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Nematic–smectic-C heat capacity near the nematic–smectic-A–smectic-C point

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An ac calorimetric technique has been used to investigate the nematic (N)–smectic-C (SmC) transition near the N-SmA-SmC multicritical point in a mixture of heptyloxypentylphenylthiolbenzoate and octyloxycyanobiphenyl ($\bar{7}$S5+8OCB). The heat-capacity data are well described by a Landau model in which the first-order character is very weak. Thus there is a classical tricritical point along the SmC transition line at (or very close to) the N-SmA-SmC point. No calorimetric indications of a biaxial N' phase were observed.

Recent scattering experiments have provided a significant characterization of liquid-crystal phase-transition behavior near the nematic (N)–smectic-A (SmA)–smectic-C (SmC) point.[1,2] These investigations were carried out on mixtures of heptyloxypentylphenylthiolbenzoate ($\bar{7}$S5) and octyloxycyanobiphenyl (8OCB), a system whose phase diagram[1] exhibits a substantial region conforming to the universal N-SmA-SmC multicritical behavior[3] for the phase boundaries. However, the nature of this multicritical point is still not clearly established. There are two types of theoretical model for the N-SmA-SmC point. The original formulation of the first type by Chen and Lubensky[4] was a mean-field theory based on a single (infinite-dimensional) order parameter for smectic ordering, and this model predicted that the N-SmA-SmC point was a $d=3$, $n=2$ (XY), $m=2$ (two soft directions) Lifshitz point. The second type of model utilizes two order parameters (TOP), one for the smectic density and one for the SmC tilt.[5,6] In this case, Grinstein and Toner[5] have shown that the N-SmA-SmC point is a decoupled tetracritical point and that a biaxial nematic (N') phase should exist between the N and SmC phases (at least in the immediate vicinity of the N-SmA-SmC point). When fluctuations are included in the Chen-Lubensky (CL) model and the possibility of a N' phase is taken into account, the CL model gives rise to the same type of phase diagram as the Grinstein-Toner model with subtle differences "at" the N-SmA-SmC point which would be difficult to distinguish experimentally.[7]

Light scattering studies of $\bar{7}$S5+8OCB agree with both types of theoretical models, in that the elastic constant K_3 scales like the longitudinal correlation length $\xi_{\parallel}$.[2] However, the observed variations in K_3 and $\xi_{\parallel}$ near the N-SmA-SmC point are not accounted for in any of the existing theoretical models. X-ray scattering studies yield mass density fluctuations very near the N-SmA-SmC point that are well described by the original CL Lifshitz model[4] and are inconsistent with current versions of TOP models.[5] There is, however, the problem that one-loop self-consistent random-phase-approximation perturbation theory predicts that the $d=3$, $m=2$ Lifshitz point should occur at 0 K.[8] It should also be noted that neither light scattering[2] nor x-ray scattering[1] provides any indication of the biaxial nematic phase predicted for TOP models.

The goal of the present work is to characterize the heat-capacity behavior through the weakly first-order N-SmC transition near the N-SmA-SmC multicritical point. Our measurements were carried out on a $\bar{7}$S5+8OCB mixture with mole fraction $X_{8OCB}=0.01945$ (weight percent 1.506), which is very close to the N-SmA-SmC composition $X_{N\text{-}A\text{-}C}=0.0217$ (1.68 wt%).[1] The observed heat-capacity variation is well described by a Landau model with a substantial sixth-order term and a very small negative fourth-order term. It should be recalled that SmA-SmC transitions are second order with small positive fourth-order terms and significant sixth-order terms.[9,10] Thus, a Landau tricritical point must occur along the SmC transition line at or very close to the N-SmA-SmC point. The heat-capacity C_p data taken above the SmC phase give no indications of the presence of a biaxial N' phase. In particular, if the proposed N-N' transition actually exists, any thermal anomaly associated with this transition is too small to detect. This conclusion is supported by data from a recent adiabatic calorimetry study of $\bar{6}O\bar{8}+\bar{6}O\bar{1}0$ mixtures near the N-SmA-SmC point.[11]

