Specific heat of the nematic, smectic-A and smectic-C phases of 4-n-pentylphenylthiol-4′-n-octyloxybenzoate: Critical behavior

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Alternating current microcalorimetry was used to measure the specific heat of 4-n-pentylphenylthiol-4′-n-octyloxybenzoate in the nematic, smectic-A, and smectic-C phases. Critical exponents were found to be consistent with the superfluid analogy of de Gennes for the nematic to smectic-A transition, i.e., $\alpha = \alpha' = 0$ (logarithmic divergence). For the smectic-C to smectic-A transition, the data were consistent with $\alpha' = -0.54$ and inconsistent with the superfluid analogy.

I. INTRODUCTION

Since de Gennes' suggestion[1] that the nematic–smectic-A (NA) and smectic-A–smectic-C (AC) phase transitions may be continuous by symmetry and ought to have superfluid-helium critical exponents, there has been much experimental and theoretical effort spent studying them. Specific-interaction mean-field models of McMillan[2] and Kobayashi[3] had previously confirmed the potential for a continuous NA transition; however, Halperin and Lubensky[4] and Halperin, Lubensky, and Ma[5] later showed that coupling between nematic director fluctuations and the smectic-A density wave,[1-3] which was left out of previous theories, always produces a first-order NA transition. For the supercooling limit T_c^* they estimate $T_c - T_c^* \gtrsim 0.01$ °K. The current experimental situation for the NA transition is confusing. There is conflicting evidence[6,7] concerning the question of a continuous transition and concerning the value of critical exponents. Both mean-field and superfluid exponents have been reported as well as exponents apparently unrelated to either model.[6] There are, in fact, light scattering data[6] which, when interpreted according to the de Gennes[1] theory, suggest the existence of more than one coherence length, although more recent x-ray experiments[7] show that this is not the case. There is clearly a need for more experimental work on the NA transition. Additional motivation for the work reported here arises from the fact that the most extensive prior work has been done on the compound cyanobenzylidene octyloxyaniline (CBOOA) which exhibits double layering[8] and, when pressure is applied[9] or a second component is added,[10] gives peculiar phase diagrams. Therefore, data on other compounds are highly desirable.

Extensive theoretical work has also been done on the AC transition. A mean-field model of McMillan,[11] though unrelated to de Gennes' phenomenological Landau model, nevertheless agrees that a continuous transition is possible, as does a mean-field model due to Wulf.[12] Priest's[13] mean-field second-rank-tensor interaction model also yields continuous AC transitions and was reported to be consistent with superfluid-helium exponents as predicted by de Gennes. DeMoura, Lubensky, Imry, and Aharony[14] have shown that the helium analogy is not destroyed by coupling to elastic degrees of freedom. Thus, theoretically there appears to be some consensus concerning the AC transition, although the specific features of the molecular interaction responsible for the phase are still very much in doubt. Experimentally, there is less data on the AC transition than on the NA transition and, as for the NA transition, the evidence which does exist is somewhat conflicting. A recent light scattering study by Delaye and Keller[15] of the softening of the tilt mode just above the AC transition in terephtal-bis-butylaniline (TBBA) suggests mean-field behavior $\gamma = 1$. On the other hand, tilt-angle studies below the AC transition reported critical behavior in two cases,[16,17] but classical behavior in another.[18]

The advantage of specific-heat measurements is clear-cut for both the NA and AC transitions. First of all very little high-resolution specific-heat data is available for the NA transition and, to our knowledge, none is available for the AC transition. Furthermore, Landau theory predicts for both the NA and AC transitions a simple finite discontinuity whereas the helium-analogy prediction is, for both cases, a λ anomaly or, more specifically, a nearly logarithmic divergence. These two cases are easily distinguished from each other experimentally.

We present specific-heat data for 4-n-pentylphenylthiol-4-n'-octyloxybenzoate, which we shall call $\overline{8}S5$.[19] For the smectic-A to smectic-C transition of $\overline{8}S5$, the data presented are consistent with a cusplike finite discontinuity and inconsistent with both the mean-field and helium-analogy predictions, whereas the nematic to smectic-A tran-

sition data are consistent with a logarithmic divergence as predicted by the helium analogy. The data come from a minicomputer-based ac-microcalorimetry experiment described below.

