# Measurements of tilt angle and heat capacity in the vicinity of one smectic-$A$–chiral–smectic-$C$ transition

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Both high-resolution heat-capacity and tilt-angle measurements have been carried out near the smectic-$A$–chiral–smectic-$C$ transition of $p$-($n$-decyloxy) benzylidene-$p$-amino-(2-methylbutyl)cinnamate (DOBAMBC). The extended mean-field theory, suggested by Huang and Viner, for the smectic-$A$–smectic-$C$ (or chiral–smectic-$C$) transition, requires a unique relationship between the tilt angle and the anomalous part of the heat capacity. Here we demonstrate this relationship by our experimental results on both heat capacity and tilt angle. This provides a strong additional support for the extended mean-field model in describing the smectic-$A$–chiral–smectic-$C$ transition.

The smectic-$A$ (Sm$A$) and smectic-$C$ (Sm$C$) liquid-crystal mesophases may be characterized as orientationally ordered two-dimensional fluids with one-dimensional mass density waves.[1] The wave vector is either along (Sm$A$) or at an angle (Sm$C$) to the unique orientational axis (long axis of the molecule). If the constituent molecules are optically active, the chiral–smectic-$C$ (Sm$C^*$) phase will be observed instead of the Sm$C$ phase.[2] In the Sm$C^*$ phase, as a consequence of the molecular chirality, the long axis of the molecule exhibits a helical structure precessing around the direction of the one-dimensional mass density wave. If the molecule has net transverse dipole moment, there will be spontaneous polarization within each smectic layer. From a symmetry argument,[2] the net spontaneous polarization will point in a direction perpendicular to both the mass density wave vector and the long axis of the molecule. Consequently, with a sufficiently high applied electric field, one can unwind the helix through the coupling between the polarization and the electric field. Reversing the applied electric field will reverse the polarity of the spontaneous polarization and change the molecular tilt angle from $\theta$ to $-\theta$, or equivalently change the azimuthal angle of the molecular tilt direction from $\phi$ to $\phi + 180°$. This is the mechanism behind our tilt-angle measurement in the Sm$C^*$ phase of $p$-($n$-decyloxy)benzylidene-$p$-amino-(2-methylbutyl)cinnamate (DOBAMBC).

In decreasing temperature many liquid-crystal compounds exhibit second-order Sm$A$-Sm$C$ (or -Sm$C^*$) transitions. Based on the symmetry of the order parameter (tilt angle in both Sm$A$-Sm$C$ and Sm$A$-Sm$C^*$ transitions), de Gennes[3] placed these transitions in the universality class of superfluid helium, that is, the three-dimensional $XY$ model. Applying Landau-Ginzburg criterion to their x-ray data on one liquid-crystal compound, Safinya et al.[4] argued that the heat-capacity jump at the transition temperature, measured by Johnson and co-worker,[5] and bare correlation lengths characterizing tilt-angle fluctuations are sufficiently large that the critical region is very small and beyond the existing experimentally accessible region. Later on, Huang and Viner[6] have pointed out the importance of adding the sixth-order term in the Landau free-energy expression in order to provide a quantitative explanation of their heat-capacity data obtained near one Sm$A$-Sm$C$ transition. Afterward the significance of the sixth-order term has been further confirmed in all the materials being studied near the

Sm$A$-Sm$C$ (or -Sm$C^*$) transition.[7–9]

In order to additionally test the validity of the extended mean-field model, suggested by Huang and Viner,[6] in describing the Sm$A$-Sm$C$ (or -Sm$C^*$) transition, we have carried out high-resolution experiments on both the tilt angle and the heat capacity of DOBAMBC near its Sm$A$-Sm$C^*$ transition. The DOBAMBC sample was purchased from Frinton Laboratories and was recrystallized twice from methanol. Details of our heat-capacity measurement procedure have been published elsewhere.[10] The measured heat capacity per unit area (sample thickness 36 $\mu$m) after subtracting the sample cell and addendum contribution is shown in Fig. 1 as a function of temperature.

The well-aligned DOBAMBC liquid-crystal sample in planar configuration was grown between a pair of glass slides which were coated with transparent and conducting indium-tin-oxide films. To achieve high-quality alignment, the glass slides were spin coated with nylon and then rubbed on cotton cloth.[11] Then the molecular tilt angle was measured by an electro-optical technique with dc applied electric fields. In the Sm$C^*$ phase, the long axis of the molecule can be switched by changing the polarity of an external applied field. Then the principal axes of the liquid-crystal sample cell could be determined from the measured angles as the cell was rotated between one pair of cross polarizers. A minimum amplitude of the electro-optical response would be detected when the molecular director was parallel or perpendicular to the principal optical axis of the polarizers. In order to reduce the finite field effect on the tilt angle, at a given temperature the tilt angles were measured with at least four different applied electric fields. An extrapolation to the zero-field limit is shown in our reported tilt-angle data which are shown in Fig. 2 as a function of $(T_c - T)$. Here $T_c$ is the Sm$A$-Sm$C^*$ transition temperature. Qualitatively, our result agrees with the one reported by Ostrovskii et al.[12]

