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# Heat-capacity studies near the smectic-*C*–smectic-*I* transition of two liquid-crystal compounds

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Detailed heat-capacity studies have been carried out in the vicinity of the smectic-*C*–smectic-*I* transition of two liquid-crystal compounds in the homologous series of racemic 4-(2′-methylbutyl)phenyl-4′-*n*-alkyloxybiphenyl-4-carboxylate (2M4P*m*OBC or *m*OSI). In contrast to the continuous smectic-*A*–hexatic-*B* transition found in many members of *n*-alkyl-4′-*n*-alkyloxybiphenyl-4-carboxylate (*nm*OBC) with symmetric and sharp heat-capacity anomalies, asymmetric and rounded ones are observed in the smectic-*C*–smectic-*I* transitions of both 2M4P8OBC and 2M4P9OBC.

The term "hexatic phase," which characterizes a two-dimensional (2D) phase with a long-range bond-orientational order and a short-range positional order, was invented in the theoretical investigations of the 2D melting processes by Halperin and Nelson around 1978.[1] Soon after that, the existence of the stacked hexatic phase in liquid-crystal materials was suggested by Birgeneau and Litster.[2] About the same time, employing the x-ray diffraction, two research groups[3] identified two liquid-crystal mesophases with a pseudohexagonal molecular in-plane packing and short-range positional order. Those two mesophases, namely, the smectic-*I* and smectic-*F* phases, turn out to be the tilted versions of the stacked hexatic phase. Both the smectic-*I* (Sm*I*) and smectic-*F* (Sm*F*) phase have a layer structure with a short-range interlayer and intralayer positional correlation and a long-range bond-orientational order. The difference between these two phases is that the long axes of the molecules tilt toward their nearest neighbors in the Sm*I* phase and toward the midpoint of the line joining nearest neighbors in the Sm*F* phase.

In the investigation of 2D melting of rodlike molecules, Nelson and Halperin[4] realized that the molecular tilt order is coupled to and can induce the bond-orientational order. Bruinsma and Nelson[5] have worked out a mean-field theory for the phase transitions between three-dimensional (3D) smectic phases. An important conclusion of the theory is that the smectic-*C*–Sm*I* (or –Sm*F*) transition cannot be a sharp one. The long-range molecular tilt order existing in the smectic-*C* (Sm*C*) phase will induce a long-range bond-orientational order through the coupling term between these two order parameters. Consequently, the Sm*C*-Sm*I* (or -Sm*F*) transition is similar to the paramagnetic-ferromagnetic transition in a nonzero applied magnetic field. If the coupling constant is temperature independent and the molecular tilt angle remains constant in the vicinity of the Sm*C*-Sm*I* (or -Sm*F*) transition, then the ordered field may be constant through the transition. Under this circumstance, the Sm*C*-Sm*I* (or -Sm*F*) transition will be more predictable than the one with a varying ordered field, e.g., through the variation of the tilt angle near or at the transition temperature. Thus the compound with a large Sm*C* phase temperature range will have a saturated molecular tilt angle just above the Sm*C*-Sm*I* (or -Sm*F*) transition and is a better candidate for the experimental investigation of these phase transitions. Several members of the homologous series of racemic 4-(2′-methylbutyl)phenyl-4′-*n*-alkyloxybiphenyl-4-carboxylate (2M4P*m*OBC or *m*OSI) have large temperature ranges for the Sm*C* phase. For example, the temperature ranges of the Sm*C* phase are 56 and 53 K for the compounds 9OSI and 8OSI, respectively. Here we will report our investigation of the nature of the Sm*C*-Sm*I* transition of both 9OSI and 8OSI compounds.

Soon after they demonstrated that the smectic-*A*–hexatic-*B* (Sm*A*-Hex*B*) transition of 65OBC was a continuous one with a large heat-capacity critical exponent,[6] Viner and Huang[7] investigated the heat-capacity anomaly associated with the Sm*C*-Sm*I* transition of 9OSI. Here 65OBC is one member of the homologous series of *n*-alkyl-4′-alkoxybiphenyl-4-carboxylate (*nm*OBC). In contrast to the case of the Sm*A*-Hex*B* transition, the Sm*C*-Sm*I* of 9OSI has a rounded and asymmetric heat-capacity anomaly. They conclude that the difference between the Sm*A*-Hex*B* and the Sm*C*-Sm*I* transition is caused by the coupling of the molecular tilt and bond-orientational order. Such a coupling does not exist in the Sm*A*-Hex*B* transition. Recently Brock and co-workers[8] have carried out an excellent x-ray diffraction experiment in the vicinity of the Sm*C*-Sm*I* transition of 8OSI and found the existence of weak bond-orientational order above the Sm*C*-Sm*I* transition. Furthermore, they found that the molecular tilt angle remains constant through the Sm*C*-Sm*I* transition.[9] Consequently, the compound 8OSI is a good candidate for exploring the nature of the Sm*C*-Sm*I* transition.