II. EXPERIMENT

The thermal configuration of the calorimeter and lumped-element model of it are shown in Figs. 1(a) and 1(b). If an appropriate electrical heater current is employed, the heat current $\dot{Q}$ will have both a sinusoidal ac and a dc component. In the steady state, the ac component $\dot{Q}_{ac}(t)$ induces an ac component in the temperature difference between the sample and the reservoir $\Delta T(t) = T_S(t) - T_R$, given by

$$\Delta T(t) = \dot{Q}_0 R\,[1+(\omega CR)^2]^{-1/2} \sin\omega t = \Delta T_m \sin\omega t \qquad (1)$$

for an appropriate choice of phase. A test of this lumped-parameter response model may be made by comparing values of $\dot{Q}_0$ and ΔT_m measured at various frequencies ω with the equation

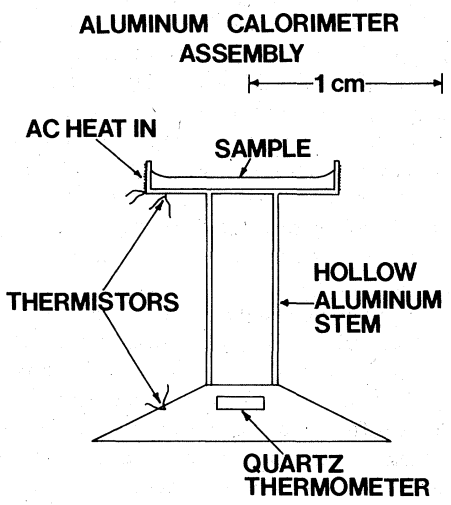
$$(\dot{Q}_0/\Delta T_m)^2 = a + b\omega^2 \quad . \qquad (2)$$

a and b are related to the model parameters R and and C by

$$a = 1/R^2, \quad b = C^2 \; . \qquad (3)$$

We tested the model first for the *empty* calorimeter at frequencies in the range $0.01 < \omega^2 < 0.06$ rad^2 sec^{-2}. ΔT was measured with thin flake thermistors and T_R was measured with a quartz thermometer. Results of the linear-regression analysis of these data are summarized in Table I. It is clear from the coefficient of determination that the lumped-parameter model explains the empty-calorimeter data very well in this frequency range. Furthermore, an examination of the last two columns of Table I shows that the empty-calorimeter heat capacity C_{add} and the thermal resistance R vary by only 0.15% and 1.0%, respectively, over the entire temperature range. Hence, systematic heat-capacity errors of less than $\pm 0.001 C_{add}$ are introduced through use of the *average* values $\bar{C}_{add}$ and $\bar{R}$ in analyzing *filled*-calorimeter data. This assumes that the data are taken at some *fixed frequency* and C_p is calculated from $C_p = C - \bar{C}_{add}$, where C is found from Eqs. (2) and (3) with R replaced by $\bar{R}$.

All this, of course, assumes that the lumped-parameter model is also valid for the filled calorimeter. Over the range of frequencies $0.02 < \omega < 0.2$ rad sec^{-1}, which brackets the fixed frequency $\omega = 0.1$ at which data presented here were taken, the lumped-parameter model was found to be valid for the filled calorimeter to within $\pm 0.2\%$; however, the optimum R was found to be 0.3% lower than the empty-calorimeter value, a negligible change. At higher frequencies, systematically lower values of C were found such that at $\omega \sim 0.4$ rad sec^{-1} this deviation reached -2%. Such a reduction of the apparent heat capacity is in the right direction and of the right magnitude to be accounted for by the thermal skin-depth effect. The frequency dependence of the filled calorimeter was measured at just one temperature 50 °C, and, of course, the skin depth is temperature dependent. However, whereas the thermal skin depth[20] depends only on the ratio $(\omega/\kappa)^{1/2}$, where κ is the thermal diffusivity, and whereas we have shown that increasing ω by a factor of 4 from 0.1 to 0.4



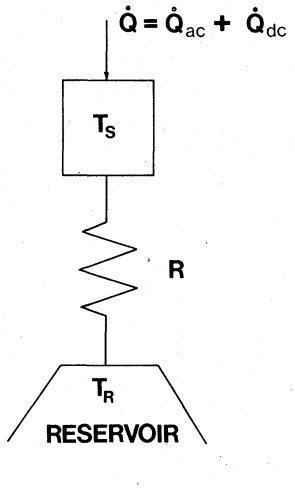


FIG. 1. (a) Schematic of ac microcalorimeter, and (b) thermal equivalent circuit of ac microcalorimeter used in analyzing heat-capacity data. $\dot{Q}$ is the heat current introduced to the sample. C is the heat capacity of the sample plus addenda which are at temperature T_S and separated thermally by resistance R from the reservoir at temperature T_R.

