing.

For the Landau-Ginzburg model, the free energy is given by

$$F = a\tau\phi^2 + b\phi^4 + c\phi^6 + \cdots + \frac{1}{2M_{\parallel}}|\nabla_{\parallel}\phi|^2 + \frac{1}{2M_{\perp}}|\nabla_{\perp}\phi|^2 + \cdots \quad . \tag{1}$$

With $t_0 = b^2/ac$, standard calculations yield

$$\phi = (b/3c)^{1/2}[(1-3\tau/t_0)^{1/2} - 1]^{1/2} \tag{2}$$

$$C = \begin{cases} 0 & \text{if } \tau > 0 \\ (a^2T/2bT_c^2)(1-3\tau/t_0)^{-1/2} & \text{if } \tau < 0 \ , \end{cases} \tag{3}$$

as well as $\chi = 1/2a\tau$ for $\tau > 0$, and $\xi_{\parallel,\perp} = (2aM_{\parallel,\perp}\tau)^{-1/2}$ for $\tau > 0$.

We now discuss the experimental results. Measurements were performed on material synthesized by CPAC-Organix and by one of us (J.G). The latter samples tended to have a wider C range. The x-ray experiments were carried out using techniques identical to those discussed in Ref. 2. The essential feature of the experiment is that by holding the director fixed with a field of 4 kG, the SmA Bragg peak evolves into a ring of scattering in the SmC phase. Azimuthal scans through the ring yield the tilt angle while longitudinal scans give the lattice constant d_c. The results obtained for a Goodby sample are shown in Fig. 1(a). Note that ϕ measured directly and deduced from a simple model with rigid rod molecules through $d_c(T) = d_A \cos[\phi(T)]$ agree absolutely. At $T_c - T = 0.9$ K there is a strong first-order transition into a crystalline-B phase.

The heat capacity was measured with an ac

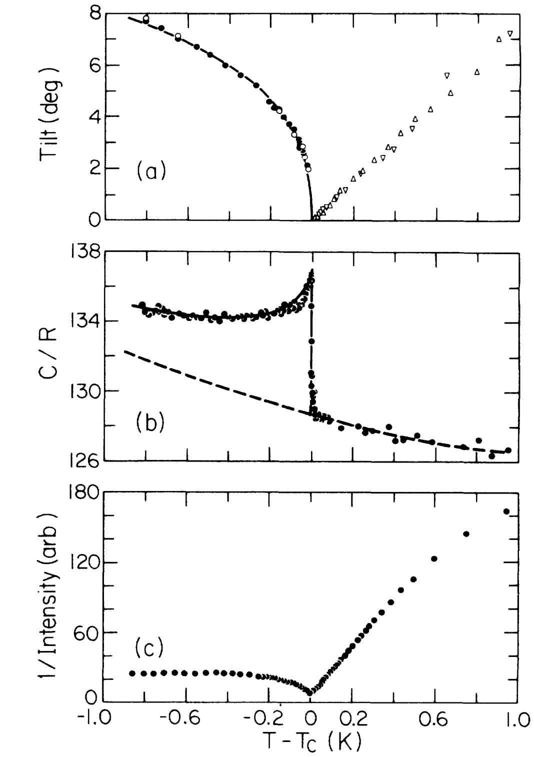

FIG. 1. (a) Tilt angle (solid circles) and $\cos^{-1}(d_c/d_A)$ in 40.7 (open circles). The solid line is a fit to Eq. (2) with $t_0 = 1.3 \times 10^{-3}$; T_c for this sample is 49.69 °C. The triangles are the reciprocal of the susceptibility (arbitrary units) measured by magnetic birefringence for two different samples. (b) Heat capacity near the A-C transition in 40.7. The dashed curve is the background scaled from 40.8, and the solid line is the Landau fit discussed in the text. $T_c = 49.96$ °C. (c) Inverse of the light scattering intensity from tilt fluctuations in 40.7. For this sample $q = q_z = 7.0 \times 10^4$ cm^{-1} and $T_c = 50.36$ °C.

