PHYSICAL REVIEW A VOLUME 25, NUMBER 1 JANUARY 1982

Nematic—smectic-A—smectic-C multicritical point

R. DeHoff,* R. Biggers, D. Brisbin, and D. L. Johnson
Department of Physics, Kent State University, Kent, Ohio 44242
(Received 17 August 1981)

A study of the phase diagram and thermal properties near the nematic—smectic-A—smectic-C (NAC) multicritical point reveals the importance of the roles that biaxiality and bare correlation lengths play in the description of this multicritical point. Comparison with models of the NAC point by Chen and Lubensky, and Chu and McMillan, indicate that these models lack qualitative agreement with the data in important areas. There are, however, certain areas of agreement.

I. INTRODUCTION

When the nematic—smectic-A—smectic-C (NAC) multicritical point was initially suggested, the two proposed explanations of it were very different. Chu and McMillan[1] (CM) proposed a model in which smectic C had 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 de Gennes.[5] Tilt of the director away from the layer normal enters the CM 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 this model and occurs when the coefficient of the transverse gradient term becomes negative.

Differences between the two models are substantial. For example, in the CL model, due to the vanishing of a twofold degenerate gradient term coefficient, the NAC point is a type ($m=2$) 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. Furthermore, the nematic—smectic-C (NC) transition entropy is zero in the CM model but is expected to be finite in the CL model because of fluctuations.[8–10]

When the NAC point was discovered experimentally,[11,12] the NC transition was indeed found to be first order with a transition entropy that went continuously to zero near the NAC point. Based on the success of the CL model in predicting both the existence of the NAC point and the finite NC entropy, the NAC point has been viewed theoretically[13–16] as an analog in liquid crystal systems of a Lifshitz point (LP), which, as originally conceived, was a magnetic multicritical point[7] where the para-, ferro-, and helically ordered phases become identical. Recent x-ray experiments,[17] however, failed to find the $k_\perp^{-4}$ angular dependence characteristic of the LP, finding instead the usual Lorentzian line shape. Furthermore, our recent thermodynamic and microscope studies[18] yielded a phase diagram having the wrong topology and heat capacity anomalies not readily explained by a LP interpretation. On the basis of these results, we suggested that the NAC point is not a LP.

The purpose of the present paper is twofold: first, to present considerable new data that more clearly characterizes the neighborhood of the NAC point and, second, to point out what may be learned about the NAC point by examining the observed phase diagram and thermal anomalies in the light of our general understanding of critical phenomena, and in the light of existing theories of the NAC point, namely, the CM and CL theories.

Section II describes the procedures unique to the present experiments and presents the experimental results in graphic form. In Sec. III the results are discussed in general terms and also in relation to (1) the theory of the liquid crystal LP, i.e., the CL theory, and (2) the CM theory.

II. EXPERIMENT AND DATA

The materials studied in this work are mixtures of $\overline{7}S5$ and $\overline{8}S5$, and 7- and 8-carbon chain members of the 4-n-pentyl-phenylthiol-4′-alkoxybenzoate ($\overline{n}S5$) homologous series. They were synthesized and recrystallized three times from ethanol by M. E. Neubert and S. Laskos of the Kent State Liquid Crystal Institute and are estimated to be 99 + % pure. In a previous study,[11] $\bar{7}S5$-$\bar{8}S5$ mixtures were shown to exhibit an NAC point at approximately 40 mol % $\bar{7}S5$. Ten mol % intervals were used leaving the question of the topology of the phase diagram near the NAC point open, notwithstanding the lines drawn as an aid to the eye in Fig. 1 of that work which turned out to be a good guess. Semiquantitative DSC calorimetric measurements were reported there; whereas, in this work, we have determined the phase diagram and thermodynamic properties with much higher resolution through the use of high resolution ac microcalorimetry and quantitative DSC measurements as well as thermal microscopy.

Specific-heat measurements in the vicinity of the nematic–smectic-*A* (NA), smectic-*A*-smectic-*C* (AC), and nematic–smectic-*C* (NC) transitions appear in Figs. 1–3, respectively. All were made using an ac microcalorimeter described previously.[19,20] The present experiments required no modification of techniques. The amplitude of the thermal oscillations was 0.005 K for all data reported.

