Calorimetric study of the smectic-A—smectic-C phase transition in liquid crystals

M. Meichle and C. W. Garland
Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 13 December 1982)

High-resolution ac calorimetric measurements have been made on azoxy-4,4'-di-undecyl-α-methylcinnamate (AMC-11), butyloxybenzylidene heptylaniline (4O.7), heptyloxybenzylidene hexylaniline (7O.6), and heptyloxybenzylidene butylaniline (7O.4). The heat capacity C_P exhibits a sharp, asymmetric peak near the second-order smectic-A—smectic-C transition. The C_P values increase in the smectic-C phase as the transition temperature T_c is approached and then decrease abruptly at T_c. These data are well described by a mean-field Landau model and are not consistent with the heliumlike critical behavior expected from the de Gennes model. It is also shown that it is very difficult to distinguish between mean-field and XY critical behavior on the basis of data obtained only in the smectic-C phase.

I. INTRODUCTION

The smectic-A (SmA) and smectic-C (SmC) phases of liquid crystals are both orientationally ordered fluids that exhibit one-dimensional translational order. The smectic layers are described by a mass-density wave along the z direction and by a director (local orientational axis) which can be either parallel to z (SmA) or at an angle to z (SmC). A simple model proposed by de Gennes[1] indicates that the second-order SmA-SmC transition should exhibit the same critical behavior as superfluid helium; i.e., this transition should be in the $d=3$, $n=2$ universality class (3D XY model). Experimentally, early heat-capacity measurements on 4-n-pentylphenylthio-4'-n-octyloxybenzoate ($\bar{8}$S5) showed classical mean-field behavior.[2] This and other indications of mean-field character were explained by Safinya *et al.*,[3] who used a Landau-Ginzburg model and argued that the bare correlation lengths characterizing tilt fluctuations are usually so large that the true critical region is unobservably small. The mean-field model is also supported by recent work by Huang and Viner,[4] who have pointed out the importance of retaining the sixth-order term in the Landau free-energy expansion. However, XY critical behavior might well be seen if the bare lengths were shorter and the critical region therefore wider. Such a situation has been reported by Galerne,[5] who has measured the tilt angle in azoxy-4,4'-di-undecyl-α-methylcinnamate (AMC-11) and has found that a power-law singularity with $\beta=0.36\pm0.005$ describes his data for $(T_c-T)/T_c \leq 5\times10^{-3}$.

Very recent measurements of the tilt-angle variation in butyloxybenzylidene heptylaniline (4O.7) show the difficulty of distinguishing critical behavior from mean-field behavior on the basis of order-parameter data alone, whereas the heat-capacity and tilt-susceptibility data are uniquely described by a mean-field Landau model.[6] Thus we have undertaken high-resolution heat-capacity measurements to test the possibility of critical behavior near the SmA-SmC transition in AMC-11 and in several N-(4-n-alkoxybenzylidene)-4'-alkylaniline (nO.m) compounds. The nO.m compounds were chosen since they exhibit significant C_P peaks, suggesting that critical energy fluctuations might be present. A preliminary report of the results for AMC-11 and 4O.7 was given in Ref. 6, but a more detailed analysis of these data is given here together with new results on heptyloxybenzylidene hexylaniline (7O.6) and heptyloxybenzylidene butylaniline (7O.4). For each compound, the heat-capacity data can be well described with a Landau model. In particular, the essentially discontinuous change in C_P that occurs at T_c is consistent with the Landau model and is not consistent with the XY model.

II. METHOD AND RESULTS

The ac calorimeter used in this work is an automated version of the technique described previously.[7] The theory and basic design features given in Ref. 7 are still pertinent, and only essential changes will be mentioned here. The body of the silver sample cell is unchanged, but the filling technique has been simplified and improved by using a cold-welded indium seal. The full cell weighs $\sim$0.6 g, of which $\sim$0.1 g is due to the liquid crystal. As a result, the heat capacity of the empty cell plus addenda is about one-half the total observed heat capacity. The system operates at a constant frequency of

TABLE I. Molecular weight and transition temperature (K) for samples studied. For first-order transitions, the coexistence range is cited.

