One of us (W.D.) acknowledges a travel grant by Deutsche Forschungsgemeinschaft.

[1]See, for example, a recent review by W. Bron, Rep. Prog. Phys. 43, 301 (1980).

[2]D. Huet, J. P. Maneval, and A. Zylberstejn, Phys. Rev. Lett. 29, 1092 (1972).

[3]W. Grill and O. Weis, Phys. Rev. Lett. 9, 588 (1975).

[4]R. G. Ulbrich, V. Narayanamurti, and M. A. Chin, Phys. Rev. Lett. 45, 1432 (1980).

[5]P. Hu, V. Narayanamurti, and M. A. Chin, Phys. Rev. Lett. 46, 192 (1981).

[6]P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1965), Vol. 7.

[7]B. Taylor, H. J. Maris, and C. Elbaum, Phys. Rev. Lett. 23, 416 (1969).

[8]J. C. Hensel and R. C. Dynes, Phys. Rev. Lett. 43, 1033 (1979).

[9]G. A. Northrop and J. P. Wolfe, Phys. Rev. Lett. 43, 1424 (1979), and Phys. Rev. B 22, 6169 (1980).

[10]W. Eisenmenger, in *Proceedings of the Third International Conference on Phonon Scattering in Condensed Matter, Providence, Rhode Island, 1979,* edited by H. J. Maris (Plenum, New York, 1980), p. 303.

[11]How does scattering affect the pattern? It should be similar to viewing a sharp optical image through fog: A weak but sharp image remains, superimposed on a smooth background.

[12]A. D. Zdetsis and C. S. Wang, Phys. Rev. B 19, 2999 (1979); A. D. Zdetsis, in *Proceedings of the International Conference on Lattice Dynamics, Paris, 1977,* edited by M. Balkanski (Flammarion, Paris, 1978) p. 45, inelastic neutron scattering data, and references herein.

[13]We did not, however, compensate for the intensity reduction by scattering.

[14]G. Northrop, to be published.

[15]J. Callaway, Phys. Rev. 113, 1046 (1959).

Nematic–Smectic-*A*–Smectic-*C* Multicritical Point

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A study of the phase diagram near the nematic–smectic-*A*–smectic-*C* multicritical point and of nematic–smectic-*C* transition entropies leads to the conclusion that this is not a Lifshitz point. It is shown that a biaxial second-rank tensor order parameter may be needed.

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When the nematic–smectic-*A*–smectic *C* (NAC) multicritical point was first suggested, the two proposed explanations of it were very different. Chu and McMillan[1] (CM) proposed a model in which smectic-*C* has the dipolar order parameter of McMillan's theory,[2] while the smectic-*A* order parameter was the one-dimensional density wave of Kobayashi,[3] McMillan,[4] and deGennes.[5] Tilt of the director away from the layer normal entered the model somewhat incidentally through a gradient term coupling the two order parameters. Chen and Lubensky[6] (CL) found an NAC point in a model where the only order parameter was the one-dimensional density wave. Tilt of the director relative to the layer normal is a central feature of the model and occurs when the coefficient of the transverse gradient term becomes negative. From the experimental point of view the differences between the two models are primarily twofold. First, in the CL model the NAC point is a type of Lifshitz point,[7] which leads to the prediction that x-ray scattering in the nematic phase near the NAC point falls off in the transverse direction as $k_\perp^{-4}$, rather than the usual $k_\perp^{-2}$ predicted by the CM model. Secondly, the nematic–smectic-*C* (NC) transition entropy is zero in the CM model but finite in the CL model because of the Brazovskii[8-10] effect. The NC entropy was found to be finite when the NAC point was discovered experimentally.[11]

In this Letter evidence is presented, based on the topology of the phase diagram and the nematic–smectic-*C* transition entropy, that for the system studied, which is the same as the one studied previously,[11] the NAC point is likely not either of the above kinds of multicritical points. Instead it conforms well with a phenomenological Landau expansion suggested recently by Benguigui,[12] for which is offered a physical interpretation.

In earlier work on mixtures of octyl- and heptyloxy-*p'*-pentylphenyl thiolbenzoate ($\overline{7}S5$-$\overline{8}S5$),[11] gross features of the phase diagram were deter-

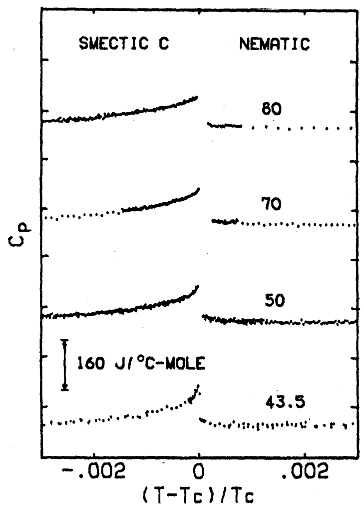

FIG. 1. Specific heat vs reduced temperature near the nematic–smectic-C transition of several mixtures. The zero of the ordinate is different for each concentration of $\overline{7}S5$, 43.5% – 80%. The baseline is approximately 1100 J/mol °C in each case.

