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Determination of the Coefficients in Landau Free Energy near the Smectic–A–Chiral Smectic–C Transition for the Liquid Crystal MBRA8

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High-resolution heat-capacity measurement has been carried out on S-4-O-(2-methyl)butyl-resorcylidene-4′-octylaniline near its smectic–A–chiral smectic–C transition. Our heat-capacity results combined with the existing tilt-angle data enable us to calculate the three leading coefficients in the Landau free energy expression for the smectic–A–chiral smectic-C transition.

A variety of organic compounds exhibit the smectic–A (SmA) and, at lower temperature, the smectic–C (SmC) liquid-crystal phase characterized by a one-dimensional density wave which has a wave vector along (A) or tilted (C) with respect to the average long molecular axis (the director $\hat{n}$). If the constituent molecules are optically active, the chiral smectic-C phase (SmC*) will be observed instead of the SmC

phase. In the SmC* phase, as a consequence of the molecular chirality, the director exhibits a helical structure with $\hat{n}$ precessing in space when an observer moves along the direction perpendicular to the smectic layers. In 1973 de Gennes[1] proposed that the SmA-SmC transition might be continuous and might exhibit helium-like critical behavior (3D XY model). In early heat capacity measurements by Shantz and Johnson on one liquid-crystal compound ($\bar{8}$S5)[2], raw data showed mean-field behavior in the vicinity of the SmA–SmC transition. Applying the Landau–Ginzburg criterion to their X-ray data on $\bar{8}$S5, Safinya *et al.*[3] argued that the heat-capacity jump at the transition temperature as well as bare correlation lengths characterizing tilt-angle fluctuations are so large that the critical region is very small and beyond experimental resolution. Furthermore, Huang and Viner[4] and later independently Carlsson and Dahl[5] have pointed out the importance of retaining the sixth-order term in the Landau free energy expansion in order to provide quantitative explanation of heat-capacity data obtained in the case of SmA–SmC transition. Afterward the significance of the sixth-order term has been confirmed in all the materials being studied near the SmA–SmC transition.[6-8]

In 1975 Meyer and coworkers[9] established the existence of liquid crystals with ferroelectric properties, the SmC* phase being the most important case. Later Clark and Lagerwall[10] showed the feasibility of a submicron electro-optical switching mechanism in a thin cell of a SmC* liquid crystal aligned homogeneously in macroscopic regions by surface stabilization. Since then, considerable effort is being concentrated on the characterization of bulk properties of the SmC* phase as well as the behavior near the continuous SmA–SmC* transition.

From the viewpoint of device application, the search for chemically stable liquid-crystal compounds which exhibit SmC* in a wide temperature range covering room temperature is very important. Recently, several room temperature SmC* compounds have been found.[11-13] Among them the S-4-O-(2-methyl)butyl-resorcylidene-4′-octylaniline (MBRA8) exhibits a SmC* phase between 35 °C and 50 °C on heating and between 50 °C and about 0 °C on cooling.[14] (The SmA-SmC* transition temperature 52 °C reported in ref. 14 is due to sample impurities.) Around 50 °C, it undergoes a continuous transition to smectic–A before becoming isotropic at about 57 °C. Technically the existence of the SmA phase is helpful for the preparation of homogeneous samples. Furthermore, the continuous SmA–SmC* transition allows us to obtain the important Landau parameters describing the SmC* ordering.

The fact that the SmA–SmC and SmA–SmC* transition from the racemic and chiral configurations of the same liquid crystal compound show only a small difference in transition temperatures[15,16] suggests that the SmA-SmC* transition is mainly driven by intermolecular forces producing the SmC phase and not by ferroelectric coupling between permanent dipoles.[15] The spontaneous polarization is thus a secondary rather than a primary order parameter.[15,17] In other words, the energy associated with the interaction between permanent dipoles is only a small perturbation of the system.

A high-resolution calorimetric investigation of MBRA8 has been carried out in the vicinity of the SmA–SmC* transition. The details of our measurement technique have been reported elsewhere.[18] The measured heat capacity per unit area (C_A) of the sample cell is shown in Figure 1 as open squares. The fact that this heat capacity anomaly is nearly a linear function of temperature in the SmA phase and has an abrupt jump indicates that the nature of this phase transition is dominantly mean-field like.