	Molecular weight	X-SmC [a]	SmC-SmA	SmA-N	N-I
4O.7	351.5	321.9–322.25	323.106	329.75	~356[b]
7O.4	351.5	335.5–336.5	337.559	347.09–347.21	349.20–349.30
7O.6	379.6	339.85–340.35	343.301	~353.5[b,c]	
AMC-11	675.0		352.360	362.5–363.2[c]	

[a]Low-temperature phase (X) is crystalline-B in 4O.7, crystalline-G in 7O.4, and smectic-F in 7O.6.

[b]Approximate value; not accurately determined in this work.

[c]There is no nematic phase; this is the SmA-I transition temperature.

$\omega=0.196$ (corresponding to a 32-sec period for the temperature oscillations). The temperature of the cell was monitored by direct readings of the thermistor resistance with a Keithley model 192 programmable digital multimeter every 0.5 sec during eight periods of oscillation. The amplitude ΔT_{ac} and phase shift of the oscillating sample temperature were determined from Fourier sine and cosine sums over the stored data after correction for any dc drift. Typical values of the amplitude were ± 5 mK (zero to peak). The temperature of the thermostat bath can be held constant during the taking of each data point or can be slowly scanned up or down in temperature. Near second-order transitions, a very slow scan rate (12 mK h^{-1}) was used. There was no indication of hysteresis on warming or cooling, and the data obtained with such scans agreed with data taken at constant bath temperatures. Thus we believe that full thermodynamic equilibrium is achieved during these slow scans.

The phase shift between the input heater voltage and the sample temperature response can provide an indication of two coexisting phases and hence a first-order transition. This is a clearly seen feature of the weakly first-order nematic (N)–isotropic (I) and strongly first-order smectic-A–crystalline-B transitions.[8] No anomalous phase shifts were observed at the SmA-SmC transitions studied here, and all our data indicate that these are second-order transitions.

The ac technique is used here as an absolute method with the results cited as values of the dimensionless ratio $\tilde{C}_P/R$. The molar heat capacity $\tilde{C}_P$ is given by the product of $\bar{C}_P$ and the molecular weight, where the specific heat $\bar{C}_P$ is obtained from $C_P(\text{obs})=m\bar{C}_P+C_P(\text{empty cell})$ for a cell containing m grams of liquid crystal. There may be systematic errors in the absolute values of $\tilde{C}_P$ due to imperfect correction for the effects of leads, possibly nonuniform heat flux, and any errors in the assessment of C_P(empty cell). However, this is not important for the present purposes. We are concerned here with the shape of the C_P variation near the SmA-SmC transition, which depends only on having good relative values.

The materials studied were (a) AMC-11 obtained from Galerne (Laboratoire de Physique des Solides, Orsay, France), (b) 4O.7 obtained from Goodby (Bell

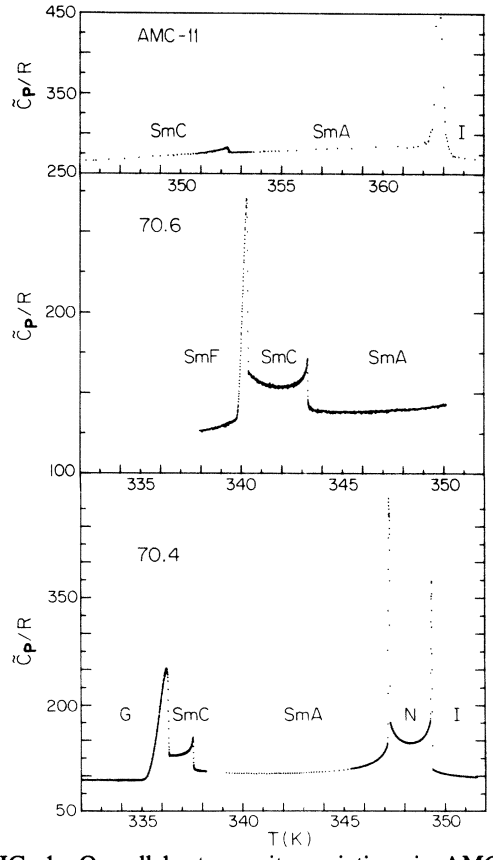

FIG. 1. Overall heat-capacity variations in AMC-11, 7O.6, and 7O.4. Anomalous phase shifts, indicating the coexistence of two phases, were observed at all the phase transitions except the SmA-SmC transition.

