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Possible general behavior in smectic-*A* –smectic-*C* (chiral smectic-*C*) transitions in liquid crystals

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From the heat-capacity studies of several different liquid-crystal compounds, each with an isotropic (I)-smectic-A (SmA)-smectic-C (SmC) [or chiral-smectic-C (SmC^*)] transition sequence, one possible general behavior is found between t_0 and T_{AC}/T_{IA}. Here T_{AC} and T_{IA} denote the SmA-SmC (-SmC^*) and I-SmA transition temperatures. The important parameter t_0 characterizes the full width at the half-height of the mean-field heat-capacity anomaly associated with the SmA-SmC or SmA-SmC^* transition and features the crossover from an ordinary mean-field-like behavior to a mean-field-tricritical-like behavior as the temperature of the system moves away from the transition temperature.

After about one decade of various heat-capacity studies by many research groups on the continuous nematic–smectic-A (N-SmA) transitions of different liquid-crystal compounds, recently one possible general trend seems to emerge.[1] Among various liquid-crystal compounds, the critical exponent α associated with the heat-capacity anomaly of the N-SmA transition is found to decrease monotonically and asymptotically toward $\alpha=0$ as T_{NA}/T_{IN} decreases. Here T_{NA} and T_{IN} are the transition temperatures of the N-SmA and isotropic-nematic (I-N) transition, respectively. Now a new possible general behavior is found in the continuous smectic-A–smectic-C (SmA-SmC) or smectic-A–chiral-smectic-C (SmA-SmC^*) transition. Here we will report this result, which may be a general behavior among all the liquid-crystal compounds with an I-SmA-SmC (or SmC^*) sequence of transitions.

A variety of organic compounds exhibit the SmA and, at lower temperature, the SmC liquid-crystal phase characterized by a one-dimensional (1D) density wave which has a wave vector along (A), or tilted with respect to (C) the average long molecular axis (director). If the constituent molecules are optically active, the SmC^* phase will be observed instead of the SmC phase. In 1973 de Gennes[2] proposed that the SmA-SmC transition might be continuous and might exhibit heliumlike critical behavior (3D XY model). In early heat-capacity measurements by Shantz and Johnson on $\overline{8}$S5 (octyloxy-p'-pentylphenylthiolbenzoate),[3] 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 $\overline{8}$S5, Safinya *et al.*[4] concluded that the critical region is very small and beyond experimental resolution because of the large heat-capacity jump at the transition temperature and the large bare correlation lengths characterizing tilt-angle fluctuations. Furthermore, Huang and Viner[5] have pointed out the importance of retaining the sixth-order term in the Landau free-energy expansion in order to provide a quantitative explanation of the heat-capacity data obtained near one SmA-SmC transition. Afterward the significance of the sixth-order term has been further confirmed in all the materials being studied near the SmA-SmC (SmC^*) transition.[6–9]

Thus far detailed heat-capacity studies and some tilt-angle measurements have been carried out on seven different liquid-crystal compounds (see Table I) which have an I-SmA-SmC (SmC^*) transition sequence. All the data can be fitted to the expression for the heat capacity (C) and tilt angle (Ψ) derived from the following Landau mean-field free energy:

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

Here, the tilt angle (Ψ) is the SmC or SmC^* order parameter,[12] $t=(T-T_{AC})/T_{AC}$ and T_{AC} is the SmA-SmC

TABLE I. Parameters obtained from heat-capacity measurements. HOBACPC: hexyloxybenzylidene p'-amino-2-chloropropylcinnamate. 2M45OBC: 2-methylbutyl 4′-n-pentyloxy-biphenyl-4-carboxylate; R: racemic version; C: chiral version. DOBAMBC: p-decyloxybenzylidene-p-amino-2-methylbutylcinnamate. 7O.6: N-(4-n-heptyloxybenzylidene)-4′-hexylaniline. AMC-11: azoxy-4,4′-di-undecyl-α-methylcinnamate. MBRA8: S-4-O-(2-methyl)butyl-resorcylidene-4′-octylaniline.

Compound	T_{AC} (K)	T_{IA} (K)	T_{AC}/T_{IA}	$t_0\times 10^3$	ΔC_J[a]	Ref.
HOBACPC	353.2	409.2	0.863	5	2.8×10^2	10
2M45OBC(R)	316.0	337.0	0.938	3.9	1.24×10^2	9
2M45OBC(C)	316.4	337.0	0.939	3.5	1.45×10^2	9
DOBAMBC	367.7	390.2	0.942	3.2	1.25×10^2	5
7O.6	343.3	353.5	0.971	1.6	2.58×10^2	8
AMC-11	352.4	362.9	0.971	1.7	82	8
MBRA8	323.2	329.2	0.982	0.9	71	11

[a] ΔC_J in J/mole K.