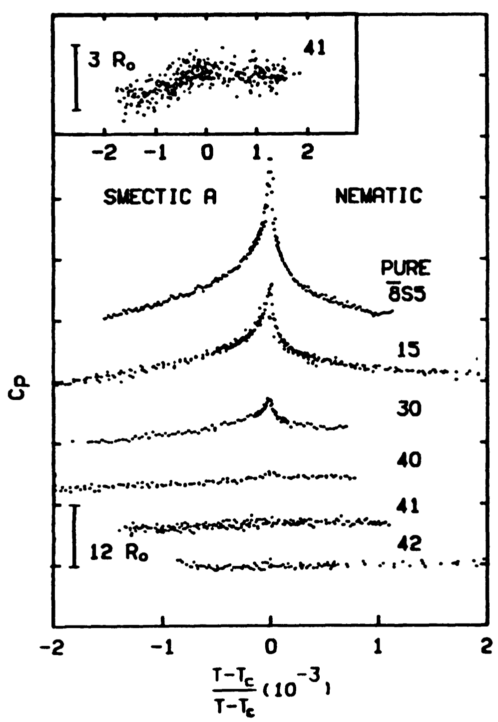

FIG. 1. Specific heat versus reduced temperature near the NA transitions of pure $\bar{8}S5$ and five mixtures (15–42 % $\bar{7}S5$). The lowest temperature point has a heat capacity of approximately 1200, 1150; 1125 J/mol °C for $x=0$, 15, 30%, respectively, and 1100 J/mol °C for the rest.

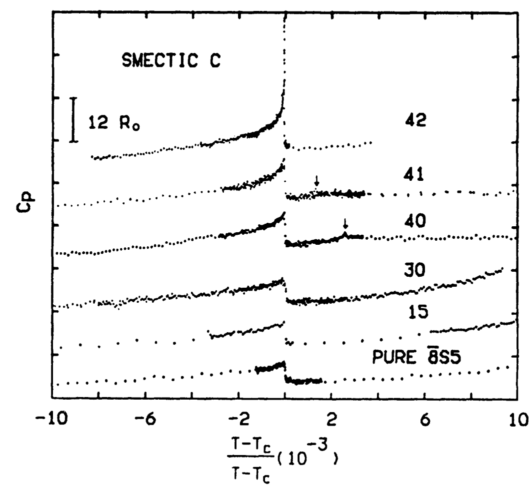

FIG. 2. Specific heat versus reduced temperature near the AC transitions of pure $\bar{8}S5$ and five mixtures (15–42 % $\bar{7}S5$). The arrows designate NA transitions. The 42% sample is very close to the NAC point.

In agreement with the previous work,[11] NA and AC transitions were found to be continuous and NC transitions first order. A Perkin-Elmer DSC-2 scanning calorimeter was used in combination with the high-resolution ac calorimeter to measure the NC transition entropies. A typical DSC scan is shown in Fig. 4 which also illustrates the technique used to separate pretransitional enthalpy from latent heat. As seen in Figs. 3 and 4, the specific

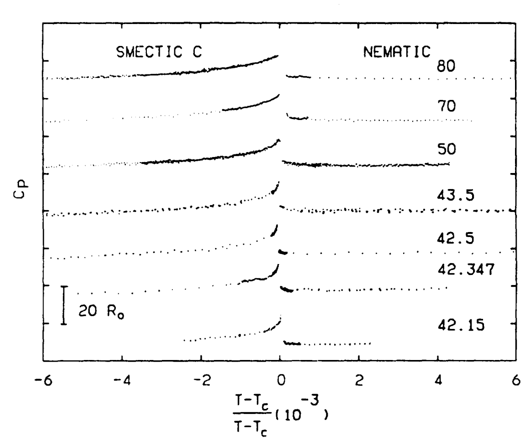

FIG. 3. Specific heat versus reduced temperature near the nematic–smectic-*C* transition of several mixtures. Zero of the ordinate is different for each concentration of $\bar{7}S5$, 43.5–80 %. The baseline is approximately 1100 J/mol °C in each case.

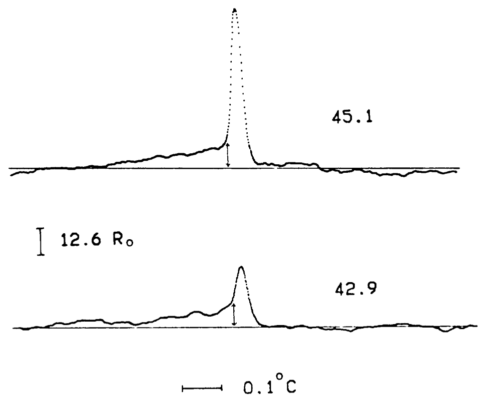

FIG. 4. DSC-2 scans of the NC transitions of 45% and 42.9% $\bar{7}S5$. Discussion of solid lines is given in the text.

