Specific Heat near the Nematic-Smectic-*A* Tricritical Point

D. Brisbin, R. DeHoff, T. E. Lockhart, and D. L. Johnson
Physics Department and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242
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Specific-heat measurements near the nematic–smectic-*A* transitions of the octyloxy, nonyloxy, and decyloxy members of the 4-*n*-pentyl-phenylthiol-4′-alkoxybenzoate ($\bar{n}$S5) homologous series reveal the presence of critical-tricritical crossover behavior upon increasing $\bar{n}$, with $\bar{n}_t \sim \bar{9}$. The results are consistent with Alben's extension of de Gennes's superfluid analogy to include superfluid-He^3-He^4-like tricritical behavior.

The question of the existence of a nematic–smectic-*A* tricritical point has motivated interest among experimentalists for several years. Since the theoretical discovery by Kobayashi[1] and McMillan[2] that coupling between the nematic and smectic order parameters may drive this transition first order, there have been several experiments that strongly suggest such a point does exist on phase diagrams of temperature versus pressure[3] or concentration.[4,5] On the theoretical side, de Gennes[6] has written a Landau theory exhibiting coupling between the smectic order parameter and the nematic director. Based on this analogy, Halperin, Lubensky, and Ma[7,8] have made calculations which predicted that the nematic–smectic-*A* transition should always be first order, thus ruling out conventional tricritical behavior. In this Letter we report specific-heat and birefringence measurements which indicate that coupling to the nematic order parameter, in the manner of Kobayashi[1] and McMillan,[2] appears to produce a conventional tricritical point. Specifically, we have made measurements on three members of the $\bar{n}$S5 homologous series,[9] namely, $\bar{8}$S5, $\bar{9}$S5, and $\bar{10}$S5.

The specific-heat data were taken on a high-resolution ac microcalorimeter described elsewhere.[10,11] The $\bar{8}$S5 data were published previously.[10] The data for all three homologs are shown in Fig. 1, where the most striking feature is seen to be the profound increase in the strength of the anomaly as $\bar{n}$ increases from $\bar{8}$ to $\bar{10}$. This may be understood as a consequence of the decreasing nematic temperature range, as seen in Fig. 2, and the consequent increase in contribution from coupling between the nematic and smectic order parameters. In the microscopic theory this coupling leads to first-order behavior for $T_{NA}/T_{NI} > 0.87$.[2] Experimentally[4] this occurs at a somewhat higher value of T_{NA}/T_{NI} (i.e., for a

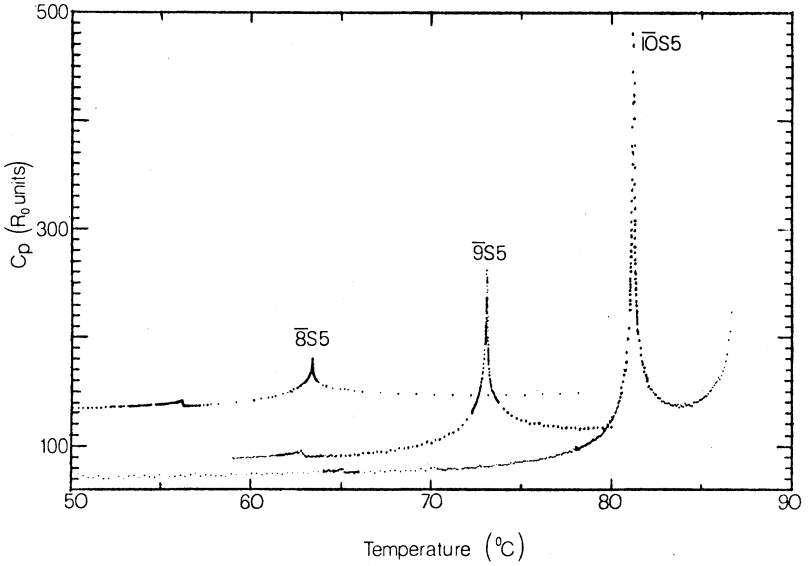

FIG. 1. Specific-heat data in units of the ideal-gas constant R_0, versus temperature for $\bar{8}$S5, $\bar{9}$S5, and $\bar{10}$S5. The very weak transition below the main nematic–smectic-*A* peaks are smectic-*A*–smectic-*C* transitions.