TABLE I. Condensed results of fitting the empty-calorimeter data taken at several temperatures and at frequencies in the range $0.01 < \omega^2 < 0.06$ rad^2 sec^{-2} to the lumped-parameter model defined in Eqs. (2) and (3).

$T_S = T_R + \dot{Q}_0 R$ (°C)	Coefficient of determination r^2	$a = 1/R^2$ (W^2 °C^{-2} ×10^{-4})	$b = C_{add}^2$ (J^2 °C^{-2})	C_{add} (J/°C)	R (°C W^{-1})
50	0.999 9991	7.1627 ±0.0585	0.261 98 ±0.001 4	0.511 85 ±0.000 14	37.36 ±0.15
55	0.999 9994	7.1607 ±0.0479	0.261 30 ±0.000 12	0.511 18 ±0.000 11	37.37 ±0.12
60	0.999 9993	7.286 ±0.050	0.261 19 ±0.000 12	0.511 07 ±0.000 13	37.05 ±0.13
65	0.999 9992	7.311 ±0.055	0.261 96 ±0.000 13	0.511 82 ±0.000 13	36.98 ±0.14
Average	...	7.230 ±0.080	0.261 61 ±0.000 42	0.511 48 ±0.000 41	37.19 ±0.20

causes a −2% error in C due to skin effect, we may conclude that a nearly fourfold increase in λ, the thermal conductivity, would be required to produce a −2% systematic error in C, since C only changes by 40% throughout our range of data. This seems unlikely even near a phase transition. The effect is highly nonlinear such that a threefold increase in λ would produce less than 1% error.

The 4-*n*-pentylphenylthiol-4′-*n*-octyloxybenzoate ($\bar{8}S5$) used in this study was synthesized and purified by Neubert. The precursors of each synthetic step were carefully purified and the final product was recrystallized three times from ethanol. Elemental analysis of the carbon, hydrogen, and sulfur content differed from the calculated values by +0.02, +0.04, and −0.02%, respectively. Based on this result and the synthetic and purification procedures used, Neubert estimates the purity to be somewhat in excess of 99.9%.

Using thermal microscopy, we have simultaneously compared the melting, smectic-C to smectic-A, smectic-A to nematic, and nematic to isotropic transition temperatures of the present material with corresponding transitions of $\bar{8}S5$ used by one of us in a previous study.[19] The latter material was synthesized and purified by the Motorola (Phoenix) group. Each of the four transition temperatures of the present material agreed with the corresponding transition temperature of the Motorola material to within experimental uncertainty of 0.05 °C. Computer analysis of the fusion curve of the Motorola $\bar{8}S5$, taken on a Perkin-Elmer (DSC-2) differential scanning calorimeter, indicated a purity of 99.9+% in agreement with Neubert's estimate for the present material. We conclude that the best estimate of the purity of the material used in this study is 99.9+%.

III. DATA

The result of our measurements are shown graphically in Figs. 2–4. From the data it is clear that the NA and AC transitions are qualitatively different from each other. In the following sections these transitions will be discussed and compared with each other and with theoretical predictions.

Figure 2 shows the specific heat of $\bar{8}S5$ in units of the ideal gas constant R_0. Distinct anomalies are found at temperatures of 56.20 and 63.43 °C, which, to within experimental uncertainty, are found by microscope observations to be the AC and NA transition temperatures, respectively. A nematic-isotropic transition is also found under the microscope at 86.5 °C, and upon cooling a monotropic smectic-C to tilted-smectic-B transition is found at 20 °C. The melting point of $\bar{8}S5$ is 56.5 °C which means that both the C and B phases are monotropic.