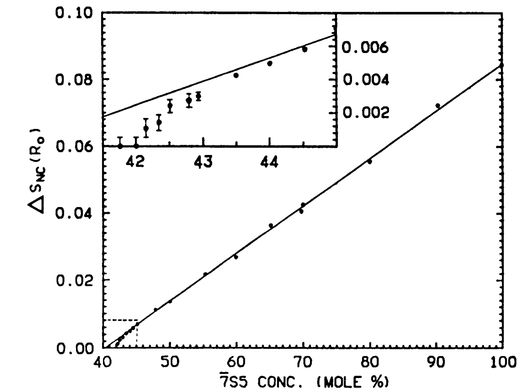

FIG. 5. NC transition entropy versus concentration. Solid lines are fits to the data at concentrations greater than 45%. Inset is an expansion of region enclosed by dotted lines. Each point represents the average of 15 to 25 scans involving several samples.

heat on the high-temperature side of the NC transition, measured by either ac or scanning calorimetry is very nearly independent of temperature. Therefore, one can extrapolate this weakly temperature-dependent specific heat to the low side of the transition with high precision (see Fig. 4). From the ac calorimetry measurements (see Fig. 3), one can accurately find the jump, ΔC_{NC}, in specific heat at the NC transition. The vertical line in Fig. 4 was drawn at a position where the DSC scan lies ΔC_{NC} above the extrapolated line; hence it divides the enthalpy into a pretransitional contribution to the left of the vertical line and a latent heat to the right of it. The error in this procedure is primarily due to the uncertainties in the extrapolation, the position of the vertical line, and, to a much lesser extent, the measurement of ΔC_{NC} by ac calorimetry. Note that the precision of this technique depends on the specific heat on the high-temperature side being weakly temperature dependent. Had there been a strong pretransitional contribution above the transition, the method would have been much less precise. The estimated precision in measuring the nematic—smectic-C transition entropy, ΔS_{NC}, by this method is $\simeq \pm 0.001 R_0$. Results are shown in Fig. 5. The error bars displayed were taken as the standard deviation of many runs (see Fig. 5 caption).

The phase diagram in the vicinity of the NAC point is shown in Fig. 6. Both thermal microscopy and ac calorimetry were used in determining this diagram because, for concentrations greater than 41%, the NA transition temperatures were undetectable by ac calorimetry as Fig. 1 suggested. Transitions to the C phase (NC,AC) were precisely measured (± 0.01 K) by ac calorimetry (see Figs. 2 and 3). They are also easily observed under the polarizing microscope using homeotropic alignment. In this configuration the field of view is dark in the nematic-and smectic-A phases but becomes suddenly bright in the C phase because the layers remain (or come in) parallel to the film while the director tilts relative to the layer normal. This brings the optic axis (acute bisectrix) away from the layer normal and produces birefringence. Thus the C line in Fig. 6 has been precisely determined by both ac calorimetry and thermal microscopy. It was necessary to shift the C-line microscope data uniformly by $+0.5$ K to gain agreement with the calorimetry data. The temperature range of the A phase for 40 and 41% samples was determined by both ac calorimetry and thermal mi-

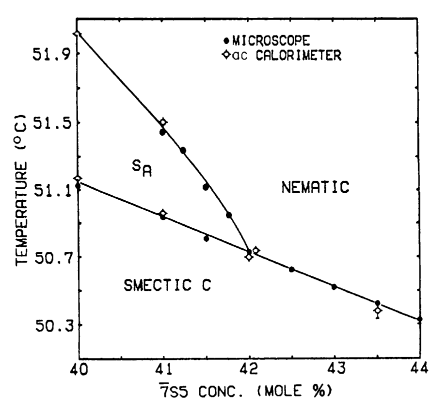

FIG. 6. Phase diagram near the NAC point. The solid line through the AC and NC data is a straight line fit but that through the NA data is an aid to the eye.

croscopy. The NA thermal anomaly, though weak, is readily observable as a small peak for the 40% sample and as a change in slope for the 41% sample. An expanded graph of the 41% data is shown in the inset of Fig. 1 where the change in the slope can be seen. The temperature width of the *A* phase for this sample was determined to ± 0.05 K with the uncertainty coming primarily from the determination of the NA transition temperature. The 40 and 41% calorimetry points on the NA line are plotted with respect to the fitted *C* line, not the corresponding calorimetry point on the *C* line. Thus the temperature interval between these points and the solid *C* line represents the width of the *A* phase determined by ac calorimetry. The microscope data on the NA line were determined by vanishing of light scattered by director fluctuations.