Here we will report our high-resolution heat-capacity study on the Sm*C*-Sm*I* transition of 8OSI. The details of our calorimetric measurement technique have been published elsewhere.[10] The measured heat capacity per unit volume of the 8OSI sample in the vicinity of the Sm*C*-Sm*I* transition is shown in Fig. 1(a). For comparison, in the same temperature interval Figs. 1(b) and 1(c) display the heat-capacity anomalies of the 9OSI compound near its Sm*C*-Sm*I* transition[7] and the 37OBC compound near its Sm*A*-Hex*B* transition,[11] respectively. Obviously, one can see that the Sm*A*-Hex*B* transition has a much sharper heat-capacity anomaly than the Sm*C*-Sm*I* transition does. The asymmetry in the heat-capacity anomalies associated with the Sm*C*-Sm*I* transition are very clear. Both the 8OSI and 9OSI show a slower drop in heat capacity on the low-temperature side of the anomaly than that on the high-temperature side.

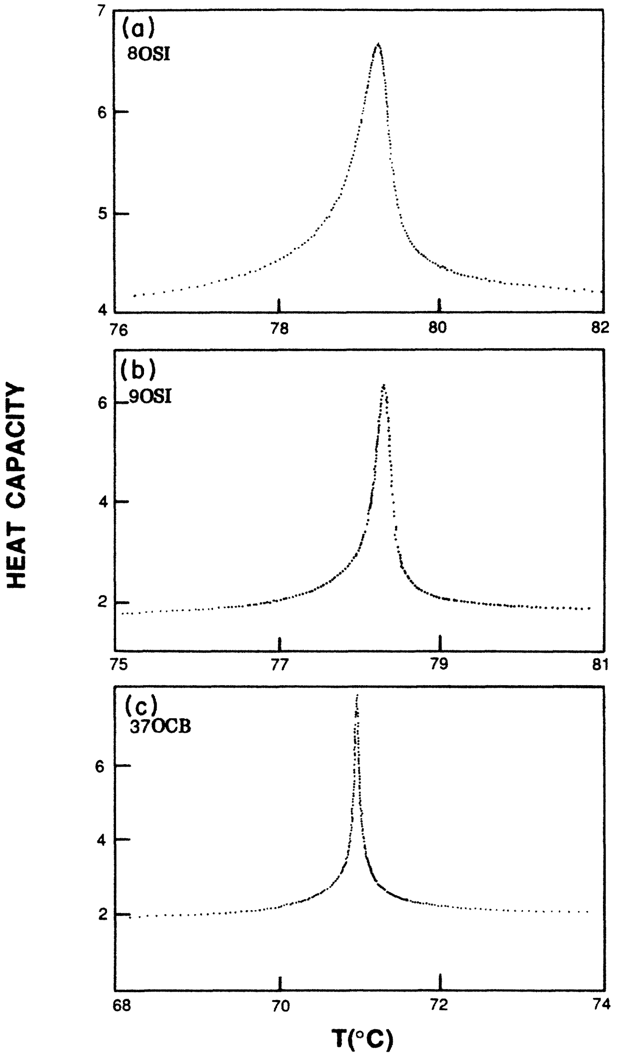

FIG. 1. Temperature variation of heat capacity near the Sm*C*-Sm*I* transition 2M4P8OBC (8OSI) (a) and 2M4P9OBC (9OSI) (b) and the Sm*A*-Hex*B* transition of 37OBC (c), respectively. Both 8OSI and 37OBC, we have measured the sample thickness and the unit for heat capacity is $J/\mathrm{cm}^3\,\mathrm{K}$. Without information of the sample thickness for 9OSI, the heat capacity is displayed in arbitrary units.