In the course of investigating the nature of the SmA–SmC transition, Huang and Viner[4] suggested that retaining the sixth-order term in the Landau free energy expansion is crucial to explain the measured heat-capacity data as well as resolve the discrepancy among the reported critical exponents associated with the tilt-angle. The heat-capacity anomaly shown in Figure 1 is characterized by the same features as the ones for the other SmA–SmC transitions. Consequently, to fit our data, we will use the heat-capacity expression obtained from the Landau free energy expansion.

$$G = G_0 + at\phi^2 + b\phi^4 + c\phi^6 \tag{1}$$

where ϕ is the order parameter (i.e., tilt-angle), $t = (T - T_c)/T_c$ and T_c is the transition temperature. G_0 is the non-singular part of the free energy and all parameters a, b, c have to be positive for a continuous transition. After minimizing the free energy with respect to ϕ, one obtains

$$\phi^2 = \begin{cases} 0 & \text{for } T > T_c \\ R\left((1 - 3t/t_0)^{1/2} - 1\right) & \text{for } T < T_c \end{cases} \tag{2}$$

where $R = b/(3c)$ and $t_0 = b^2/(ac)$. Then one can calculate the heat

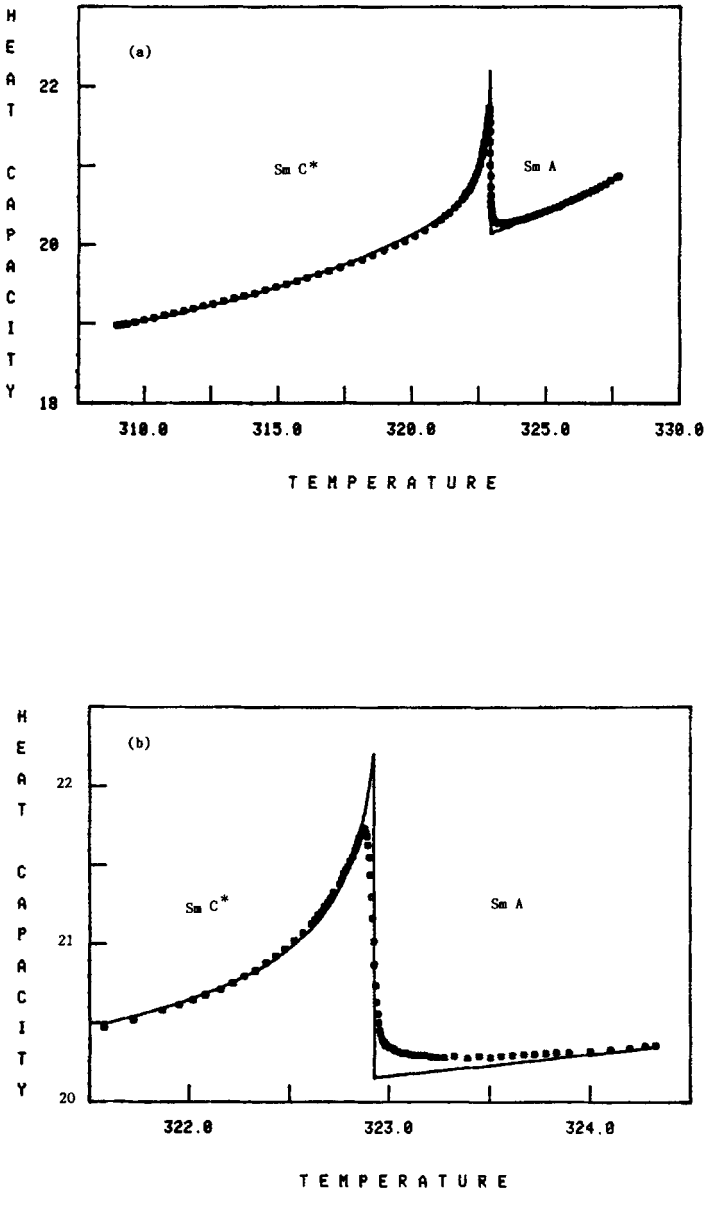

FIGURE 1 Total heat capacity per unit area in J/cm^2-K as a function of temperature near the SmA–SmC* transition of MBRA8. Squares: experimental data; solid line: best fit to Eqs. (3) and (4). (a) The data were plotted in the entire measured temperature range. (b) The data with $|T - T_c| \leq 1.5$ K were displayed to show the rounding effect near T_c

capacity associated with this free energy to obtain

$$C = \begin{cases} C_0 & \text{for } T > T_c \\ C_0 + AT(T_m - T)^{-1/2} & \text{for } T < T_c \end{cases} \quad (3)$$

where C_0 is the background heat capacity obtained from G_0, $A = a^{3/2}/(2(3c)^{1/2}T_c^{3/2})$ and $T_m = T_c(1 + t_0/3)$. Because of the large fitting range ($\simeq$ 18 K), we have here assumed that

$$C_0 = B + Dt + Et^2 \quad (4)$$

for both above and below T_c. The transition temperature T_c is chosen to be the midpoint of the mean-field heat-capacity jump. Then the measured heat-capacity data were fitted to Eqs. (3) and (4) with one set of fitting parameters, i.e., T_m, A, B, D and E. The fitted result is shown as a solid line in Figure 1. It is clear that Eqs. (3) and (4) provide an excellent fit to the data except very close to T_c. The commonly observed excess heat capacity above the fitted curve for $T > T_c$ may be interpreted as short range SmC order fluctuations in the SmA phase. Immediately below T_c, the experimental curve is rounded and several of the experimental points are below the fitted curve. We believe that this may be caused by either a very weak first-order character of this transition which is driven by the fluctuations of the nearby isotropic-SmA transition or more likely a macroscopically inhomogeneous distribution of impurities. The rounding caused by either finite size or temperature gradient effect is believed to be small because of the earlier experience with the same calorimeter where the observed rounding in similar transitions[4,16] has been found to be much smaller.