III. DISCUSSION OF EXPERIMENTAL RESULTS

Present theoretical understanding of the three phase transitions studied here is deficient. In spite of vigorous experimental and theoretical efforts, the NA transition remains one of the least understood and most interesting examples of critical phenomena. Though currently less intensely studied, the NC transition is likely to be at least as difficult and interesting as the NA. Both transitions involve the onset of translational ordering in one spatial direction: parallel to the director for the NA transition but skewed to it for the NC. It is, therefore, natural to think of the line of nematic–smectic transitions (NA and NC) as a line of order-disorder transitions and the AC line as a line of more subtle order-order transitions analogous to certain structural transitions in solids[21] or the spin-reorientation transition in certain magnetic systems.[22] The analogy gains further appeal when pursued in some detail[23] as it would appear to explain the apparent mean-field behavior of the AC transition on the basis of a Ginzburg criterion.[24]

From the discussion that follows, however, it will be seen that the above view of the NAC phase diagram may at best be somewhat naive in that the thermal properties are, to say the least, not readily explained by such a picture. The data suggest that it is rotational ordering that dominates thermal behavior in the vicinity of the NAC point while the onset of layering is subtle indeed. This point will be illustrated by discussing first the line of nematic–smectic transitions (NA and NC lines) and second the line of smectic-*C* transitions (AC and NC lines) with emphasis on the continuity, or lack thereof, of thermal properties and phase boundaries.

A. Nematic–smectic transitions (NA and NC lines)

According to the phase diagram of Fig. 6, the nematic–smectic line has a sharp discontinuity in slope at the NAC point. Furthermore, examination of Figs. 1 and 3 reveals a profound difference between NA and NC thermal anomalies. Whereas the NA anomalies appear to be lambdalike indicating strong fluctuation effects and a broad critical regime, the NC anomalies indicate very weak fluctuations and a pronounced specific heat jump, suggestive of mean-field or near mean-field (Gaussian) behavior. It is, therefore, tempting to characterize the nematic–smectic (NS) line as exhibiting abrupt crossover between critical and classical behavior at the NAC point. However, the truth will not be known until the bare coherence lengths have been measured (they are model dependent) and a Ginzburg criterion examined. This point is discussed further below. In any case it is true that the introduction of tilt (biaxiality) profoundly alters the nature of the nematic-to-smectic transition in a way which, as we shall show, is not immediately suggested by current models[1,6] of the NA and NC transitions. Clues to the significance of this may be found by considering the NA and NC transitions separately.

1. NA transitions

Although the NA transitions are lambdalike, indicating strong fluctuations, the amplitude of the anomaly is observed to decrease very rapidly as the NAC point is approached and has nearly vanished at 41% (Fig. 1). Even after the thermal anomaly has become undetectable the transition can still be observed under the microscope; or by light scattering, or by Freedericksz transition measurements of the divergence of the bend (or twist) curvature coefficients. The latter two kinds of measurements were performed on a sample having a smectic-*A* range of 0.18 K ($\simeq$41.7%), and established that the NA transition remains sharp on a scale of a few millidegrees.

The disappearance of the thermal anomaly is probably not directly related to the NAC point as similar behavior has been observed in systems having no such point[25,26] and indeed no *C* phases. A unifying characteristic of the systems studied is that the strength of the NA anomaly decreases rapidly with increasing nematic range, suggesting that the degree of nematic order near the NA transition is important. Another unifying feature is that the amplitude of the anomaly decreases as the bare smectic-A coherence lengths,[17,18,26] measured by x-ray scattering, increase. For example, in the present study these lengths are $\xi_\perp^0 \sim 1.6$ Å, $\xi_\parallel^0 \sim 50$ Å for a sample with an A range of 0.28 K ($X \sim 41.6\%$) (similar values are found for a 41% sample),[17] whereas the corresponding values found for pure $\overline{8}S5$ were only ~ 0.9Å and ~ 6Å, respectively.[27] Thus the bare lengths increase rapidly with nematic range. This particular result can explain why the anomaly vanishes, as shown by the following discussion.

Whereas scattering probes of critical phenomena sample a narrow range in wave-vector space, specific-heat measurements sample fluctuations at all wave vectors. Therefore, and because there is no characteristic length in the problem, fluctuations in all wavelength ranges between some smallest and some largest length, i.e., ξ_0 and $\xi(t)=\xi_0 t^{-\nu}$, contribute. From the simple argument that the largest fluctuation should have a free energy cost $\sim k_B T$, it follows that near a critical point the free energy density should scale as[28]

$$F \sim \xi_\parallel^{-1} \xi_\perp^{-2} \tag{1}$$

in units of $k_B T$ per unit volume, where

$$\xi_\parallel = \xi_\parallel^0 t^{-\nu} \tag{2a}$$

and

$$\xi_\perp = \xi_\perp^0 t^{-\nu} . \tag{2b}$$

Now $C = -\partial^2 F/\partial t^2 = A \mid t \mid^{-\alpha}$. Therefore, $F \sim A t^{2-\alpha}$ and $A\xi_\parallel^0(\xi_\perp^0)^2 t^{2-\alpha-3\nu} = \text{const}$. This implies that $3\nu = 2-\alpha$, which is the $d=3$ version of the so-called hyperscaling law $d\nu = 2-\alpha$. Hence we have the interesting result

$$A\xi_\parallel^0(\xi_\perp^0)^2 = \text{const} , \tag{3}$$

i.e., that the specific-heat amplitude, A, scales inversely as $\xi_\parallel^0(\xi_\perp^0)^2$, in qualitative agreement with our experiments. The constant in Eq. (3) is believed on theoretical grounds to be universal,[29] a result known as two-scale factor universality because it reduces from three to two the number of independent scale factors needed to describe an ordinary critical point. For the bare lengths given above, Eq. (3) predicts that pure $\overline{8}S5$ has an anomaly 27 times stronger than the 41% sample. A look at Fig. 1 suggests that this is not an unreasonable prediction.