Laboratories), (c) 7O.6 obtained from CPAC-Organix, and (d) 7O.4 obtained from Smith (General Motors Research Laboratory). The molecular weight and observed transition temperatures for these samples are given in Table I. Comparison of the nO.m temperatures with literature values[9] indicates that our samples were of high purity. Furthermore, the transition temperatures were stable over a considerable time span; in particular, the SmA-SmC temperatures showed no detectable drift with time (i.e., less than 5 mK/week).

The heat-capacity variation over a wide range of temperature is shown in Fig. 1 for AMC-11, 7O.6, and 7O.4. The overall C_P variation for 4O.7 has been reported previously.[10] In that earlier work, a narrow range of SmC phase was discovered in 4O.7, but a detailed study was not made of this feature. In the present work we have repeated the investigation of the SmA-SmC region on a new 4O.7 sample of higher purity. The heat-capacity data for all four samples in the immediate vicinity of the SmA-SmC transition are presented and discussed in Sec. III along with comparisons of fits with the XY and Landau models.

III. DATA ANALYSIS AND DISCUSSION

We shall begin this section with a brief review of the heat-capacity behavior expected from the 3D XY model and a Landau model. For the $d=3$, $n=2$ universality class one has

$$\tilde{C}_P/R=\begin{cases}At^{-\alpha}(1+Dt^{0.5})+B+E(T-T_c) & \text{for } T>T_c\\ A'|t|^{-\alpha'}(1+D'|t|^{0.5})+B'+E'(T-T_c) & \text{for } T<T_c\end{cases} \tag{1}$$

where the reduced temperature is defined by $t\equiv(T-T_c)/T_c$, the critical exponents $\alpha=\alpha'=-0.026$, and $A/A'=1.11$, $D/D'\simeq 1$, $B=B'$.[11] One also expects $E=E'$ since the linear term arises from the regular (noncritical) contributions to the free energy. For the Landau-Ginzburg model, the free energy can be taken to have the form

$$G=G_0+at\phi^2+b\phi^4+c\phi^6+\frac{1}{2M_{\|}}|\vec{\nabla}_{\|}\phi|^2+\frac{1}{2M_{\perp}}|\vec{\nabla}_{\perp}\phi|^2, \tag{2}$$

where ϕ is the tilt order parameter. From Eq. (2), one obtains

$$\tilde{C}_P/R=\begin{cases}\tilde{C}_P^0/R & \text{for } T>T_c\\ \tilde{C}_P^0/R+A\dfrac{T}{T_c}\left[\dfrac{T_m-T_c}{T_m-T}\right]^{1/2} & \text{for } T<T_c\end{cases} \tag{3}$$

where $A\equiv a^2/2bRT_c$, $T_m\equiv T_c+(b^2T_c/3ac)$, and $\tilde{C}_P^0$ is the background heat capacity arising from G_0. If $b>0$, one has a second-order Landau transition that may be quite close to a classical tricritical point if A is large and T_m-T_c is small. This form was first given by Landau and Lifshitz.[12] It has recently been applied to the SmA-SmC transition in racemic 4-(2'-methylbutyl)phenyl-4'-n-nonyloxybiphenyl-4-carboxylate (2M4P9OBC) by Huang and Viner,[4] who have defined a convenient quantity $t_0\equiv 3(T_m-T_c)/T_c=b^2/ac$ which characterizes the shape of the excess heat capacity. Note that in the Landau expression, the *excess* $\tilde{C}_P/R$ (i.e., the contribution due to the transition) jumps discontinuously from 0 to A at T_c. This excess $\tilde{C}_P/R$ drops to $\frac{1}{2}A$ at $t=-t_0$; thus t_0 characterizes the sharpness of the C_P peak. The usual form for the background contribution both above and below T_c is

$$\tilde{C}_P^0/R=B+E(T-T_c), \tag{4}$$

corresponding to the slow linear increase in heat capacity observed in normal fluids.