calorimeter technique which has been described elsewhere[5]; the absolute accuracy is better than 20%. We show in Fig. 1(b) the specific heat of 40.7 in the immediate neighborhood of the A-C transition. In the measurements, no phase shift was detected between the input heater power and the sample temperature response, providing strong evidence that there was no coexistence of two phases, and hence the transition is second order. We note qualitatively that the heat capacity shows a sharp jump at T_c, indicative of mean-field behavior. The behavior below T_c is, however, anomalous. We shall present quantitative fits to these data below.

From light scattering it is possible to obtain both the tilt susceptibility and the tilt correlation lengths.[1,6] The light scattering was performed on a planar aligned sample, 50 μm thick, between Corning 7059 glass slides with 3000-Å period surface relief gratings. The laser wavelength was 6328 Å and the power about 1 mW. The geometry of the beam was chosen such that the inverse scattering intensity was given by

$$I^{-1}=\frac{\tau^{\gamma}}{\epsilon_a^2 kT\chi_0}+\frac{(\xi_\perp^0 q_x)^2+(\xi_\parallel^0 q_z)^2}{\epsilon_a^2 kT_0\chi_0}\ , \quad (4)$$

where we have assumed $\gamma=2\nu$. The results for a scattering geometry with $q_x=0$ are shown in Fig. 1(c). In addition, we show in Fig. 1(a) results for the susceptibility obtained using a magnetically induced birefringence technique.[7]

We now discuss the combined results shown in Fig. 1 in the context of the mean-field and critical models. A fit of the order-parameter data to the power-law form yields $\beta=0.377\pm0.01$, in reasonable agreement with the helium value 0.35 and with Galerne's AMC-11 value of 0.36 ± 0.005. The data, however, are equally well described by the mean-field form, Eq. (2), with a crossover temperature t_0 in the range of 1×10^{-3} to 2×10^{-3}. It is evident from Fig. 1 that the specific-heat results are incompatible with a power-law description. Therefore this cannot be a conventional critical transition. Attempts to fit the data to the mean-field form, Eq. (3), are complicated by a strong background variation associated with precursor effects near the transition into the crystalline-*B* phase. Such precursor effects have been observed in 40.8, and a scaled version of the 40.8 behavior can be used as the background variation in 40.7.[8] The resulting fit shown in Fig. 1(b) was then obtained using Eq. (3) with $a^2/2bT_c=7.7R_0$ and $t_0=1.3\times10^{-3}$; see Ref. 8(b) for further details. The result of fitting the order-parameter data using Eq. (2) with the same t_0 value is shown by the solid line in Fig. 1(a).

Clearly, the mean-field form with the crossover temperature of $t_0=1.3\times10^{-3}$ works well for both the order parameter and the heat capacity. The order-parameter and specific-heat data are consistent with a mean-field description containing an unusually large sixth-order term, but one cannot claim uniqueness based on these data alone.

In mean-field theory, the susceptibility and correlation lengths above T_c do not depend on the relative magnitudes of the fourth- and sixth-order terms. Thus measurements of these quantities can choose uniquely between the two descriptions. It is evident from Fig. 1(a) that $1/\chi$ indeed varies linearly with $T-T_c$. A least-squares fit of the power-law form yields $\gamma=0.98\pm0.04$ in agreement wtih the mean-field value $\gamma=1$ and excluding the $d=3$, $n=2$ value $\gamma=1.32$. From Fig. 1(c) and Eq. (4) we conclude that the light scattering data are also consistent with $\gamma=1$. The deviation from linearity for $T-T_c>0.5$ K is due to extra background scattering which has not been corrected for. Using Eq. (4) it is also possible to extract the bare lengths $\xi_\parallel^0$ and $\xi_\perp^0$ from the data. This gives $\xi_\parallel^0=20.4\pm0.7$ Å with a comparable, but less accurately determined, value for $\xi_\perp^0$. As discussed by Safinya *et al.*,[2] a bare length of this size implies a critical region inside of 10^{-5}. Thus the mean-field behavior we observe is necessitated by the Ginzburg criterion.