It would appear, then, that the NA line is a line of critical points and that specific-heat and x-ray results are at least in qualitative agreement with general scaling concepts. The precise kind of critical behavior displayed by the NA transition is, of course, the subject of intense current study. Earlier work[19] suggested that the heat capacity anomaly for pure $\overline{8}S5$ is very nearly heliumlike [$\alpha \sim O(\log)$]. One would like to know whether this behavior persists along the NA line, but such a study is complicated by the rapid decrease in amplitude. Nevertheless, by using mixtures to study what appears to be a crossover from tricritical to critical behavior in the $\overline{n}S5$ homologous series[30] ($\overline{10}S5$, $\overline{9}S5$, $\overline{8}S5$), it may be possible to establish the value of α and other critical exponents and amplitude ratios necessary for a complete characterization of critical behavior near the NA line. Such work is in progress.

2. NC transitions

Thermal behavior near the NC line is sharply different from that near the NA line. Whereas the NA transitions are continuous and exhibit strong fluctuations, the NC transitions are discontinuous (first order) and exhibit very weak fluctuations. According to accepted concepts of fluctuation phenomena, a crossover between strong and weak fluctuation regimes could be explainable by some Ginzburg criterion[24]

$$t_G = \frac{k_B^2}{32\pi^2(\Delta C)^2 \xi_0^6} , \tag{4}$$

where ΔC is the specific heat jump, ξ_0 is the bare coherence length [$\xi_0^6 \to (\xi_\parallel^0)^2(\xi_\perp^0)^4$ for the uniaxial system], and t_G is the width of the critical regime in reduced temperature units. For the 41% sample $\Delta C_{\text{NA}} << R_0$ (Fig. 1). Taking $\xi_\parallel^0 = 50$ Å and $\xi_\perp^0 = 1.6$ Å from x-ray measurements[17] leads to $t_G > 0.1$, i.e., a wide critical regime. The NC critical regime appears by contrast to be very narrow. Figure 3 suggests that $t_G < 10^{-4}$ which, for $\Delta C_{\text{NC}} \sim 10R_0$ (see Fig. 3), gives $\xi_0^C > 8.3$ Å. This is to be compared with the average smectic-A coherence length defined by $\xi_0^A = (\xi_\parallel^0 \xi_\perp^{0^2})^{1/3}$ which for the 41% sample is 5.0 Å. Clearly, therefore, a Ginzburg criterion explanation of the change in nematic−smectic thermal properties at the NAC point implies a rather abrupt and substantial increase of the bare correlation lengths. In a one-order parameter model such as the Lifshitz point model[7] of Chen and Lubensky,[6] the imposition of such a sudden change in bare lengths would seem rather *ad hoc*. Had $\Delta C_{\rm NC}$ gradually vanished on approach to the NAC point so as to match smoothly into NA behavior, or had there developed a finite $\Delta C_{\rm NA}$ on the NA line such that $\Delta C_{\rm NA} \to \Delta C_{\rm NAC} = \Delta C_{\rm NC}$, a one-parameter model would be more plausible. But, in fact, $\Delta C_{\rm NC}$ remains constant ($\sim 10 \pm 1.2 R_0$) and $\Delta C_{NA} \sim 0$ right up to the NAC point as can be seen in Figs. 1 and 7. There may, of course, be a reason other than the Ginzburg criterion for the abrupt change in properties. In particular, it should be noted that the above arguments rest on the assumptions that the discontinuities in C_p at the NC transitions and the absence of a divergence in C_p above $T_{\rm NC}$ are the signatures of a weak fluctuation, or near mean-field regime. Alternatively, the divergence may be cut out by the first-order phase transition. One would then expect the disappearance of the latent heat to be accompanied by a growth of pretransitional heat capacity anomaly, which does not happen. However, the absence of such an anomaly may result from large bare coherence lengths *à la* Eq. (3) for the NA transition. Then by definition, the critical regime would obtain. Such an interpretation of the data introduces a degree of continuity to the thermal properties along the line of nematic—smectic transitions; hence, it should not be ignored. However, large bare lengths *coupled with large jumps in heat capacity* are normally the signature of mean-field, not critical, behavior. Of course, the application of either the Ginzburg criterion or two-scale factor universality [Eq. (3)] in a region of first-order phase transitions must be considered tentative.