A. AMC-11

In view of the report that the order-parameter variation in this compound is consistent with the critical behavior expected for the $d=3$, $n=2$ universality class,[5] we have carried out a careful comparison of our C_P data with both the XY and Landau models. The C_P variation in the range $|t|<2\times10^{-2}$ is shown in Fig. 2, and the parameters for various XY fits with Eqs. (1) and Landau fits with Eqs. (3) and (4) are given in Table II.

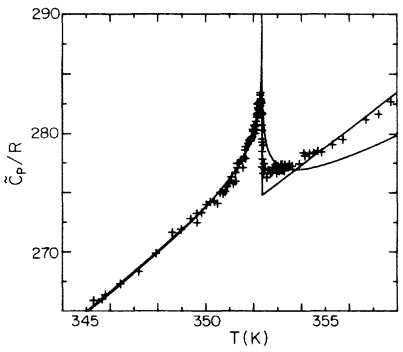

FIG. 2. Molar heat capacity near the SmA-SmC transition in AMC-11. Lines represent fits with the XY model and the Landau model. Below T_c these models predict almost identical values except very close to T_c (see Fig. 3).

Simultaneous fits with both of Eqs. (1) to data above and below T_c when $B=B'$ was imposed gave 352.360 K as the best value for T_c, but such fits were poor. In essence, the inability of the model to give a good representation above T_c caused systematic deviations on both sides. Since $T_c=352.360$ K was also obtained for Landau fit 3, we have fixed T_c at this value for a series of one-sided fits.

For SmC phase data with $T \leq 352.310$ K (i.e., $|t|_{\min}=1.4\times10^{-4}$), one can obtain good fits with the XY model. Note that the XY heat capacity with a negative exponent α corresponds to a sharp cusp, and B represents the peak $\tilde{C}_P/R$ value at T_c. XY fit 1 for the range $|t| \leq 2\times10^{-2}$ gives a physically reasonable slope $E=1.35$, but XY fit 2a for the range $|t| \leq 5\times10^{-3}$ gives an artificially high E value which is inconsistent with the remaining data below T_c and all the data above T_c. However, XY fit 2b shows that a fairly good fit that is close to XY fit 1 can be obtained for $|t| \leq 5\times10^{-3}$ when the slope E is held fixed at 1.35. In contrast, the data above T_c are very poorly represented by the XY model. If one uses parameters based on XY fit 1 with the scaling equalities $\alpha=\alpha'$, $B=B'$, $E=E'$, and the expected ratio $A=1.11A'$, the fit for $T>T_c$ is terrible ($\chi^2_\nu \simeq 100$). On allowing A to be a free parameter but retaining the scaling values for the other parameters, XY fit 3 is obtained, for which $A/A'=1.04$ and the χ^2_ν value is still very poor. Only by allowing A, B, and E to be free parameters can one find a good fit above T_c (XY fit 4), but this fit is highly artificial and involves an unacceptable violation of scaling. In all of the above fits the corrections-to-scaling amplitudes D and D' were held equal to zero; trial fits including nonzero D and D' values showed that the inclusion of correction terms did not make any significant improvement in the fit to these AMC-11 data. In summary, the XY model can provide a fairly good representation for most of the data below T_c but cannot represent data above T_c in any theoretically consistent manner. The smooth XY curves shown in Figs. 2 and 3 are based on fits 1 and 3, which preserve the scaling equalities.

The Landau model based on Eqs. (3) and (4) gives a good representation to all the data with the exception of a small range of data just above T_c ($0<t<3\times10^{-3}$). The smooth Landau curves in Figs. 2 and 3 represent Landau fit 3 in Table II, for which the characteristic temperature parameter t_0 has the small value 1.7×10^{-3}. This fit also yields a physically reasonable slope $E=1.54$. In order to compare Landau fits with the XY fits below T_c, Landau fits 1 and 2 were made as direct analogs of XY fits 1 and 2. For such Landau fits to SmC data alone, good fits can be achieved with a fairly wide

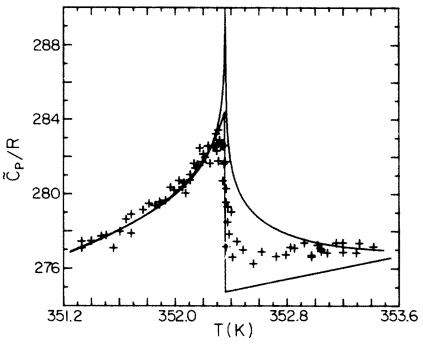

FIG. 3. Detailed view of the fits to the AMC-11 data near T_c.

range of E values (1.25–1.7) so we have held E fixed at the value 1.54 that is consistent with the data above T_c. Note that Landau fits 1 and 2 have somewhat better χ^2_ν values than XY fits 1 and 2.