The extended mean-field model has the following free-energy expansion near the Sm$A$-Sm$C$ (or -Sm$C^*$) transition:

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

where $\Psi = \theta e^{i\phi}$ is the order parameter and $\theta$ and $\phi$ are the molecular tilt angle and azimuthal angle. The reduced temperature $t = (T - T_c)/T_c$. $G_0$ is the nonsingular part of the
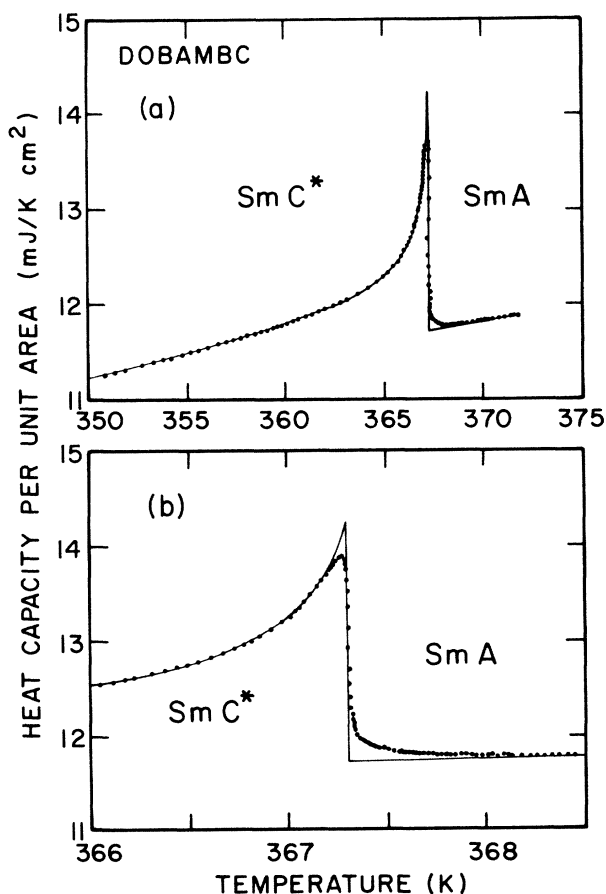
FIG. 1. Heat capacity per unit area (sample thickness 36 $\mu$m) as a function of temperature near the Sm$A$-Sm$C^*$ transition of DOBAMBC. Dots: experimental data; solid line: best fit to Eq. (3). (a) The data are plotted in the entire measured temperature range. (b) The data close to $T_c$ are displayed to show the rounding effect near $T_c$.

free energy, and the constants $(a,b,c) > 0$ for a continuous transition. After minimizing $G$ with respect to $|\Psi|$, $|\Psi|$ is zero for $T > T_c$, and we have

$$|\Psi| = \{(b/3c)[(1-3t/t_0)^{1/2}-1]\}^{1/2} \qquad (2)$$

for $T < T_c$, where the dimensionless parameter $t_0 = b^2/(ac)$. The second derivative of $G$ with respect to $T$ leads to the following expression for heat capacity:

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

Here $C_0$ is the background heat capacity obtained from $G_0$, $A = a^{3/2}/[2(3c)^{1/2}T_c^{3/2}]$, and $T_m = T_c(1+t_0/3)$, where $T_c$ is chosen to be the midpoint of the mean-field heat-capacity jump. Our measured $T_c$ is 94.15 °C. Because of a wide temperature range ($\sim 22$ K) for our data, we used $C_0 = B + Dt + Et^2$ as our background term. The fitting of heat-capacity data to Eq. (3) are shown as a solid line in Fig. 1. The fitting is very good except very close to $T_c$, where some roundings exist. So far, we have studied six different liquid-crystal compounds near the Sm$A$-Sm$C^*$ transitions of chiral compounds or the Sm$A$-Sm$C$ transitions of racemic mixtures.[9] All these compounds have shown much larger
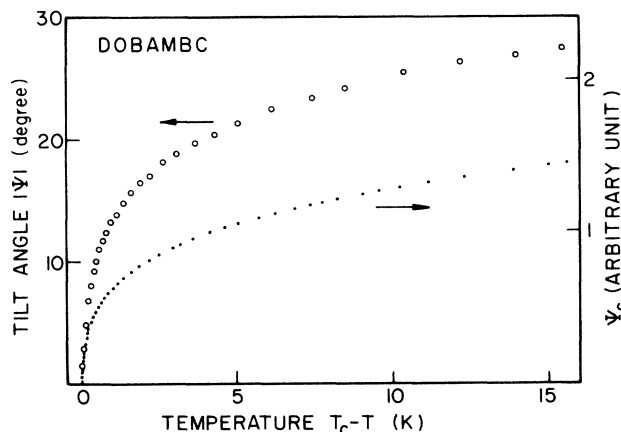