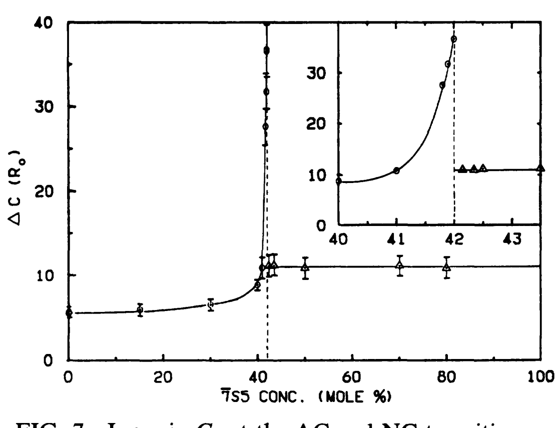

FIG. 7. Jump in C_p at the AC and NC transitions. The three highest points are probably underestimated because of rounding due to finite temperature resolution. As discussed in the text, C_p (42%)$=C_{\rm NAC}(T)$ diverges below T_c but is regular above T_c to within experimental uncertainties. Hence, $\Delta C_{\rm NAC}$ is actually infinite if the effects of rounding are properly treated. It would appear, then, that $\Delta C_{\rm AC}$ diverges at the NAC point.

Coupled to the question of the nature of the NAC point is the question of why the NC transition is first order since Landau theory allows it to be continuous. If the NAC point is a LP of the CL type then the answer is presumably that fluctuations drive it first order as a result of the degeneracy of such fluctuations[8] on a ring in $\vec{k}$ space.[6,9,10,13,31] Swift[9] and Swift and Mulvaney[13] have extended the perturbation calculation of Brazovskii[8] to the NC problem and found $\Delta S_{\rm NC} \sim k_B q_\perp^0 / 4\pi \xi_\parallel^0 \xi_\perp^0$, where $q_\perp^0$ is the component of the density wave perpendicular to the director, i.e., $q_\perp^0 / q_0 = \tan\omega$, where $q_0 = 2\pi/$(layer spacing) and ω is the tilt angle. Unfortunately, it is not currently possible to test this result since $q_\perp^0$, $\xi_\parallel^0$, and $\xi_\perp^0$, which come directly from x-ray data, are not yet known. The appropriate x-ray experiments are in progress,[32] but their interpretation will be model dependent.

B. Smectic-C transitions

In contrast to the line of nematic—smectic transitions which exhibits a kink at the NAC point, the line of smectic-C transitions (AC and NC) is continuous as Fig. 6 shows. Furthermore the AC and NC thermal anomalies are very similar, as Figs. 2 and 3 show. Weak fluctuation contributions characterize these transitions and distinguish them from the NA transitions.

It is of interest to compare the magnitude of the specific-heat jumps along the smectic-C line. The results are shown in Fig. 7. Far from the NAC point $\Delta C_{\rm NC} \sim 2\Delta C_{\rm AC} \sim 10 R_0$, a result for which we have no explanation, and which may not be of great consequence. Perhaps it is related to the additional molecular degrees of freedom involved at the NC transition.

As discussed above, $\Delta C_{\rm NC}$ is constant to within experimental uncertainties all the way to the NAC point. In contrast, $\Delta C_{\rm AC}$ diverges sharply in the range $40\% < X < X_{\rm NAC} = 42\%$. Outside of this narrow range ΔC_{AC} varies slowly with concentration and C_p shows little evidence of a divergence above or below $T_{\rm AC}$. Instead one observes the step discontinuity characteristic of a mean-field transition. In earlier work[19] on pure $\overline{8}S5$ the somewhat cusplike nature of the AC transition led the authors to consider the possibility of critical behavior. Later x-ray measurements[23] of the tilt exponent ($\beta \sim 0.47$), however, suggested mean-field behavior. A Ginzburg criterion argument based on de Gennes's Ginzburg-Landau functional led to the conclusion that an average bare coherence length $\bar{\xi}_0=(\xi_{\parallel}^0 \xi_{\perp}^{0^2})^{1/3} > 13$ Å would lead to a critical regime less than 10^{-5} wide ($t_G < 10^{-5}$). Very recent light scattering measurements[33] just above the AC transition of pure $\bar{8}S5$ yielded $\xi_{\parallel}^0 \sim 13.5$ Å, $\xi_{\perp}^0 \sim 21$ Å($\bar{\xi}_0 \sim 18$ Å), and $\nu \sim 0.55$ for $10^{-3} \gtrsim t \gtrsim 2\times 10^{-5}$ in essential agreement with a mean-field or near mean-field description of the AC transition. Similar results were obtained from an $X=36\%$ sample. It appears, therefore, that the AC line, at least for $X<40\%$, is a line of nearly mean-field transitions. Such a statement is supported by exponents and the Ginzburg criterion. It is clear from the above discussions that the AC and NC lines have a great deal more in common than the NA and NC lines.