Our ac calorimetric technique has been described elsewhere.[12] The N-SmC transition for 1.5 wt% 8OCB is monotropic. On cooling at a slow constant rate ($dT/dt \simeq -1.0$ K/h) from 335 K, the N phase freezes into the crystal K phase in the range 317.5–321 K. Subsequent cooling runs were carried out by cooling very rapidly from 335 to 320 K and then scanning through the region of the N-SmC transition at a rate of approximately -1.5 K/h. Three separate runs were in good agreement, with the N-SmC transition occurring at 314.9 K and the SmC phase freezing at $\sim$310.5 K. An overview of the C_p data from all of our runs is shown in Fig. 1. The inset gives the phase diagram in the range $X_{8OCB}=0$ to 0.0387 (3 wt%).[1,13] The specific heat $\bar{C}_p$ is displayed in Fig. 1 rather than the dimensionless quantity $\bar{C}_p/R$ (where $\bar{C}_p$ is the molar heat capacity). This choice is convenient since $\bar{C}_p$ values for liquid crystals away from any transition are fairly insensitive to molecular mass or structure; typical $\bar{C}_p$ values lie in the range 2.0–2.4 $\mathrm{J\,K^{-1}\,g^{-1}}$.

Figure 2 shows in detail the $\bar{C}_p$ variation near the N-SmC transition. For the scan rate used, each data point represents the specific heat averaged over a temperature range of $\sim$0.1 K. Data points below 311.6 K are not in-

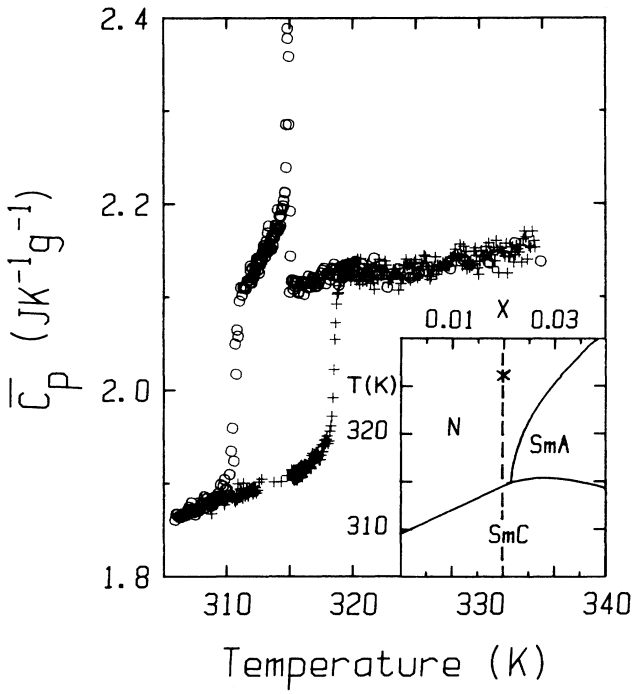

FIG. 1. Specific heat $\bar{C}_p$ for a 7S5+8OCB mixture with $X_{8OCB}=0.01945$ (1.506 wt%). All data were obtained on cooling; the drop of $\sim 10\%$ in $\bar{C}_p$ is associated with freezing of the sample into the crystal K phase. The + points were obtained on slow cooling runs and show $N \rightarrow K$ freezing. Open points obtained on rapid cooling runs show the monotropic $N \rightarrow$ SmC transition prior to Sm$C \rightarrow K$ freezing. The inset shows the phase diagram near the N-SmA-SmC point, where X denotes the mole fraction of 8OCB. Heat-capacity measurements were made along the path marked by a dashed vertical line.