In summary, the Landau model provides a satisfactory description for all the data except for a short range just above T_c (which may indicate the presence of very weak 3D Gaussian fluctuation effects[13]). The XY model also provides a reasonable fit for data at $T \leq 352.31$ K, which is the temperature for the maximum observed C_P value. However, the XY model cannot provide a consistent description of the SmA phase data or of the data very close to T_c. Figure 3 shows a detailed view of the data near T_c. The deviation between the data and the XY model in the range 352.31–352.36 K is significant and cannot be improved by any change in the T_c value. Thus measurements made only in the SmC phase, such as the tilt-angle order-parameter variation, may not be able to distinguish between helium-like behavior and a Landau description in which the coefficient of the sixth-order term is unusually large. Indeed, the order-parameter data in Ref. 5 can be

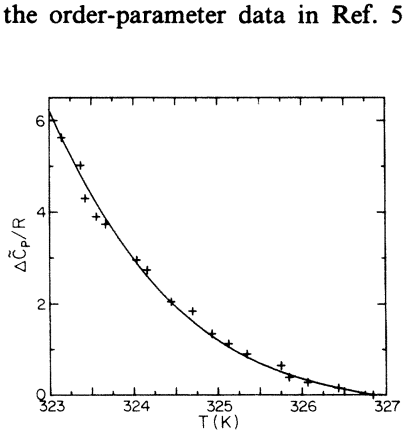

FIG. 4. Anomalous heat capacity in 4O.8 associated with precursor effects near the transition into the crystalline-B phase (see Ref. 8). Curve represents an empirical fit with Eq. (5).

reasonably described by such a Landau model as well as by the XY model.[6,14]

B. nO.m compounds

The analysis of the C_P data in these compounds is complicated by the presence of a crystalline phase that occurs only one or two degrees below the SmA-SmC transition temperature (see Table I). In 4O.7 this phase is a B phase, in 7O.4 it is a G phase, and in 7O.6 it is a SmF (2D crystalline) phase.[9] Precursor effects associated with the transition into such crystalline phases give rise to an anomalous background variation, and Eq. (4) does not provide a good description of $\tilde{C}_p^0/R$. Fortunately, such effects have already been observed in butyloxybenzylidene octylaniline (4O.8) where there is a SmA to crystalline-B transition,[8] and a scaled version of the 4O.8 behavior has been used to assign the background variation in the nO.m compounds studied here.

Figure 4 shows the anomalous variation in the SmA phase of 4O.8 as the transition into the B phase at 322.91 K is approached. This 4O.8 precursor effect has been fitted with the simple empirical form

$$\Delta\tilde{C}_P/R = \begin{cases} 0 \text{ for } T > T_x \\ 0.360[(T_x - T) + 0.236(T_x - T)^3] \text{ for } T < T_x \end{cases} \quad (5)$$

where $\Delta\tilde{C}_P = \tilde{C}_P(\text{obs}) - \tilde{C}_P(\text{normal background})$,[8] and $T_x = T_{AB} + 4$ characterizes the range of this effect. For the present nO.m compounds, we have assumed that the background contribution to C_P can be represented by

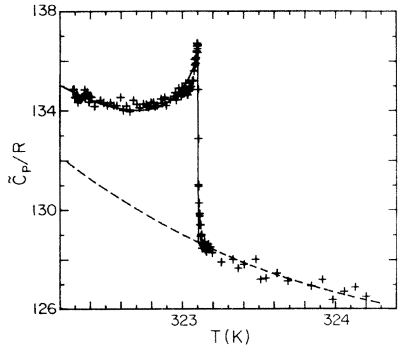

FIG. 5. Molar heat capacity near the SmA-SmC transition in 4O.7. Dashed curve represents the background scaled from 4O.8, as given by Eq. (6), and the solid line is the Landau fit.