Figure 8 is an expansion of the NAC point specific-heat data ($X_{\mathrm{NAC}}=42\%$). It was suspected that the rather curious shape of this anomaly was due to finite temperature resolution (± 0.005) of the apparatus. Therefore, the data were fit to a function of the form

$$\bar{C}_p(t)=\frac{1}{2\Delta}\int_{t-\Delta}^{t+\Delta} C_p dt \ , \tag{5}$$

where $t=(T-T_c)/T_c$, $\Delta=0.005$ K, and

$$C_p=\begin{cases} A'\,|\,t\,|^{-\alpha'}+B', & T<T_c \quad (6a)\\ B, \ (A=0), & T>T_c \quad (6b)\end{cases}$$

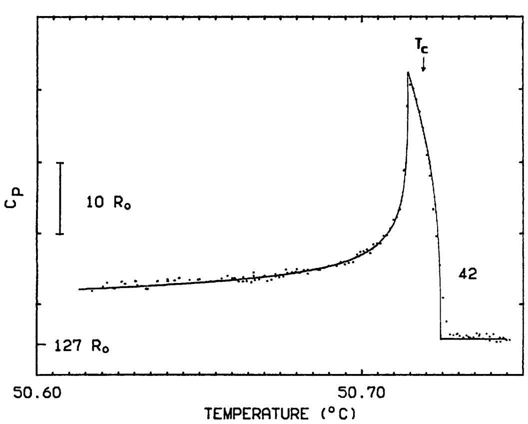

FIG. 8. Specific heat versus temperature very near the NAC point, 42% $\bar{7}S5$. The solid line is a fit to a simple power law with integral averaging to account for finite temperature resolution. Discussion of results is in the text.

This method of averaging over the finite temperature interval of the measurements was quite successful as the results of the fit show in Fig. 8. $\alpha'=0.67\pm 0.1$ was derived from the best fit. It appears that fluctuations above T_c are weak even at the NAC point. Conceivably, however, the often universal ratio A/A', which has not yet been calculated for any NAC point models, is just very small. It is of interest, therefore, to compare the measured value of α' with the value predicted by the $m=2$ LP. To order $\epsilon_l=1+m/2=2$, α is calculated[34] to be 0.6. The good agreement may be fortuitous inasmuch as several other experimental features of the NAC phase diagram seem to be in disagreement with the concept of an NAC Lifshitz point. Specifically, the phase diagram topology and continuity of thermal properties near the NAC point, as discussed at length above, as well as the x-ray line shapes,[17] are not explained by any LP model. In support of the Lifshitz point interpretation is this value of α and the finite NC entropy[11]; the latter is not directly related to the Lifshitz point as such but does arise naturally in the CL model of the NAC point as a result of fluctuations.[8,9]

C. Chu McMillan model

Unlike the CL model this model employs two-order parameters to describe the NAC phase diagram. The free energy, ignoring gradient terms, is

$$F=a\psi_0^2+\tfrac{1}{2}b\psi_0^4+e\beta_0^2\psi_0^2+\tfrac{1}{2}f\beta_0^4\psi_0^2 \ ,$$

where

$$a=a_o(T-T_1), \quad e=e_0(T-T_2), \quad b,f>0 \ .$$

ψ_0 is the usual density wave amplitude. β_0 is the dipolar order parameter introduced by McMillan[2] to describe the smectic-C phase. Although this model has two-order parameters they are not introduced symmetrically. Both terms involving β_0 are scaled by ψ_0^2 because β_0 is only defined in a layered phase. Scaling β_0 terms by the density wave amplitude rules out the unwanted biaxial nematic. The phase diagram predicted by the CM free energy has a continuous NS line and an oblique AC line much like the CL model but unlike the present experimental results. Adding gradient terms but ignoring director fluctuations, the model predicts Lorentzian x-ray scattering in the plane perpendicular to the director in the nematic phase above the NAC point. This agrees with experimental results but is different from the distinctive $k_{\perp}^{-4}$ prediction of a LP theory like that of CL. Finally, the CM model predicts $\Delta S_{NC}=0$ in disagreement with the present experimental results and with the CL theory.