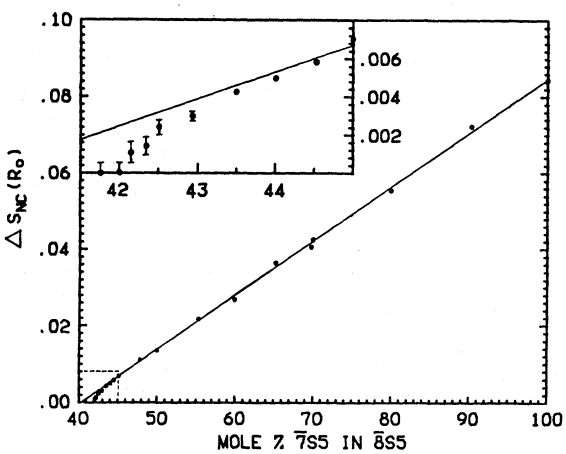

FIG. 2. Scanning calorimetry measurements of nematic–smectic-C transition entropy vs concentration. Lines are fits to data at concentrations greater than 45%. Inset is an expansion of the region indicated by dotted lines. The pretransitional part was excluded from the enthalpy calculations by dropping a vertical line from a point on the low-temperature side of the scanning curve lying ΔC_{NC} above the extrapolated high-temperature baseline and including area only on the high-temperature side of this line. ΔC_{NC} comes from the ac calorimetry data.

mined, and it was found that the NC transition line in the temperature-concentration plane was first order. The NC transition entropy, measured by scanning calorimetry alone, was found to decrease with $\overline{8}S5$ concentration and vanish near the NAC point. This Letter reports the results of high-resolution ac calorimetry measurements of heat capacity near the nematic–smectic-A (NA), smectic-A–smectic-C (AC), and NC transitions, and scanning calorimetry measurements which, combined with the ac calorimetry, allow for a much more precise determination of NC transition entropies than was possible before.[11] Also reported is a determination of the phase diagram in an expanded region near the NAC point.

The ac calorimetry measurements of heat capacity near the NC transitions are presented in Fig. 1. Pretransitional entropy contributions near these transitions are clearly very weak. At the AC transition, samples with $0 < x \leq 41\%$ exhibited small clear jumps in heat capacity similar to those in Fig. 1 but with jumps approximately one half the size. The 42% sample showed a much larger jump, clear evidence of an NA transition by light scattering, but no evidence of latent heat. A 42.15% sample, shown in Fig. 2 but not Fig. 1, had a small jump as in Fig. 1 and showed latent heat but no evidence of an NA transition by light scattering. Hence, the NAC point is between 42% and 42.15%.

Because of the weakness of the NC heat-capacity anomalies accurate separation of pretransition and transition entropies was feasible. The concentration dependence of the resulting NC transition entropies is shown in Fig. 2. Figure 3 shows the phase diagram near the NAC point.

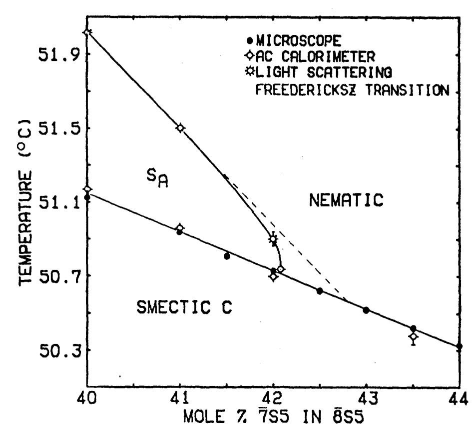

FIG. 3. Phase diagram near the NAC point. The calorimetric NA transition temperature for the 41% sample was obtained from a graph with a coarser temperature scale and expanded C_p scale where an abrupt change in slope could be seen. The solid line through the AC and NC data is a straight line fit but that through the NA line is an aid to the eye.

Transition temperatures were determined by ac calorimetry, thermal microscopy, light scattering, and Fréedericksz transition measurements. Need for the latter two kinds of experiments is evident from Fig. 4 where it is seen that the NA heat-capacity anomaly is very weak near the NAC point. Thermal microscopy is an extremely sensitive method of determining the smectic-C line.