Our heat-capacity data near the Sm*A*-Hex*B* transition of many *nm*OBC compounds can be well described by a power-law expression with a small scaling correction term.[11] Assuming that the coupling between the molecular tilt and bond-orientational order is sufficiently small, the heat-capacity anomaly may still be described by a simple power law, namely,

$$C_p=\begin{cases} A^+|t|^{-\alpha}+B+Dt, & T>T_c \\ A^-|t|^{-\alpha}+B+Dt, & T<T_c\ . \end{cases} \tag{1}$$

The nonlinear least-squares fitting of our data to this power law over slightly less than two decades is displayed in Figs. 2(a) and 2(b) for 8OSI and 9OSI, respectively. The fitting results are $\alpha=0.52$ and $A^+/A^-=0.62$ for 8OSI and $\alpha=0.76$ and $A^+/A^-=0.59$ for 9OSI. It is obvious that the fitting results are more reasonable for both compounds on the high-temperature side. The fitting results seem to suggest that the ordered field for both 8OSI and 9OSI is sufficiently weak such that the simple power-law remains a reasonable approximation in the region $T-T_c>0.1$ K.[12] Just like the Sm*A*-Hex*B* transition,[13] a large value of the critical exponent $\alpha$ is found in the Sm*C*-Sm*I* transition, but we don't have a good explanation for why the values of $\alpha$ for 8OSI and 9OSI have such a large difference. In principle, if the ordered field is constant throughout the transition region,

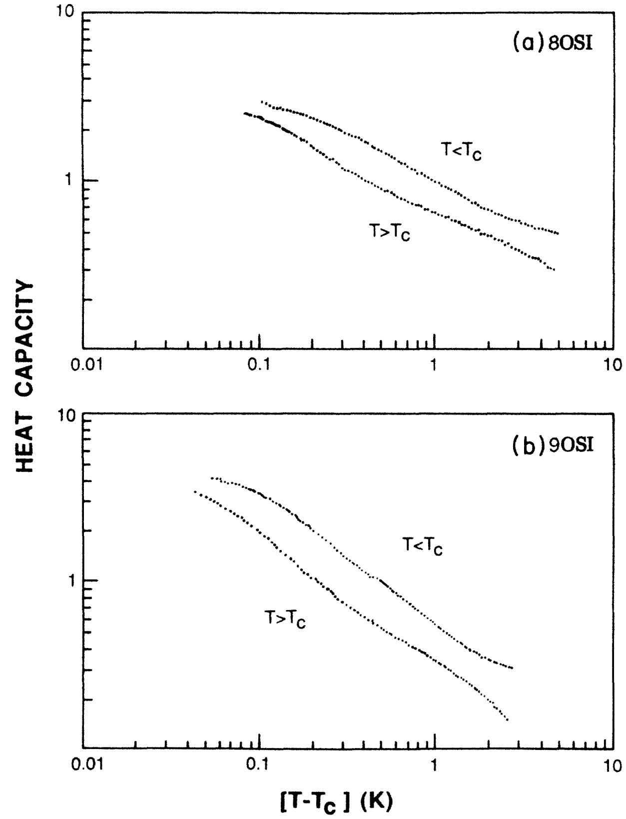

FIG. 2. Anomalous part of the heat capacity $\Delta C_p=C_p-B-Dt$ vs $|T-T_c|$ for 2M4P8OBC (8OSI) (a) and 2M4P9OBC (9OSI) (b) near the Sm*C*-Sm*I* transition, respectively.

one should be able to carry out the fitting to the heat-capacity data with some model.

Using the parametric representations suggested by Schofield[14] and the "linear model" approximation,[15] we have derived an expression for the heat capacity in the presence of a weak coupling field. To lowest order in the coupling $h$, the expression is

$$C_h \simeq A\,|t|^{-\alpha}\left[1+E\frac{h^2}{|t|^{2\beta\delta}}\right] . \qquad (2)$$

Here $\beta$ and $\delta$ are the usual critical exponents describing the asymptotic shape of the coexistence curve and critical isotherm, respectively. The relevant scaling relation among the exponents is $\alpha=2-\beta(\delta+1)$. To do a meaningful fit to this expression $\beta$ and $\delta$ should be known *a priori*[16] leaving $\alpha$ as a fitting parameter and the scaling form for $\alpha$ as a check for self-consistency.

Equation (2) will only be valid in a region far enough away from $T_c$ such that $Eh^2/|t|^{2\beta\delta} \ll 1$. As $T$ approaches $T_c$, there will be a crossover to a rounded, coupling-dominated regime at a temperature $|t_0| \simeq (Eh^2)^{1/2\beta\delta}$. For a rough approximation we may take $|t_0|$ as the temperature closest to $T_c$ which gave us a reasonable (i.e., smallest $\chi^2$) fit to Eq. (1), and we may estimate the relative strength of the coupling between tilt and bond-orientational order for the two compounds. Taking $|t_0|$ to be $2.8\times10^{-4}$ and $1.7\times10^{-4}$ for the 8OSI and 9OSI, respectively, one finds that the coupling field $h$ is roughly four times stronger in the 9OSI.[17] Although this estimate is relatively crude, it would be interesting to perform x-ray diffraction on 9OSI near its Sm*C*-Sm*I* transition to compare the strength of hexatic order just above the Sm*C*-Sm*I* transition of 9OSI with that of 8OSI.