Clearly, it is now important to reexamine the situation in AMC-11. We show in Fig. 2(b) new heat-capacity measurements near the *A*-*C* transition in AMC-11. Again one obtains a mean-field-like jump. We have fitted these data to Eq. (3) together with a linear background. The free parameters in the fit were the background magnitude and slope, a^2/b and t_0. We show in Fig. 2(b) the results of the best fit with $t_0=1.7\times10^{-3}$; clearly the fit is very good. We show in Fig. 2(a) the results of a fit of the order-parameter data[4] to Eq. (2) with t_0 fixed at the value determined above and with T_c and $a/2b$ as adjustable parameters. Again, this gives a good description although there are subtle systematic deviations. A value of t_0 approximately a factor of 2 smaller gives results indistinguishable from the power-law fit. We believe that this discrepancy is within the overall uncertainties in both measurements. Measurements by Delaye and Keller[9] in the nematic phase also favor mean-field behavior. We conclude that AMC-11 is better described by mean-field theory with a large sixth-order term than by the helium critical model.

We list in Table I the heat-capacity jumps and crossover temperatures at the *A*-*C* transitions for ma-

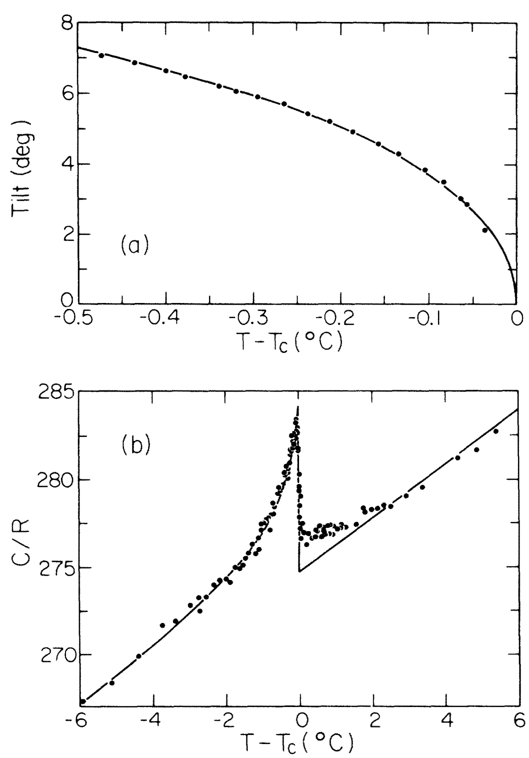

FIG. 2. (a) Order parameter for AMC-11 from Ref. 4. The solid line is a fit to Eq. (2) with $t_0=1.7\times10^{-3}$. (b) Heat capacity of AMC-11. The solid line is a fit to Eq. (3), as discussed in the text, with $t_0=1.7\times10^{-3}$.

TABLE I. Heat-capacity jump and crossover temperatures at the A-C transition.

Material	$\Delta C = \frac{a^2}{2bT_c}$ (R_0 units)	$t_0 = \frac{b^2}{ac}$ (units of 10^{-3})
$\overline{8}S5$[a]	5	6.5
2M4P90BC[b]	16	5.5
AMC-11	10	1.7
40.7	8	1.3

[a]Reference 2 and C. A. Shantz and D. L. Johnson, Phys. Rev. A 17, 1504 (1978).
[b]Reference 3.