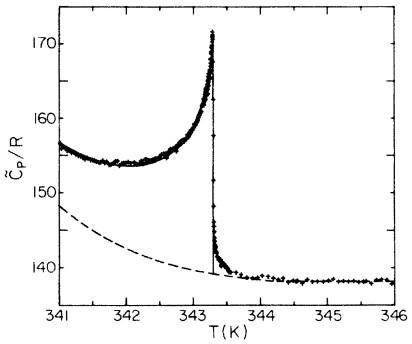

FIG. 6. Molar heat capacity near the SmA-SmC transition in 7O.6. Dashed curve represents the background scaled from 4O.8, as given by Eq. (6), and the solid line is the Landau fit.

$$\tilde{C}_P^0/R = \begin{cases} B \text{ for } T > T_x \\ B + C[(T_x - T) + 0.236(T_x - T)^3] \text{ for } T < T_x \end{cases} \quad (6)$$

where T_x is taken to be $T_{CB} + 4$ for 4O.7, $T_{CG} + 4$ for 7O.4, and $T_{CF} + 4$ for 7O.6. Thus the *shape* and range of the precursor effects in 4O.8 have been maintained, and only the magnitude of this background variation is allowed to vary by taking C as an adjustable parameter. The values taken for T_x were 326.0 K in 4O.7, 340.0 K in 7O.4, and 344.2 K in 7O.6. As shown below, this scaled 4O.8 background is completely consistent with the observed data. Indeed, there was no significant improvement in the fits if T_x and the coefficient of the $(T_x - T)^3$ term were allowed to be freely adjustable parameters (in which case, their least-squares values were found to be quite close to the fixed values chosen above).

It is clear from Figs. 5–7 that in the nO.m compounds the jumps in C_P at T_c are very abrupt,[15] and

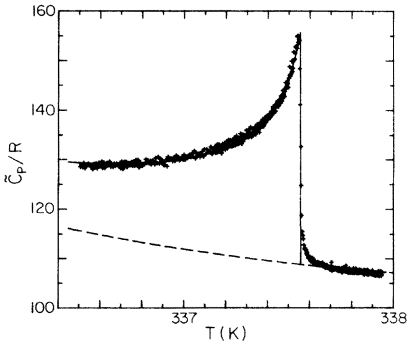

FIG. 7. Molar heat capacity near the SmA-SmC transition in 7O.4. Dashed curve represents the background scaled from 4O.8, as given by Eq. (6), and the solid line is the Landau fit.

TABLE II. Parameter values obtained from least-squares fitting of $\tilde{C}_P/R$ data with the XY model, Eq. (1), and the Landau model, Eq. (3) and Eq. (4) or (6). Values in parentheses were held fixed during the fit. Coefficients D and D' in Eq. (1) were set equal to zero.

	B	A	T_m (K)	T_c (K)	C or E (K^{-1})	$10^3 t_{max}$	χ^2_ν
			AMC-11				
XY fit1 ($T<T_c$)	349.79	−82.93		(352.360)	$E=1.35$	−20	1.45
2a ($T<T_c$)	326.91	−54.57		(352.360)	$E=2.86$	−5	1.07
2b ($T<T_c$)	351.77	−85.30		(352.360)	$E=(1.35)$	−5	1.59
3 ($T>T_c$)	(349.79)	−86.30		(352.360)	$E=(1.35)$	+15	17.3
4 ($T>T_c$)	291.90	−18.66		(352.360)	$E=1.33$	+15	0.55
L fit 1 ($T<T_c$)	274.37	9.95	352.602	(352.360)	$E=(1.54)$	−20	1.04
2 ($T<T_c$)	271.73	12.04	352.850	(352.360)	$E=(1.54)$	−5	0.90
3	274.75	9.80	352.560	352.360	$E=1.54$	−20/+15	1.25
			nO.m compounds				
4O.7	(125.0)	7.66	323.255	(323.106)	$C=0.429$	±2.5	1.34
4O.7	(125.0)	7.75	323.242	(323.106)	$C=0.427$	±1.0	1.59
7O.6	(138.2)	31.43	343.484	(343.301)	$C=0.924$	±6.5	1.76
7O.6	(138.2)	30.81	343.399	(343.301)	$C=3.258$	+2/−1	1.20
7O.4	(103.5)	47.59	337.655	(337.559)	$C=0.857$	+1/−3	1.54
7O.4	(103.5)	47.94	337.650	(337.559)	$C=0.922$	±1	1.64
7O.4	109.23	47.80	337.646	(337.559)	$E=-6.34$	+1/−3	1.28
7O.4	109.36	48.03	337.641	(337.559)	$E=-7.11$	±1	1.4