One important difference in the heat-capacity anomaly between the Sm*A*-Hex*B* and Sm*C*-Sm*I* transition is that the former one has a much sharper anomaly than the latter one. There exist two possible sources of rounding for the Sm*C*-Sm*I* transition being reported here. First, as mentioned earlier, the intrinsic coupling between the tilt-angle and bond-orientation order will lead to a rounded Sm*C*-Sm*I* transition. Secondly, both 9OSI and 8OSI compounds are racemic mixtures of chiral compounds. From our experience in the investigations of the nature of the Sm*A*-Sm*C* (or -Sm*C**) transition, both the Sm*A*-Sm*C** transition and the Sm*A*-Sm*C* from the racemic compounds show more rounded mean-field transitions than the Sm*A*-Sm*C* transition from nonchiral compounds. For example, widths in the reduced temperature of the 10%–90% mean-field heat-capacity jump are about $6\times10^{-5}$ and $9\times10^{-4}$ for 70.4 (Ref. 18) and 9OSI (Ref. 19), respectively. [Here 70.4 refers to *n*-(4-*n*-heptyloxybenzylidene)-4′-*n*-butylaniline.] For a compound with a chiral part, one can usually obtain samples only about 90% pure in the optically active part of the molecule. Comparing the Sm*A*-Sm*C* transitions from 70.4 and 9OSI we find that the rounding in the mean-field jump due to the impurities in the optically active part of the chiral compound increases roughly by sevenfold. In the case of the Sm*A*-Hex*B* and the Sm*C*-Sm*I* transition we will use the closest data point to the transition temperature which can be fitted to the simple power law as the criterion for the rounding. Then in the reduced temperature the rounding occurs about $4\times10^{-5}$ and $1.7\times10^{-4}$ for the Sm*A*-Hex*B* transition of 37OBC and the Sm*C*-Sm*I* transition of 9OSI, respectively. Approximately, this is about a fourfold increase in rounding. Thus we believe that the effect of the impurity rounding due to the impurities related to the optically active part of the molecules cannot be neglected in explaining the observed rounding in the Sm*C*-Sm*I* transition. Consequently, it would be much better to study the Sm*C*-Sm*I* (or -Sm*F*) transition in a nonchiral compound with a large Sm*C* phase temperature range and without a change in the tilt angle through the Sm*C*-Sm*I* transition. The second distinct feature shown in Figs. 1(a) and 1(b) is the slower increase in heat capacity on the Sm*I* side of the anomaly as a function of temperature. We believe that this is the result of coupling between the hexatic order and the molecule tilt angle. Judging from the quality of the fitting to the simple power-law expression, we do not know why this coupling seems to have a larger effect on the Sm*I* phase than on the Sm*C* phase.

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[12] The 8OSI data were fit with a $\chi^2$ of about 4, and the 9OSI data were fit with a $\chi^2$ of about 20. This would seem to indicate that the fit is better for the former, although this is not very apparent from Fig. 2. The relatively large $\chi^2$ for the 9OSI explains why the authors in Ref. 7 were unable to get a conver-

gent fit for the 9OSI data, as the technique used for this fitting is a bit more sophisticated. For reference, the 37OBC can be fit to Eq. (1) with a $\chi^2$ of about one over more than two decades in reduced temperature.

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[17] Taking $\beta \simeq 0.2$ (see Ref. 16) and using $\delta = (2-\alpha)/\beta - 1$ one obtains $\delta_{8\mathrm{OSI}} \simeq 6.4$ and $\delta_{9\mathrm{OSI}} \simeq 5.2$. Thus $[(Eh^2)_{8\mathrm{OSI}}]/[(Eh^2)_{9\mathrm{OSI}}] \simeq (|t_0|^{2\beta\delta}_{8\mathrm{OSI}})/(|t_0|^{2\beta\delta}_{9\mathrm{OSI}}) \simeq 0.055$. The coefficient $E$ can be expressed in terms of $\delta, \beta$ and the parameters $a$ and $k$ of the linear model. Since these are roughly the same for both compounds, $E$ will be the same order of magnitude in each case and we have $h_{8\mathrm{OSI}} \sim (0.23) h_{9\mathrm{OSI}}$. It is not clear, however, whether $\alpha$ for the 8OSI and 9OSI should be different, as the data suggest. If it is different, then the assumption that $\beta$ is the same is questionable. The above argument would stem from a picture in which $\beta$ were unaffected by the coupling $h$, but $\delta$ (and hence $\alpha$) were.

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