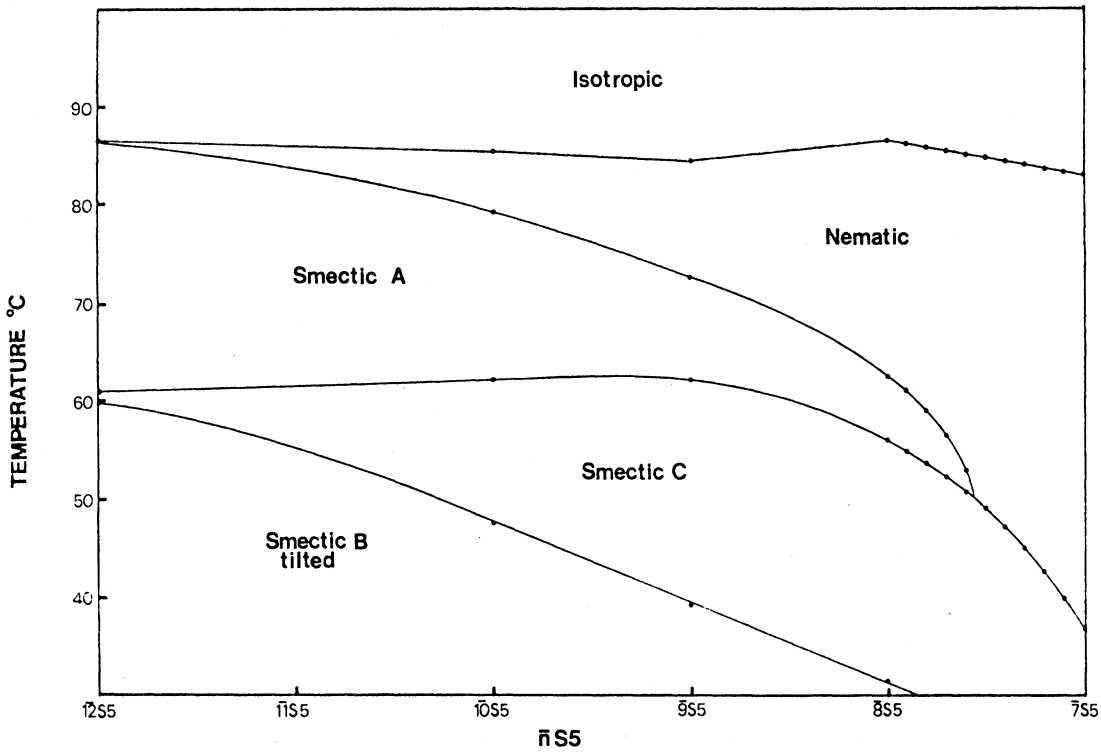

FIG. 2. Temperature versus $\bar{n}$ phase diagram for $\bar{n}$S5 homologous series. Fractional values of $\bar{n}$ between $\bar{7}$S5 and $\bar{8}$S5 correspond to binary mixtures of these compounds.

more narrow nematic range). The effect of such coupling has been illustrated by the following Landau theory[6]:

$$F = F_0 + \alpha|\psi|^2 + \tfrac{1}{2}\beta_0|\psi|^4 - C|\psi|^2\delta S + (1/2\chi)\delta S^2, \quad (1)$$

where $\alpha = \alpha_0(T - T_{NA})$, $\beta, C, \chi > 0$. $S = \langle\frac{1}{2}(3\cos^2\theta - 1)\rangle$ is the nematic order parameter,[12] where θ is the angle between the long molecular axis and the preferred molecular direction. $\delta S = S - S_0$, where S_0 is the value that S would take on in the absence of any short- or long-range smectic order. The negative sign before the coupling forces $\delta S > 0$ as observed experimentally.[13] Eliminating δS by setting $\delta F/\partial\delta S = 0$ gives