there are only very weak indications of fluctuation effects[13] above T_c. Furthermore, the C_P variations in the SmC phase are very well described by the Landau model with Eqs. (3) and (6). The least-squares values of the adjustable parameters A, T_m, and C are shown in Table II along with the fixed values used for B and T_c. The T_c values were taken to be the location of the midpoints of the jumps in C_P, and the B values were determined from the constant $\tilde{C}_P/R$ background values observed a few degress above T_x. Note that the values of the free parameters are stable when the range of data is reduced. The fits shown in Figs. 6 and 7 as well as the χ^2_ν values listed for 7O.6 and 7O.4 in Table II were obtained by omitting data in the range $0<t<5\times10^{-4}$, where small fluctuation effects occur.

Since the data in the SmC phase of 7O.4 do not clearly require a curved background such as the scaled 4O.8 background, we also tried 7O.4 Landau fits with an assumed linear background, i.e., using Eqs. (3) and (4). The results given in the last two lines of Table II are in good agreement with the previous fits. In fact, the two types of background do not differ much over the 1.5-K range of data used in the fits.[16]

No effort has been made to fit these nO.m data with the XY model. Even if reasonable fits could be achieved below T_c, it is obvious that the discontinuous drop in C_P and the extremely small excess heat capacity above T_c are inconsistent with heliumlike behavior.

IV. CONCLUSION

All four investigated compounds show heat-capacity variations near the SmA-SmC transitions that are well represented by a Landau model and are not consistent with XY critical behavior like that observed in superfluid helium. In the case of 4O.7 this mean-field behavior can be explained in terms of the Ginzburg criterion, which shows that critical behavior in 4O.7 occurs for reduced temperatures less than 10^{-5}.[6] Light scattering investigations to determine the bare correlation lengths would allow the Ginzburg criterion to be checked in the other materials. Tilt-susceptibility measurements in the SmA phase would also be of value in confirming the mean-field behavior.

Values for the heat-capacity jump at T_c and the characteristic reduced temperature t_0 are given in Table III for several compounds. Note that the C_P peaks observed here are sharper (smaller t_0) than those reported previously for other SmA-SmC transitions. It is thus of interest to ask whether the investigated compounds are perhaps close to a classical tricritical point. Although one cannot determine the individual Landau coefficients a,b,c from heat-

TABLE III. Heat-capacity jump $A=a^2/2bRT_c$ and the characteristic reduced temperature $t_0=b^2/ac$ associated with the SmA-SmC transition.

Material	A	$10^3 t_0$	$10^3 A^{1/2} t_0$
$\bar{8}$S5[a]	5	6.5	14.5
2M4P9OBC[b]	16	5.5	22.0
DOBAMBC[b]	~15	3.2	12.4
AMC-11	9.8	1.7	5.3
4O.7	7.7	1.3	3.6
7O.6	30.8	1.6	8.9
7O.4	47.8	0.8	5.5

[a]Reference 2.

[b]Reference 4. DOBAMBC stands for *p*-decyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate.

capacity data alone, it is of value to look at trends in the parameters $A=a^2/2bRT_c$ and $t_0=b^2/ac$ and also in the quantity $A^{1/2}t_0=b^{3/2}/c(2RT_c)^{1/2}$.