($-$SmC^*) transition temperature. G_0 is the nonsingular part of the free energy and the constants $(a,b,c)>0$ for a continuous transition. After minimizing G with respect to Ψ, Ψ is zero for $T > T_{AC}$. In the case of $T < T_{AC}$, one obtains

$$\Psi^2 = R[(1-3t/t_0)^{1/2}-1] \ , \tag{2}$$

where $R=b/(3c)$ and $t_0=b^2/(ac)$. Then the second derivative of G with respect to T leads to the following expression for heat capacity;

$$C=\begin{cases} C_0 & T > T_{AC} \\ C_0 + AT(T_m - T)^{-1/2} & T < T_{AC} \ . \end{cases} \tag{3}$$

Here, C_0 is the background heat capacity obtained from G_0, $A=a^{3/2}/[2(3c)^{1/2}T_{AC}^{3/2}]$ and $T_m = T_{AC}(1+t_0/3)$, where T_{AC} is chosen to be the midpoint of the mean-field heat-capacity jump. In reduced temperature, t_0 is the full width at half-height of $(C-C_0)/T$ vs T curve.

Because the measurement of tilt angles requires a well aligned sample, it is much easier to obtain high-quality heat-capacity data than high-quality tilt-angle data. Consequently, the heat-capacity jump at T_c $[\Delta C_J = a^2/(2bT_{AC})]$ and the important parameter t_0 were obtained from the heat-capacity data. Equation (2) enables us to figure out the constant $R[=b/(3c)]$ from tilt-angle data. Thus, very careful heat-capacity studies have been carried out on seven different liquid-crystal compounds with an I-SmA-SmC (SmC^*) transition sequence. In Table I the parameters t_0 and ΔC_J obtained from the heat-capacity measurements are listed along with T_{AC} and T_{IA}. Here, T_{IA} is the I-SmA transition temperature. A plot of t_0 vs $r_{AC}(=1-T_{AC}/T_{IA})$ is given in Fig. 1. For these seven different compounds which have been studied, there seems to exist one general relation between t_0 and r_{AC}. Furthermore, for the compounds with small temperature ranges for the SmA phase, an approximately linear relationship exists between t_0 and r_{AC}. The value of t_0 for HOBACPC, which has the largest value of r_{AC} among these compounds, cannot be determined accurately. The small temperature range for the SmC^* phase and the large heat-capacity anomaly associated with the SmC^*-SmI^* transition make the determination of t_0 nontrivial.[10] Nevertheless, the value of t_0 for HOBACPC may represent the asymptotic value of t_0 for large values of r_{AC}. A linear least-squares fit to the rest of the six data points gives $t_0 = -2.0\times10^{-4} + 6.23\times10^{-2}(1-T_{AC}/T_{IA})$. This result suggests that as T_{AC}/T_{IA} increases toward one, the parameter t_0 decreases toward zero. This does not necessarily imply that b approaches zero, as the mean-field-tricritical point requires, because the parameter c and/or a can be abnormally large with b remaining finite such that t_0 apparently approaches zero. To get further insight into this point, existing tilt-angle data from four compounds[13–15] were used to determine the parameter R [in the unit of (radian)^2]. Then the following three relations—$t_0=b^2/ac$, $\Delta C_J = a^2/(2bT_{AC})$, and $R=b/(3c)$—enable us to calculate all three coefficients, i.e., a, b, and c. The results are listed in Table II. With the exception of MBRA8, the coefficients of the other three compounds monotonically decrease as T_{AC}/T_{IA} increases. In the case of MBRA8, the coefficients a and b are comparable to that of HOBACPC, but the coefficient c is about 30 times larger.[16] This is the major reason that t_0 of MBRA8 is so small.

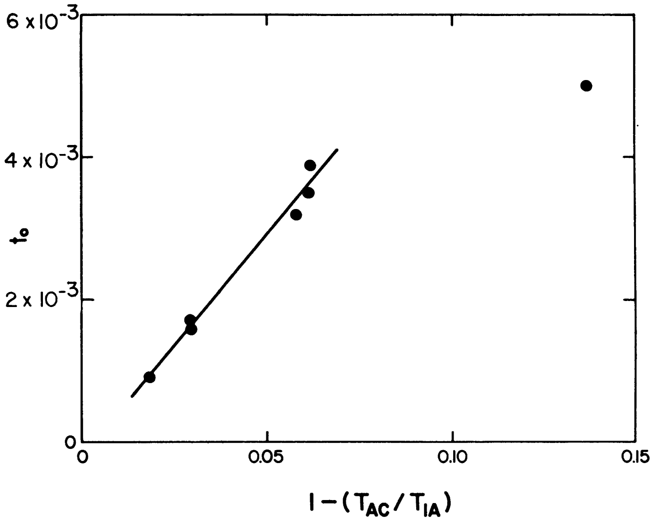

FIG. 1. Plot of t_0 vs $(1-T_{AC}/T_{IA})$ for seven different liquid-crystal compounds. The solid line is the best linear least-squares fit to six data points with small value in $(1-T_{AC}/T_{IA})$.