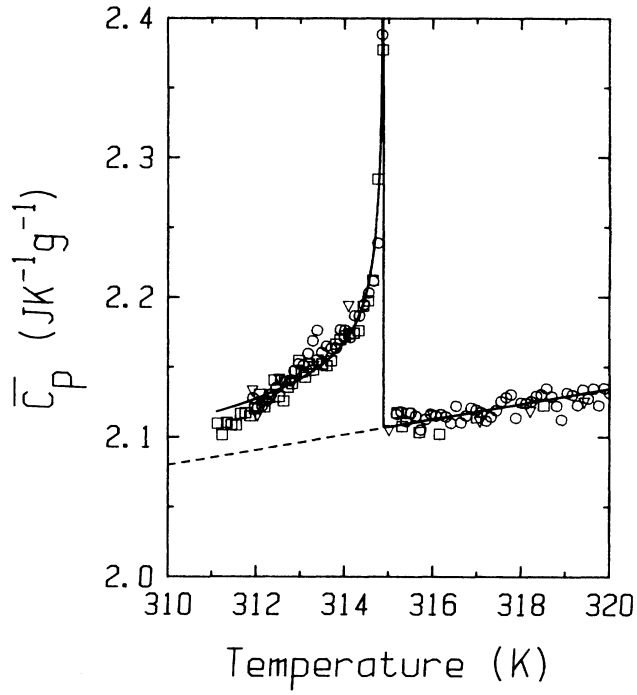

FIG. 2. Detailed view of the N-SmC specific-heat peak shown in Fig. 1. Data from three separate cooling runs are distinguished by different symbols. The line represents the best least-squares fit to the data with Eq. (2) and $\bar{C}_p^0=2.11+0.006(T-315)$, which was determined from the regular specific-heat variation observed in the nematic phase. The value of T_1 was taken to be 314.884 K, which lies at the center of the small gap between the points just above and just below the transition.

cluded since these points are influenced by the onset of freezing. The highly asymmetric $\bar{C}_p$ peak with no excess heat capacity above the transition is exactly what one expect from a Landau model near a tricritical point.[9,14]

The Landau free energy can be written as

$$\bar{G}=\bar{G}_0+at\psi^2+b\psi^4+c\psi^6 , \tag{1}$$

where $t\equiv(T-T_0)/T_0$, $\bar{G}_0$ is the free energy per gram in the disordered phase, and ψ is the order parameter. Explicit gradient terms are suppressed in Eq. (1); thus the coefficients a,b,c are effective values with $a>0$, $c>0$, and b allowed to be either positive, zero, or negative. It follows directly from Eq. (1) that below the transition temperature the excess specific heat $\Delta\bar{C}_p\equiv\bar{C}_p-\bar{C}_p^0$ and the order parameter are given by[14]

$$\Delta\bar{C}_p=A^*(T/T_0)(T_k-T)^{-1/2}\simeq A^*(T_k-T)^{-1/2} , \tag{2}$$

$$\psi^2=-(b/3c)+(2A^*/a)(T_k-T)^{1/2} , \tag{3}$$

where $T_k\equiv T_0+(b^2T_0/3ac)$ and $A^*\equiv(a^3/12cT_0)^{1/2}$. When $b>0$, a second-order transition takes place at T_0. When $b<0$, a first-order transition takes place at $T_1=T_0+(b^2T_0/4ac)$ and T_k represents the metastability limit for the ordered phase ($T_0<T_1<T_k$). When $b=0$, a Landau tricritical point occurs at $T_k=T_0$. It is sometimes convenient to rewrite Eq. (2) in either of the following forms:[9]

$$\Delta\bar{C}_p=2|A|\left(\frac{T}{T_0}\right)\left(\frac{T_k-T_1}{T_k-T}\right)^{1/2}$$
$$=|A|\left(\frac{T}{T_0}\right)\left(\frac{T_k-T_0}{T_k-T}\right)^{1/2} , \tag{4}$$

where $A=a^2/2bT_0$. Since (T/T_0) ranges from 0.99 to 1.015 for the present data, this trivial temperature dependence can be neglected in Eqs. (2) and (4) by setting (T/T_0) equal to unity.

In the analysis of second-order SmA-SmC transitions, it has become common to use a quantity $t_0\equiv b^2/ac=3(T_k-T_0)/T_0$. It is more convenient here for the analysis of a first-order N-SmC transition to introduce a parameter δ defined by

$$\delta\equiv b^2T_0/4ac=t_0T_0/4=(T_1-T_0)=3(T_k-T_1) . \tag{5}$$

Note that $2|A|\equiv A^*(3/\delta)^{1/2}$ is the value of $\Delta\bar{C}_pT/T_0\simeq\Delta\bar{C}_p$ at T_1 and $|A|$ is the value of $\Delta\bar{C}_p$ at $T_0=T_1-\delta$. In order to fit the $\bar{C}_p$ data, one needs the regular contribution $\bar{C}_p^0(T)$, which comes from the term $\bar{G}_0$ in Eq. (1), and the excess contribution $\Delta\bar{C}_p$ given by either Eq. (2) or (4).

The regular part is determined by fitting the observed $\bar{C}_p$ data in the nematic phase and extrapolating this linear variation below the transition (see Fig. 2). The most attractive choice for representing $\bar{C}_p$ is to use Eq. (2) with A^*, T_k, and T_1 as the adjustable parameters. The shape and size of $\Delta\bar{C}_p$ are fixed by the choice of A^* and T_k alone; the parameter T_1 only specifies the temperature where the excess heat capacity drops to zero.