In comparing the above results with theory, first note that the AC and NC lines (the smectic-C line) in Fig. 3 are continuous through the NAC point, while the NA line approaches obliquely. This result is contrary to the predictions of both the CM and CL theories which have the NA and NC lines continuous at the NAC point with the AC line coming in obliquely. It must be noted that the theoretical phase diagrams are based on mean-field theories, and so the effect of fluctuations is not considered. However, multicritical fluctuations may not be an important feature of this system except in the immediate vicinity of the NAC point. To see this, note that the NC transition entropy of Fig. 2 approaches zero with a concentration dependence that is linear over the entire range from 100% $\overline{7}S5$ to within a few percent of $x_{\rm NAC}$ (~42%). It is only within the last percent or so that the $\Delta S_{\rm NC}$ line curves downward to zero. Extrapolating the linear segment of this curve to zero entropy, the entropy would vanish at $x \sim 40.3\%$, clearly to the left of the observed NAC point. It should be noted that the linear extrapolation of the NA line shown in Fig. 3 would predict a mean-field NAC point at $x = 42.75\%$, clearly to the right of the observed NAC point. If this downward curvature of $\Delta S_{\rm NC}$ and of the NA line is assumed to be due to multicritical fluctuations, these data suggest that the correct mean-field theory would have a tricritical point on the AC line at ~40.3% and an NAC point at ~42.75% where the smectic-C line is met obliquely by the NA line. The reason why the smectic-C line is undistorted even very near the NAC point may be that the NA fluctuations (Fig. 4) have already become small well away from the NAC point. This may also explain the extreme smallness of the multicritical region of the x-T plane. We do not believe that the vanishing of the NA heat-capacity anomaly is directly related to the NAC point, but that it is related instead, through two-scale-factor universality,[13,14] to the increase in the smectic-A coherence length amplitude evidenced in x-ray scattering experiments.[15]

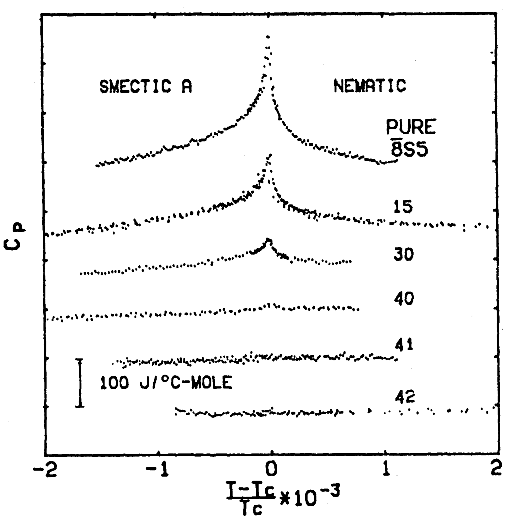

FIG. 4. Specific heat vs reduced temperature of pure $\overline{8}S5$ and four mixtures (15% – 42% $\overline{7}S5$). The zero of the ordinate is different for each concentration. The lowest temperature point has a heat capacity of approximately 1200, 1150, 1125 J/mol °C for $x = 0\%$, 15%, 30%, respectively; and 1100 J/mol °C for the rest.

The data presented provide a test of mean-field theories of the NAC point. They are in disagreement with both the CM and CL theories which predict the wrong topology.[16]

It is interesting that a recent free-energy expansion by Benguigui[12] is consistent with the present results in that it predicts *a tricritical point on the AC line near the NAC point and the correct phase diagram.* The free energy is a two-parameter expansion,

$$F = \alpha\psi_0^2 + \tfrac{1}{2}\beta\psi_0^4 + \tfrac{1}{3}\gamma\psi_0^6 + a\eta^2 + \tfrac{1}{2}b\eta^4 - c\eta^2\psi_0^2, \qquad (1)$$

where $\alpha = \alpha_0(T - T^*)$, and $(\beta, \gamma, a, b, c) > 0$. ψ_0 is associated with the smectic density wave and η with the tilt. Unlike the above expansion, the CM and CL theories introduce the tilt *only in terms scaled by* ψ_0^2 since tilt cannot be defined in the absence of layers. Such scaling prevents these models from producing the correct phase diagram. What appears to be needed is an order parameter that can properly reflect the rotational and translational symmetries of the nematic, smectic-A, and *biaxial* smectic-C phases and which leads to the above free-energy expansion.