In analyzing both the x-ray and heat-capacity data near the SmA-SmC transition line of $(\overline{8}S5)_{1-x}-(\overline{7}S5)_x$ mixtures, we have found a linear relationship between t_0 for the mean-field SmA-SmC transition and T_{AC}/T_{NA}.[6] Here, $\overline{7}$S5 refers to heptyloxy-p'-pentylphenylthiolbenzoate. Similarly, the parameter t_0 decreases toward zero as T_{AC}/T_{NA} approaches one, i.e., the temperature range for the SmA phase vanishes. Further data analysis demonstrates that the smallest value of t_0, found in the mixture with $x=0.42$, in which the SmA phase only exists in a very small temperature interval ($\simeq 0.3$ K), is due to the increase in coefficients a and c, but not the decrease in the coefficient b.[17] Similar to what we have found here, the coefficient b actually increases relative to the general trend as t_0 becomes small enough.

There exist several high-resolution heat-capacity measurements on the SmA-SmC transition of pure compounds with an I-N-SmA-SmC transition sequence.[3,5,8] Among these

TABLE II. Coefficients of Landau free energy. a, b, and c in J/mole.

Compound	R	$a\times10^{-3}$	$b\times10^{-2}$	$c\times10^{-3}$
HOBACPC	1.7×10^{-2}	19	19	36
DOBAMBC	2.8×10^{-2}	3.5	1.4	1.6
AMC-11	1.7×10^{-2}	1.8	0.58	1.1
MBRA8	0.11	13	35	1100

compounds no systematic behavior of t_0 could be found. This observation suggests that the simple Landau theory,[18] by including coupling of the nematic ordering to tilt angle, is not sufficient to describe the general behavior we reported here.

Thus, by far most of the experimental work on phase transitions has been carried out on systems with given transitions, which bear the interesting critical phenomena, being well separated from the other transitions. In other words, the disordered phase, associated with a given continuous phase transition at T_c, may undergo another transition, occurring at a higher temperature T_1, to a more disordered phase. Usually these two transition temperatures, i.e., T_c and T_1, are well separated and the ratio T_c/T_1 is much smaller than one. In the case of liquid crystals, a cascade of transitions from the isotropic phase to various mesophases can occur in a relatively narrow temperature range. This will provide us with unique cases to investigate the effect of one transition on the other transition in a systematic way. Here, the possible general behavior between t_0 and T_{AC}/T_{IA} clearly demonstrates that the ratio (T_{AC}/T_{IA}) affects the behavior of the Sm*A*-Sm*C* transition in an important way. For the seven compounds reported here, there are four chiral compounds, one racemic version, and two other kinds. As far as the molecular structures are concerned, one compound (AMC-11) is not an aromatic mesogen and the rest of the six compounds have four entirely different aromatic arrangements in the central parts of their molecules. The variety of the molecular structures among these seven compounds leads us to believe that the relation between t_0 and T_{AC}/T_{IA} is a general one and independent of the molecular structure.

In the light of the recent results on the *N*-Sm*A* transition,[19,20] we would suggest that before r_{AC} reaches zero, the Sm*A*-Sm*C* transition will be driven to become first order by the large fluctuations of the nearby *I*-Sm*A* transition. Thus, the IAC point, where isotropic, Sm*A*, and Sm*C* phases coexist, is an ordinary triple point. Then along the Sm*A*-Sm*C* transition line of various liquid-crystal compounds, there may exist one fluctuation-induced tricritical point. In the vicinity of this tricritical point, the mean-field model, proposed by us to describe the Sm*A*-Sm*C* transition, should fail and the corresponding Landau coefficients become meaningless. The observed anomalous behavior in the Landau coefficients of MBRA8 may indicate the closeness of this compound to the fluctuation-induced tricritical point.

Further experimental work is in progress to confirm this possible general behavior and to study the behavior of the Sm*A*-Sm*C* transition as r_{AC} decreasing.

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[16] 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 $c\Psi^6$ unjustifies. The measured tilt angle at $T_{AC}-T\simeq 25$ K is about 7°($\simeq 0.12$ rad). Consequently, at this temperature the three leading terms in the Landau free-energy expansion (i.e., at Ψ^2, $b\Psi^4$, and $c\Psi^6$) have values of 14.5, 0.73, and 3.17 J/mole, respectively. Thus, even in this wide temperature range the expansion up to $c\Psi^6$ is a reasonable approximation.

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