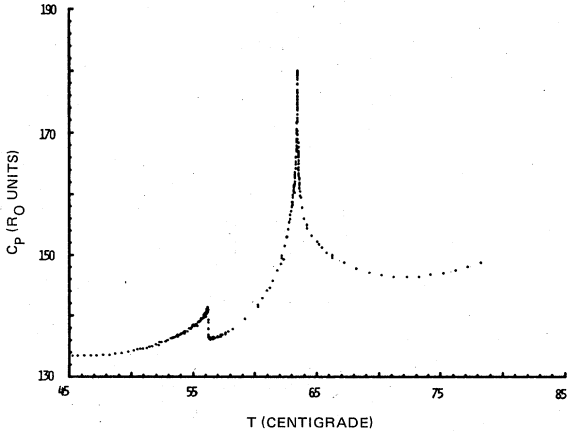


FIG. 2. Measured specific heat in units of R_0, the ideal gas constant, vs temperature in degrees celsius.

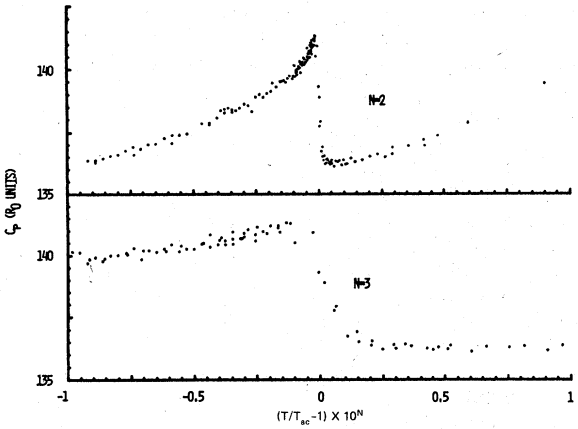


FIG. 3. Measured specific heat near the smectic-A–smectic-C transition vs reduced temperature $t \equiv [T/T_{AC}-1]\times 10^N$, where $T_{AC}=329.348\,^\circ$K is the temperature, where dC_p/dT is maximum. For $N=2$ one tic mark on the horizontal axis represents 0.165 °K.

The present measurements indicate that any entropy discontinuity at the NA or AC transitions is less than $0.002R_0$. This estimate recognizes that the rounding of the transitions could be due to the coupled effects of latent heat and finite temperature resolution or to sample-inhomogeneity-induced two-phase regions. However, the amplitude of the applied temperature oscillations ranged from $0.045 < \Delta T_m < 0.01\,^\circ$C depending upon the *distance* $|\Delta T| = |T - T_c|$ from the transition temperature T_c. This finite temperature resolution is of the right magnitude to account for the rounding of the transitions seen in Figs. 3(b) and 4. Further evidence favoring instrumental rounding for the NA transition is that Freedericksz transition and light scattering studies[21] of the bend curvature coefficient enhancement indicate that $T_c^* - T_c < 0.006\,^\circ$K. This is less than the observed rounding. Therefore the rounding may be entirely instrumental. We return to this point in Sec. IV A.

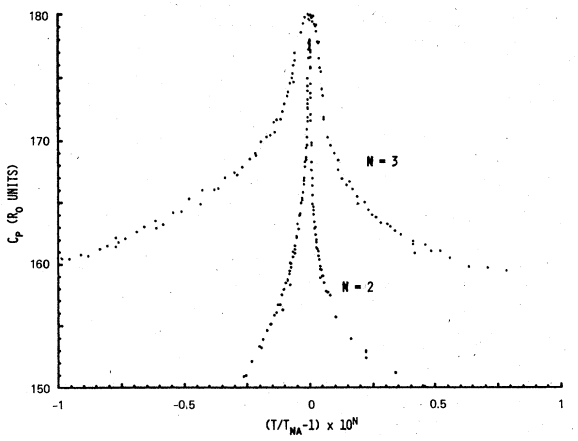


FIG. 4. Measured specific heat near the nematic–smectic-A transition vs reduced temperature times 10^N. The reduced temperature is defined as $t \equiv [T/T_{NA} - 1]$ and $T_{NA}=336.578$ is the temperature where a smoothed C_p vs T is maximum. For $N=3$ the data were all increased by $2R_0$ for clarity.