terials which have been studied in some detail. Since a scales with $k_B T_c$, it should vary by less than 10% for the different materials. It is evident from the ΔC data that the fourth-order coefficient b shows no systematic trend. Further, the heat-capacity jump itself at the A-C transition is relatively small. Thus there is no evidence that b is unusually small, say, because of coupling to another order parameter.[10] Rather, the early crossover from the usual mean-field behavior seen in many other transitions such as ferroelectrics and superconductivity seems to be caused by an anomalously large sixth-order term c in the Landau free energy. This means physically that the liquid crystal resists large tilt fluctuations. It might be noted that in 40.7 at the crossover temperature $t_0 = 1.3 \times 10^{-3}$ the tilt is 6°. This corresponds to a relative displacement of the molecules of only 0.5 Å. We do not have a reasonable physical explanation for the appearance of saturation effects at such small displacements.

In conclusion, we find that in 40.7, even though the order-parameter behavior is consistent with true helium critical behavior over the reduced temperature range $3 \times 10^{-3} > \tau > 5 \times 10^{-5}$, the data as a whole are uniquely described by a mean-field model with an unusually large sixth-order term. The measured bare length is consistent with this result. Further, we find that the available data on AMC-11 are also consistent with mean-field behavior. We conclude therefore that in the vast majority of cases,[11] although de Gennes's original helium model may be correct, the true critical region is inaccessible by current experimental techniques. Further, the model of Safinya *et al.*[2] satisfactorily accounts for this narrow critical region.

We should like to thank D. L. Johnson and C. C. Huang for helpful discussions. The work at MIT was supported by the National Science Foundation under Grants No. DMR78-24185 and No. DMR78-23555 and by the Joint Services Electronics Program No. DAAG-29-80-C-0104. The Francis Bitter National Magnet Laboratory is supported by the National Science Foundation.

[1]P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974); J. D. Litster and R. J. Birgeneau, Phys. Today 35, 26 (1982).

[2]C. R. Safinya, M. Kaplan, J. Als-Nielsen, R. J. Birgeneau, D. Davidov, J. D. Litster, D. L. Johnson, and M. Neubert, Phys. Rev. B 21, 4149 (1980), and references therein.

[3]C. C. Huang and J. M. Viner, Phys. Rev. A 25, 3385 (1982); C. C. Huang and S. C. Lien, Phys. Rev. Lett. 47, 1917 (1981). In the latter paper these authors use the mean-field model discussed here to describe the tilt in the immediate vicinity of an nematic–smectic-A–smectic-C (NAC) multicritical point. Since the tilt may be described as the transverse gradient of the order parameter and the order parameter shows true critical behavior at the NAC point, a mean-field model would seem to be inappropriate.

[4]Y. Galerne, Phys. Rev. A 24, 2284 (1981).

[5]G. B. Kasting, K. J. Lushington, and C. W. Garland, Phys. Rev. B 22, 321 (1980).

[6]P. G. de Gennes, C. R. Acad. Sci. Ser. B 274, 758 (1972).

[7]C. Rosenblatt and J. D. Litster, Phys. Rev. A 26, 1809 (1982).

[8](a) K. L. Lushington, G. B. Kasting, and C. W. Garland, J. Phys. (Paris) Lett. 41, L419 (1980); (b) C. W. Garland and M. Meichle (unpublished).

[9]M. Delaye and P. Keller, Phys. Rev. Lett. 37, 1065 (1976).

[10]A. Wulf, Mol. Cryst. and Liq. Cryst. 56, L123 (1979). Wulf's model also predicts a crossover of the sort reported here. However, his mechanism requires $\phi \sim 1.4 \cos^{-1} dc/d_A$ whereas we find to high accuracy $\phi = \cos^{-1} dc/d_A$.

[11]The only well-documented exception seems to be the work by M. Delaye, J. Phys. (Paris) Colloq. 40, C3-350 (1979), in p-nonyloxybenzoate-p-butyloxyphenol. She measures both heliumlike critical behavior and small bare lengths. High-resolution heat-capacity and x-ray measurements on this material would be valuable.