From the measured T_c and the fitted T_m one gets $t_0 = 3((T_m/T_c) - 1) = 9.0 \times 10^{-4}$, a value comparable to the smallest t_0 found in the other measured SmA–SmC transitions.[8] Because of the rounding near T_c, the mean-field heat capacity jump (C_J) at T_c is obtained from the fitted curve. After dividing by the sample thickness ($= 1.2 \times 10^{-2}$ cm), C_J is found to be equal to 0.18 J/K-cm^3 ($= 71$ J/mole-K) which is comparable to that of other SmA–SmC transitions. Finally, Eq. (2) enables us to calculate $R = b/3c$ from the measured tilt-angles, using the t_0 obtained from our heat capacity measurement. Of the six reported values[14] of tilt-angle five give fairly consistent values in R. From these $R = 1.1 \times 10^{-3}$ (in radians) is obtained with 15% standard deviation.

Employing the three relations

$$C_J = a^2/(2bT_c),\ t_0 = b^2/(ac) \quad \text{and} \quad R = b/(3c),$$

one obtains separately the three relevant Landau parameters which are given in Table I.[19]

Since the first separate estimates of the parameters a, b, c were made,[5] the data from Ref. 4 can be used to get a corresponding set of values for DOBAMBC (the estimations in Ref. 5 differ from these more accurate values). These values are also given in Table I.

The question whether b is small or large seems, at first thought, to give an idea about the character of the transition because, as is well known, the transition changes from second to first order when b changes sign. A compound with a negative b value would therefore be a good starting point to prepare a system, by mixing, exhibiting a tricritical point. However, it is not clear if such a b value can or will be actually measured. Therefore it seems safer to judge the nature of the transition by not regarding the absolute values of a, b and c but instead the dimensionless parameter $b^2/ac = t_0$ which can also be expected to be much more comparable in size from system to system.[20]

As can be seen, in MBRA8 the coefficient a is slightly larger, b larger by one order of magnitude, c again larger by about three orders of magnitude than in DOBAMBC. As the value of t_0 becomes sufficiently small, an increase in these three Landau coefficients was obtained in the mixture system of $\bar{8}$S5 and $\bar{7}$S5 near the nematic-SmA-SmC multicritical point.[21] Nevertheless, the combined weight of the parameters gives for $t_0 = b^2/ac$ in MBRA8 a value of only 0.9×10^{-3} in comparison with 3.0×10^{-3} in DOBAMBC. The smallness of t_0 seems to indicate that the SmA–SmC* transition is approaching the mean-field tricritical point in MBRA8, and it would seem desirable to correlate the values exhibited by a sequence of members of the MBRA series with the change in the temperature range for the SmA phase.[20] Further studies on mixtures and pure compounds are in progress.

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TABLE I

Landau parameters for MBRA8 and DOBAMBC

	MBRA8 (this work)	DOBAMBC (Huang and Viner[4])	DOBAMBC (Carlsson and Dahl[5])
a [J/mole]	1.3×10^4	3.5×10^3	4.3×10^3
b [J/mole]	3.5×10^3	1.4×10^2	1.0×10^2
c [J/mole]	1.1×10^6	1.6×10^3	1.1×10^3
$t_0 = b^2/ac$	0.9×10^{-3}	3.2×10^{-3}	2.1×10^{-3}

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19. In the case of MBRA8, the anomalously large value in the Landau coefficient c seems to suggest that the truncation of the power-series expansion at $c\phi^6$ unjustifies. The measured tilt-angle at $T_{AC} - T \simeq 25$ K is about 7° ($\simeq 0.12$ radian). Consequently, at this temperature the three leading terms in the Landau free energy expansion (i.e., $at\phi^2$, $b\phi^4$, and $c\phi^6$) have values of 14.5, 0.73, and 3.17 J/mole, respectively. Thus even in this wide temperature range the expansion up to $c\phi^6$ is a reasonable approximation.
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21. C. C. Huang and S. C. Lien, NATO ASI conference proceedings on "Multicritical Phenomena," Ed. R. Pynn and A. Skjeltorp (Plenum Publishing Corp., 1984) p. 73, $\bar{7}$S5 is heptyloxy-*p'*-pentylphenylthiolbenzoate.