FIG. 2. Measured tilt angle (open circle) and calculated $\Psi_c$ (solid dot) (see the text for the calculation) are plotted as a function of $(T_c - T)$.

excess heat capacity above the mean-field expression for $T > T_c$ than our results on the Sm$A$-Sm$C$ transition of heptyloxybenzylidene butylaniline (70.4), which does not contain any optically active part. Based on this fact, we believe that the rounding is not caused by our measurement technique and may be caused by a small amount of optical isomers existing in the chiral liquid-cyrstal compounds and acting like impurities.

Furthermore, within the extended mean-field model, there exists one unique relationship between the order parameter $|\Psi|$ and the anomalous part of heat capacity $\Delta C (= C - C_0)$, i.e.,

$$|\Psi| = \left[ \frac{T_c}{a} \int_T^{T_c} \frac{\Delta C}{T} dT \right]^{1/2} . \qquad (4)$$

In order to check this important relationship, we have calculated

$$\Psi_c = \left[ \int_T^{T_c} \frac{\Delta C}{T} dT \right]^{1/2}$$

from our heat-capacity data. The result is also shown in Fig. 2. The temperature dependence of $\Psi_c$ looks similar to that of the tilt-angle data. In Fig. 3, the ratio $|\Psi|/\Psi_c$ is plotted as a function of $(T_c - T)$. It is obvious that $|\Psi|/\Psi_c$ remains fairly constant over more than two and a half de-
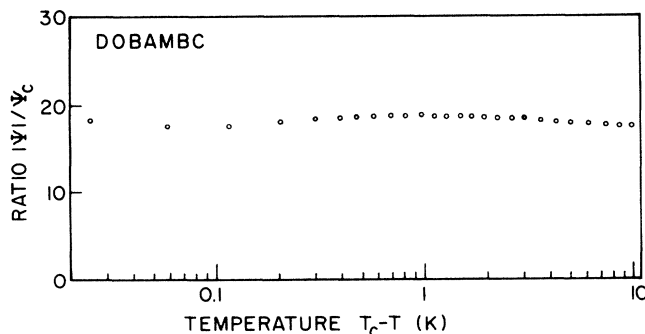


FIG. 3. The ratio $|\Psi|/\Psi_c$ is plotted as a function of $(T_c - T)$.

cades in $(T_c - T)$. This confirms the relationship in Eq. (4) and provides additional strong support for the validity of the extended mean-field model for the Sm$A$-Sm$C$ (or -Sm$C^*$) transitions. To the contrary, in the three-dimensional $XY$ model, the anomalous part of heat capacity and the order parameter have the following temperature dependence:

$$\Delta C = A_0 |t|^{-\alpha}$$

and

$$|\Psi| = \Psi_0 |t|^{\beta} \quad ,$$

with $\alpha \simeq -0.02$ and $\beta = 0.35$. The simple relation [Eq. (4)] does not hold in this model.

In conclusion, additional measurements have been carried out to support the extended mean-field model in describing the Sm$A$-Sm$C$ (or -Sm$C^*$) transition. Theoretically, to our knowledge, only in two cases one can, a priori, predict a mean-field-like behavior for a given phase transition. First, the spatial dimension of the system is equal to or higher than the upper critical dimensionality of the given ordering at the transition. One typical example is the paramagnetic-ferromagnetic transition of LiTbF$_4$ (Ref. 13). Secondly, the ordering near the given transition has a large bare correlation length; in other words, it has long-range interaction associated with the order parameter ordering. The examples

are normal-superconducting transition and Jahn-Teller–type transition mediated by acoustic phonons (e.g., TmVO$_4$) (Ref. 14). With its bare correlation lengths[8] slightly larger than those of smectic-$A$ ordering near the nematic-Sm$A$ transition,[15] the Sm$A$-Sm$C$ (or -Sm$C^*$) transition does not satisfy those two criteria for being mean-field like. In other words, in comparison with the fluctuation-dominant nematic-smectic-$A$ transition, why is the heat-capacity jump at the Sm$A$-Sm$C$ (or -Sm$C^*$) transition so large such that the critical fluctuation region is diminishingly small ($\leq 10^{-7}$ in reduced temperature) for the Sm$A$-Sm$C$ (or -Sm$C^*$) transition? The importance of the $|\Psi|^6$ term may be related to a relatively "small" temperature range for the Sm$A$ (disordered phase) temperature range.[9] Theoretical understanding of the smallness of the critical fluctuation region, with a large $|\Psi|^6$ term in free-energy expansion for the Sm$A$-Sm$C$ (or -Sm$C^*$) transition, is very important.

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