The parameters for the least-squares fit shown in Fig. 2 are

$$A^* = 0.063\ \mathrm{J\,K^{-1}\,g^{-1}},\quad T_k = 314.907\ \mathrm{K}\ ; \tag{6}$$

T_1 can lie anywhere in the range 314.860–314.907 K (which represents the gap between T_k and the position of the point with the largest $\bar{C}_p$ value). Thus $(T_k - T_1) = \delta/3$ can have any value between 0 and 47 mK, or $0 < t_0 < 1.79\times10^{-3}$. This magnitude for t_0 at a first-order N-SmC transition is with the range of t_0 values $(0.5 - 6.5\times10^{-3})$ reported for second-order SmA-SmC transitions in typical pure liquid crystals[9] and in the $\bar{7}$S5+$\bar{8}$S5 mixture.[10] We believe that an even smaller upper bound on $(T_k - T_1)$ could be established if slower scans and therefore higher resolution near T_1 were possible, but the present data make it clear that the first-order character of the transition in a 1.5-wt.% sample is very weak. Thus a Landau tricritical point exists at (or very close to) the N-SmA-SmC multicritical point.

No pretransitional energy (entropy) fluctuations are observed in the N phase, in spite of the presence of large and unusual critical variations seen in $\xi_{\parallel}$ and $\xi_{\perp}$.[1,2] Two-scale-factor universality[15] allows us to show that these primarily SmA-like fluctuations in the N phase should not lead to an observable excess heat capacity. Measurements of $\Delta\bar{C}_p$ near the N-SmA transition in a 2.5-wt.% sample[16] combined with the correlation length variations measured at 1.5 and 2.5 wt.% (Ref. 13) indicate that $\Delta\bar{C}_p$ due to SmA fluctuations in the N phase should be less than 0.004 $\mathrm{J\,K^{-1}\,g^{-1}}$ for this 1.5-wt.% sample.

Our major conclusion is that the thermal behavior along the first-order N-SmC line evolves toward a tricritical point at (or near) the N-SmA-SmC point where it joins the second-order SmA-SmC line. Thus the N-SmA-SmC multicritical point exhibits simultaneously the characteristics of a Lifshitz point and those of a mean-field tricritical point. X-ray measurements of the temperature variation of the tilt angle[13] support this conclusion and are consistent with the Landau parameters found here. Earlier measurements[10,17] on the system $\bar{7}$S5+$\bar{8}$S5 ($\bar{8}$S5 is octyloxypentylphenylthiolbenzoate) are qualitatively consistent with this description although that system exhibits an unusually small multicritical N-SmA-SmC region and the tricritical nature of the heat capacity cannot be demonstrated. However, differential scanning calorimetry measurements on $\bar{7}$S5+$\bar{8}$S5 do indicate that the *latent heat* along the first-order N-SmC line approaches zero at (or very close to) the N-SmA-SmC point.[17] The combination of a N-SmC latent heat that goes to zero at the N-SmA-SmC point and a large asymmetric N-SmC heat-capacity peak near that point has also been observed in $\bar{6}\bar{O}\bar{8}+\bar{6}\bar{O}\bar{10}$ mixtures[11] and $\bar{5}\bar{O}\bar{8}+\bar{6}\bar{O}\bar{8}$ mixtures.[18] The present experiment does not rule out the possibility that the tricritical point could actually lie on either the N-SmC or SmA-SmC line very close to rather than exactly at the N-SmA-SmC point, but all the available information suggests that the SmC transition changes from first to second order *at* the N-SmA-SmC multicritical point.[1,2,10,11,13,17–19] Thus it appears that a more general treatment of multicritical Lifshift points in "incommensurate" liquid-crystal systems is needed, perhaps along the lines suggested in Ref. 20.

Finally, the data shown in Figs. 1 and 2 show no indication of a biaxial N' phase for a sample with $X = 0.01945$. It is perhaps possible such a phase exists but is stable only over a very narrow range of compositions extremely close to $X_{N\text{-}A\text{-}C}$. However, it should be noted that such a restricted N' phase will be difficult to observe due to the large SmA fluctuations above the N-SmA-SmC point. It seems more likely that the tricritical nature of the N-SmA-SmC point destroys the stability of the N' phase (which should exhibit layer orientational order among SmC cybotactic groups[7]).

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