IV. CONCLUSION

Extensive data have been presented which provide a rather thorough characterization of the NAC phase diagram topology and thermal properties, both globally and near the NAC point. Comparison of these data, and complementary x-ray[17,23,32] and light scattering data,[33] with two hypotheses central to phase transition phenomena, namely, the Ginzburg criterion[24] and two-scale factor universality,[29] suggest that the NC and AC transitions have more in common than the NA and NC transitions. This suggests that biaxiality plays a more important role in the description of the NAC phase diagram and thermal properties than had previously been thought.

If our application of the above hypotheses is correct then the conclusion is that the *C* line is a line of nearly mean-field transitions because of the Ginzburg criterion. It may well be, therefore, that thermal properties along the *C* line are continuous and along the NS line discontinuous at the NAC point because the onset of layering has been washed out by two-scale factor universality leaving the onset of biaxiality as the primary contributor to C_p. If so, this leads to the interesting question of whether one can have systems where the bare lengths are shorter near the NAC point resulting in strong multicritical fluctuation phenomena.

As a final point it should be mentioned that another potential reason for nearly mean-field behavior is dimensionality. For example, certain structural transitions involving soft acoustic modes are at or above the upper critical marginal dimensionality,[21] d_u. Although the AC transition has similarities with such transitions, especially in the presence of a magnetic field,[35] d_u is actually four in the de Gennes model,[5] so its mean-field behavior is likely not related to dimensionality. d_u for the $m=2$ LP is five.[7]

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation under Grant No. DMR79-06330. We wish to thank J. D. Litster for making available to us the results of light scattering experiments prior to publication.

---

*Present address: Tektronix, Inc., P.O. Box 500, Beaverton, Oregon 97077.

[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. de Gennes, Solid State Commun. 10, 753 (1972); Mol. Cryst. Liq. Cryst. 21, 49 (1973).
[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. Teor. 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]G. Sigaud, F. Hardouin, and M. Achard, Solid State Commun. 23, 35 (1977).
[13]J. Swift and B. Mulvaney, J. Chem. Phys. 72, 3430 (1980).
[14]R. M. Hornreich, J. Mag. Magnet. Mat. (to be published).
[15]S. Redner and H. Stanley, Phys. Rev. B 16, 4901 (1977).
[16]G. Grinstein (unpublished).
[17]C. R. Safinya, R. J. Birgeneau, J. D. Litster, and M. E. Neubert, Phys. Rev. Lett. 41, 668 (1981).
[18]R. DeHoff, R. Biggers, D. Brisbin, R. Mahmood, C. Gooden, and D. Johnson, Phys. Rev. Lett. 47, 664 (1981).
[19]C. A. Schantz and D. L. Johnson, Phys. Rev. A 17, 1504 (1978).
[20]D. L. Johnson, C. F. Hayes, R. J. DeHoff, and C. A. Schantz, Phys. Rev. B 18, 4902 (1978).
[21]R. A. Cowley, Phys. Rev. B 13, 4877 (1976).
[22]L. M. Levinson, M. Luban, and S. Shtrikman, Phys. Rev. 187, 715 (1969).
[23]C. Safinya, M. Kaplan, J. Als-Nielsen, R. Birgeneau, D. Davidov, J. Litster, D. Johnson, and M. Neubert, Phys. Rev. B 21, 4149 (1980).
[24]V. L. Ginzburg, Fiz. Tverd. Tela (Leningrad) 2, 2031 (1960) [Sov. Phys. Solid State 2, 1824 (1960)].
[25]D. L. Johnson, C. Maze, E. Oppenheim, and R. Rey-

nolds, Phys. Rev. Lett. 34, 1143 (1975).
[26]C. W. Garland, G. B. Kasting, and K. J. Lushington, Phys. Rev. Lett. 43, 1420 (1979); K. J. Lushington, G. B. Kasting, and C. W. Garland, Phys. Rev. B 22, 2569 (1980).
[27]C. R. Safinya (private communication).
[28]See, for example, L. Kadanoff, in *Phase Transitions and Critical Phenomena,* Vol. 5A, edited by C. Domb and M. S. Green (Academic, London, 1976), p. 10ff.
[29]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).
[30]D. Brisbin, R. De Hoff, T. Lockhart, and D. Johnson, Phys. Rev. Lett. 43, 1171 (1979).
[31]J. Swift and P. Leitner, Phys. Rev. B 16, 4137 (1977).
[32]C. R. Safinya and R. Birgeneau (private communication).
[33]R. Schaetzing, Ph.D. dissertation, MIT, 1980 (unpublished).
[34]R. M. Hornreich, M. Luban, and S. Shtrikman, Phys. Rev. Lett. 35, 1678 (1975); D. Mukamel, J. Phys. A 10, L249 (1977); R. M. Hornreich and A. D. Bruce, *ibid.* 11, 595 (1978).
[35]R. Hornreich, and S. Shtrikman, Phys. Lett. 63A, 39 (1977).