$$\delta S = C\chi|\psi|^2, \quad (2a)$$

and

$$F = F_0 + \alpha|\psi|^2 + \tfrac{1}{2}\beta|\psi|^4, \quad (2b)$$

where

$$\beta = \beta_0 - \tfrac{1}{2}C^2\chi. \quad (2c)$$

χ is the nematic susceptibility and is a function of the degree of saturation of the nematic order parameter and, therefore, of the "distance" in temperature below the nematic-isotropic transition T_{NI}. Thus if the nematic range is wide, $\chi(T_{NA})$ is small, $\beta > 0$, and the transition is second order. On the other hand, for a sufficiently narrow nematic range, $\chi(T_{NA})$ is large, $\beta < 0$, and the transition is first order. A tricritical point, $\beta = 0$, occurs when $\chi(T_{NA}) = 2\beta_0/C^2$. The growth of the specific-heat anomaly is reflected in the divergence of the specific-heat *discontinuity* as $\beta \to 0$. Specifically,

$$\Delta C(T_{NA}) = -\alpha_0^2/\beta = \alpha_0^2/(\tfrac{1}{2}C^2\chi - \beta_0). \quad (3)$$

Physically the growth of the anomaly arises because the nematic fluctuation entropy contained under the transition grows with $\chi(T_{NA})$.

The validity of this interpretation can be qualitatively tested by a measurement of the nematic order parameter, or a quantity proportional to it, near the nematic–smectic-A transition. We have measured the optical birefringence $\Delta n(T) = n_e - n_0 \sim S$ throughout the nematic and smectic-A ranges. The results are shown in Fig. 3. These data show quite clearly that Δn is enhanced by smectic order ($\delta S > 0$) by an amount that increases with $\bar{n}$,

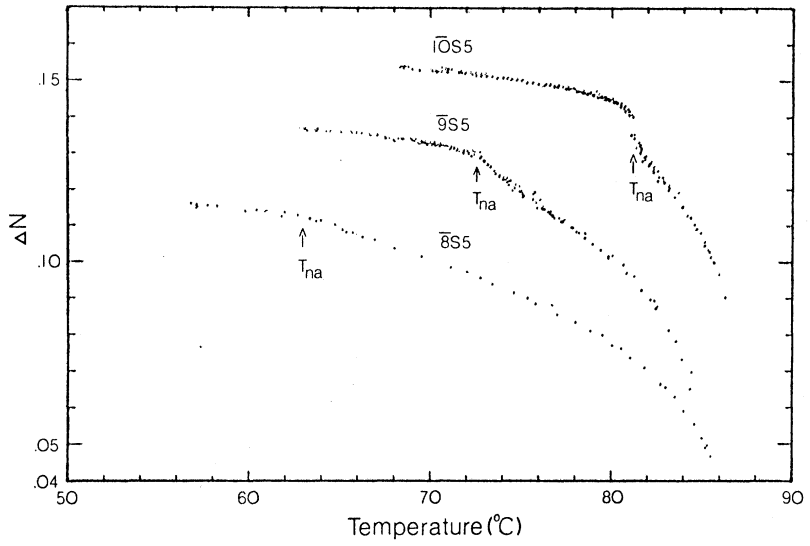

FIG. 3. Birefringence data ($\Delta n \equiv n_e - n_0$) vs temperature for $\overline{8}$S5, $\overline{9}$S5, and $\overline{10}$S5. The ordinate is correct for $\overline{10}$S5, whereas $\overline{9}$S5 and $\overline{8}$S5 data are shifted down by 0.02 and 0.05, respectively.

as predicted by Eq. (2a). In spite of the qualitative success of this simple Landau model, fluctuations clearly play an important role and mean-field theory is not adequate to describe these transitions. If one ignores the complication of director fluctuations[7,8] and also anisotropy, the problem reduces to that of superfluid helium which we shall show is consistent with our results. In this limit our system would be analogous to ^{3}He-^{4}He mixtures,[14] where coupling to concentration fluctuations drives the superfluid transition first order. The ^{3}He-^{4}He tricritical point separates the lambda line from a phase separation region in the T-X_3 (^{3}He concentration) plane; X_3 is the so-called nonordering density and the chemical-potential difference, Δ, between ^{3}He and ^{4}He is the conjugate field h.[15] In the present case, δS is the nonordering density, n, analogous to the concentration X_3. The field g conjugate to δS would be any that tends to align the long molecular axes such as a magnetic field.