A tensor order parameter, closely related to one suggested by Lubensky,[17] can lead to the above expansion. It derives from the polarizability density of an anisotropic layered medium given by

$$\overleftrightarrow{P} = n_0(1+\psi)(K_0\overleftrightarrow{I} + K_A\overleftrightarrow{Q}), \qquad (2)$$

where n_0 is the average molecular density, ψ is the smectic density wave given by $\psi = \psi_0 \cos(\vec{q}\cdot\vec{r})$, K_0 and K_A are the isotropic and anisotropic parts of the polarizability, and $\overleftrightarrow{Q}$ is a symmetric traceless tensor. As noted by Lubensky,[17] $\overleftrightarrow{Q}$ *may be biaxial even for cylindrical molecules if the layer normal is not parallel to the director*, $\hat{n}$. In the biaxial case $\overleftrightarrow{Q}$, diagonalized, has the elements $\frac{2}{3}Q_z$, $-\frac{1}{3}Q_z+\eta$, and $-\frac{1}{3}Q_z-\eta$, where in a simple interpretation Q_z is the Maier-Saupe order parameter[18] and, *for cylindrical molecules*, η *is a measure of the asymmetry of long-axis fluctuations*. There is now strong evidence[19] that for the systems studied here *asymmetry is the source of biaxiality* rather than condensation of rotations about the long axis of noncylindrical molecules.[20] Taking for the order parameter the anisotropic part of $\overleftrightarrow{P}$, namely,

$$\overleftrightarrow{S} \equiv \overleftrightarrow{P} - n_0K_0\overleftrightarrow{I}, \qquad (3)$$

Eq. (1) can result since only terms *even* in η and ψ_0, though, of course, mixed Q_z, survive.[21] In such a model the tilt enters, as in the CM theory, through a gradient term. Gradient terms must vanish for rotations that leave the orientation of the *biaxial* tensor ellipsoid relative to the layer normal unchanged. Therefore, a second director, perpendicular to $\hat{n}$, enters the problem with the result that, as in the CM theory and as observed,[15] x rays exhibit $k_\perp^{-2}$ scattering instead of the $k_\perp^{-4}$ predicted by a Lifshitz-point theory. Because of this agreement and because the predicted phase diagram and NC entropies agree with the results reported here, we conclude that the NAC point is not a Lifshitz point but may instead be a more complicated multicritical point involving a multicomponent tensor order parameter.

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[1]K. Chu and W. McMillan, Phys. Rev. A 15, 1181 (1977).

[2]W. McMillan, Phys. Rev. A 8, 1921 (1973).

[3]K. Kobayashi, Mol. Cryst. Liq. Cryst. 13, 137 (1971).

[4]W. McMillan, Phys. Rev. A 4, 1238 (1971).

[5]P. deGennes, Solid State Commun. 10, 753 (1972).

[6]J. Chen and T. Lubensky, Phys. Rev. A 14, 1202 (1976).

[7]R. Hornreich, M. Luban, and S. Shtrikman, Phys. Rev. Lett. 35, 1678 (1975).

[8]S. Brazovskii, Zh. Eksp. Theor. Fiz. 68, 175 (1975) [Sov. Phys. JETP 41, 85 (1975)].

[9]J. Swift, Phys. Rev. A 14, 2274 (1976).

[10]D. Mukamel and R. Hornreich, J. Phys. C 13, 161 (1980).

[11]D. Johnson, D. Allender, R. DeHoff, C. Maze, E. Oppenheim, and R. Reynolds, Phys. Rev. B 16, 470 (1977).

[12]L. Benguigui, J. Phys. (Paris), Colloq. 40, C3-419 (1979).

[13]D. Stauffer, M. Ferrer, and M. Wortis, Phys. Rev. Lett. 29, 345 (1972); P. Hohenberg, A. Aharony, B. Halperin, and E. Siggia, Phys. Rev. B 13, 2986 (1976).

[14]C. Garland, G. Kasting, and K. Lushington, Phys. Rev. Lett. 43, 1420 (1979).

[15]C. Safinya, R. Birgeneau, J. D. Litster, and M. E. Neubert, following Letter [Phys. Rev. Lett. 47, 668 (1981)].

[16]Other experimentally observed NAC points may have the topology of the CM and CL theories. See G. Sigaud, F. Hardouin, and M. Achard, Solid State Commun. 23, 35 (1977).

[17]T. Lubensky, Phys. Rev. A 2, 2497 (1970).

[18]W. Maier and A. Saupe, Z. Naturforsch. A 13, 564 (1958), and 14, 882 (1959), and 15, 287 (1960).

[19]T. Lockhart, D. Allender, E. Gelerinter, and D. Johnson, Phys. Rev. A 20, 1655 (1979); T. Lockhart, Ph.D. thesis, Kent State University, 1981 (unpublished).

[20]Certainly the molecules are *not* cylindrical but their thermal average conformation may be.

[21]Terms odd in ψ vanish upon spatial integration since $\psi \sim \cos(\vec{q}\cdot\vec{r})$. The important invariants of $\overleftrightarrow{S}$, namely $\mathrm{Tr}\overleftrightarrow{S}$, $\mathrm{Tr}(\overleftrightarrow{S})^2$, and $\det\overleftrightarrow{S}$ are even in η. Note that $\mathrm{Tr}\overleftrightarrow{S} \neq 0$ although $\mathrm{Tr}\overleftrightarrow{Q} = 0$.