In the case of AMC-11 and 4O.7, the moderate size of the jump A and the small t_0 value strongly suggest that the coefficient c of the sixth-order term is anomalously large rather than the coefficient b of the fourth-order term being unusually small.[6] In the case of 7O.6 and especially 7O.4, the large A value suggests that b might be quite small compared to its value in the other compounds. However, we cannot eliminate the alternative possibility that the coefficient a is larger in 7O.6 and 7O.4 than in the other compounds. Another way to consider the question of possible tricriticality is to consider the relative magnitudes of the coefficients b and c. The $A^{1/2}t_0$ values, which are independent of a, do not suggest any significant differences among AMC-11, 4O.7, 7O.6, and 7O.4. In all four materials, the term $c\phi^6$ must play an important role in Eq. (2). If the large heat-capacity jump in 7O.6 and 7O.4 were to be explained by a very small b value then it would be also necessary to postulate a parallel decrease in c. We have not been able to find an explanation, say in terms of coupling between the tilt order parameter and some other order parameter, for very small b *and* c values in 7O.6 and 7O.4. Nor does there seem to be any obvious correlation based on the molecular structure or phase diagrams of 7O.6 and 7O.4 to expect quasitricritical behavior in these compounds. Thus it seems more reasonable to consider all four compounds to have similar Landau second-order transitions.

In order to realize a SmA-SmC transition that exhibits heliumlike critical behavior it will be necessary to find a material which has fairly short bare correlation lengths so that the true critical region is accessible. A possible candidate for such a material is *p*-nonyloxybenzoate-*p*-butyloxyphenol ($\bar{9}O\bar{4}$), for which light scattering studies yield XY critical values for the correlation exponent ν.[17] However, a recent calorimetric investigation[18] has shown that the C_P variation in this compound is mean-field-like and not significantly different in character from that shown here for AMC-11. X-ray and tilt-susceptibility investigations of $\bar{9}O\bar{4}$ would be helpful in clarifying the nature of this SmA-SmC transition.

Note added in proof. A subsequent redetermination of C_P(empty cell) for the 4O.7 run has revealed a systematic error in our earlier evaluation of this quantity. As a result, the $\tilde{C}_P/R$ values reported here for 4O.7 are too high by a temperature-independent constant amount equal to 30. The only effect this has on the 4O.7 model parameters in Table II is to reduce B from 125.0 to 95.0. Comparable but unknown additive errors are also present for all the other materials, but this does not influence the conclusion about the character of the phase transitions since only the parameter B is affected.

ACKNOWLEDGMENTS

We are indebted to Y. Galerne for stimulating discussions and for providing a sample of AMC-11. We also wish to thank R. J. Birgeneau, G. Durand, and J. D. Litster for helpful discussions. The work was supported by National Science Foundation Grant No. DMR-81-19295.

[1]P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).

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

[3]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.

[4]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); S. C. Lien, J. M. Viner, and C. C. Huang (unpublished).

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

[6]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).

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

[8]K. J. Lushington, G. B. Kasting, and C. W. Garland, J. Phys. (Paris) Lett. 41, L-419 (1980).

[9]G. W. Smith and Z. G. Gardlund, J. Chem. Phys. 59, 3214 (1973); A. Wiegeleben, L. Richter, J. Deresch, and D. Demus, Mol. Cryst. Liq. Cryst. 59, 329 (1980).

[10]E. Bloemen and C. W. Garland, J. Phys. (Paris) 42, 1299 (1981).

[11]G. Ahlers, Phys. Rev. A 8, 530 (1973); K. H. Mueller, G. Ahlers, and F. Pobell, Phys. Rev. B 14, 2096 (1976).

[12]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958), Sec. 138.

[13]S. K. Ma, *Modern Theory of Critical Phenomena* (Benjamin, New York, 1976), Chap. III.

[14]Y. Galerne (private communication).

[15]The width of these $\tilde{C}_P$ jumps can be characterized by citing the reduced temperature $t_1 = \Delta T / T_c$ corresponding to the range ΔT in which $\tilde{C}_P$ goes from 10% to 90% of the jump. These values are $t_1 = 4.6 \times 10^{-5}$ in 4O.7, 7.3×10^{-5} in 7O.6, and 5.0×10^{-5} in 7O.4. Thus the jumps are much more abrupt than that in 2M4P9OBC, for which $t_1 = 90 \times 10^{-5}$ (Ref. 4).

[16]It should be noted that when Eq. (4) is used, the parameter B corresponds to the background value *at* T_c. This quantity calculated from the 7O.4 parameters obtained with Eq. (6) has the value 108.7, which is very close to the 109.3 value from the fits with Eq. (4).

[17]M. Delaye, J. Phys. (Paris) Colloq. 40, C3 (1979).

[18]R. Biggers and D. L. Johnson (unpublished).