To avoid dealing with renormalized exponents,[16] it is convenient to study critical-to-tricritical crossover phenomena in the T-g plane rather than the T-n plane. This was impossible in the ^{3}He-^{4}He experiments since $g = \Delta = \mu_3 - \mu_4$ cannot be controlled independently.[17] The liquid-crystal case is more favorable since one may independently apply a field g conjugate to the nonordering parameter, $n = \delta S$. As indicated above, this may be done by applying any field that couples to the orientation of the molecular long axis such as a magnetic or electric field. We have acted independently on δS by changing the number of CH_2 groups in the alkoxy chain of $\overline{n}$S5, i.e., by changing $\overline{n}$. Thus for our experiments we may consider $g = \overline{n}$; thus g is a discrete variable[18] and Fig. 2 is the T-g plane in which one may study critical-to-tricritical crossover of unrenormalized exponents. This tricritical model predicts[15] the specific-heat exponents to crossover from the superfluid ($n = 2, d = 3$) value of $\alpha = \alpha' \sim 0$ (log) for $\overline{n} < \overline{n}_t$, where n_t is the tricritical value of $\overline{n}$, to the tricritical value $\alpha_t = \alpha_t' \sim 0.5$ for $\overline{n} = \overline{n}_t$. We have analyzed the data shown in Fig. 1 for specific-heat exponents and the results are shown in Table I. The exponenst listed in Table I show that the ^{3}He-^{4}He superfluid model is consistent with our specific-heat results and that there appears to be a tricritical point at $\overline{n}_t \gtrsim \overline{9}$. Whereas for $\overline{8}$S5 we found no evidence of first-order behavior, i.e., of a two-phase region, we do find a very

TABLE I. Results of analysis of $\overline{n}$S5 specific-heat data. Scaling ($\alpha = \alpha'$) was statistically allowed by the data and was assumed in determing the values listed here. Here $t \equiv (T - T_c)/T_c$, and $\alpha \equiv \alpha' = 0$ (log) denotes a logarithmic divergence.

$\overline{n}$S5	$\alpha = \alpha'$	$T_c - T_c'$ (K)	t_{min}	t_{max}
$\overline{8}$S5	0.0 (log) ± 0.02	0 ± 0.007	6.8×10^{-5}	4.9×10^{-3}
$\overline{9}$S5	0.22 ± 0.03	0.002 ± 0.01	1.3×10^{-4}	2.3×10^{-2}
$\overline{10}$S5	0.45 ± 0.05	0.02 ± 0.01	9.7×10^{-5}	9.0×10^{-3}

narrow two-phase region (<0.04 °K) for $\bar{9}$S5 and a slightly wider one for $\overline{10}$S5. A two-phase region has been found previously in 8OCB (see Ref. 11) and strongly implies, though does not prove the existence of a first-order, impurity-broadened transition. Assuming that is the case, we find transition entropies of $\Delta S \lesssim 10^{-4} R_0$ for $\bar{9}$S5 and $\Delta S \sim 5\times10^{-2} R_0$ for $\overline{10}$S5. Very near the tricritical point impurity concentration fluctuations play a role, the character of which depends on the relative solubility and mobility of the impurity in the two phases. These fluctuations are expected to diverge at the tricritical point as a result of coupling to the order-parameter fluctuations. Thus the very narrow two-phase region in $\bar{9}$S5 may be a *nonequilibrium effect* due to macroscopic inhomogeneities arising from the critical divergence of order-concentration fluctuations. Therefore, $\bar{9}$ may be less than, but extremely close to, $\bar{n}_t$. Further study is required to clarify this point.

An interesting conclusion from this experimental observation of superfluid-^{3}He-^{4}He-like behavior is that in spite of the complications of anisotropy and coupling to the director, which have been theoretically predicted to destroy the superfluid analogy,[6,8] it appears that the analogy holds, at least for specific-heat measurements. It would be interesting to have x-ray measurements of the smectic-A susceptibility and correlation length for the $\bar{n}$S5 system. High-precision measurements of Δn on $\bar{9}$S5,[18] such as those of Lim and Ho,[19] may show a divergence of χ(nematic) at $T_{NA}{}^t$ if performed in the presence of a magnetic field since then one can measure $\partial(\Delta n)/\partial g \sim |t|^{-\alpha}$.[15]

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[9]$\bar{n}$S5 is an abbreviation for 4-n-pentylphenylthiol-4′-n-alkyloxybenzoate, which has the chemical structure $C_{\bar{n}}H_{2\bar{n}+1}$-$C_6H_4$-COS-$C_6H_4$-$C_5H_{11}$.

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