The features of these transitions that stand out quite clearly in Fig. 2 are (i) the NA transition discloses a λ-like anomaly, whereas (ii) the AC transition appears much more like a simple discontinuity, namely, an Ehrenfest second-order transition. Upon closer examination of the AC transition [see Fig. 3(a)] we see that there may be a very weak divergence or, as in nickel, a cusp-like singularity. The truth about this is obscured somewhat by the rounding of the transition and the temperature dependence of the smectic-A contribution on the high-temperature side. Note, however, that Fig. 3(a) shows an increasing slope on approach to the AC transition from below. Indeed the slope is seen to become quite steep and is increasing quite rapidly just before the rounding begins at $|T/T_{AC} - 1| \sim 1.2\times 10^{-4}$. The implications of a very weak divergence or cusp are important and will be discussed in Sec. IV. If we assume a simple discontinuity and linearly extrapolate the data to the midpoint of the rounded region, we find $\Delta C = 6R_0$ and $T_{AC} = 56.20\,^\circ$C for the specific-heat discontinuity and the transition temperature, respectively.

IV. ANALYSIS AND DISCUSSION

Both microscopic mean-field theories and Landau theories have been written for the NA and the AC phase transitions. Critical exponents have been predicted and discussed. We proceed to compare these theories with the data presented.

A. Nematic–smectic-A transition

De Gennes[1] has predicted a superfluidlike anomaly in the specific heat rather than a simple discontinuity as in superconductor. In his theory the specific heat should behave as

$$C_p^- = \frac{A}{\alpha'}\left(|t'|^{-\alpha'} - 1\right) + B' + E't' \quad \text{for } T < T_c\,, \tag{4a}$$

$$C_p^+ = \frac{A}{\alpha}\left(|t|^{-\alpha} - 1\right) + B + Et \quad \text{for } T > T_c\,, \tag{4b}$$

with $\alpha = \alpha' \sim 0$, $A \sim A'$. For CBOOA, Djurek *et al.*[22] found $\alpha = 0.16 \pm 0.01$ with $\alpha' = 0.14 \pm 0.02$ so that, to within their estimated experimental uncertainty, $\alpha = \alpha' = 0.15$. This is *not* consistent with the superfluid analogy, but is consistent with the three-dimensional Ising model.

In our analysis we have included the E and B terms to account for the background contribution

TABLE II. Results of fitting the specific-heat data for $\overline{8}S5$ near the nematic–smectic-A transition to Eqs. (4a) and (4b). The first two columns give the range of reduced temperatures included in each fit and the third gives the standard deviation of the data from the best fit. The last five columns list the best-fit parameter values and their standard errors.

$\lvert t'\rvert_{\min}$ [a]	$\lvert t'\rvert_{\max}$	σ' (R_0)	A' (R_0)	α'	T_c' (°K)	B' (R_0)	E' (R_0)
5.79×10^{-5}	1.27×10^{-2}	0.48	6.198	0.0012	336.588	117.67	524
			±2.98	±0.07	±0.0084	±11	±151
5.79×10^{-5}	6.12×10^{-3}	0.35	4.998	0.0042	336.576	126.84	1271
			±0.638	±0.017	±0.002	±2.64	±107
5.79×10^{-5}	3.15×10^{-3}	0.29	4.74	0.0041	336.574	128.96	1586
			±0.71	±0.018	±0.0018	±3.07	±185
$\lvert t\rvert_{\min}$	$\lvert t\rvert_{\max}$	σ	A	α	T_c	B	E
6.98×10^{-5}	1.41×10^{-2}	0.24	4.129	0.0001	336.585	129.45	60.7
			±0.128	±0.003	±0.0014	±0.77	±32
6.98×10^{-5}	5.76×10^{-3}	0.23	4.043	0.01	336.582	129.89	183.5
			±2.87	±0.09	±0.0064	±11.3	±255
6.98×10^{-5}	3.39×10^{-3}	0.25	4.297	0.0014	336.583	127.99	183.8
			±4.04	±0.12	±0.0063	±16.4	±522

[a] $t\equiv1-T/T_0$, where $T_0=336.578$ is the temperature at the center of the rounded peak (see Fig. 4).

which we shall call the *regular contribution*.[23] The data were fitted by Eqs. (4a) and (4b), using a nonlinear least-squares fitting technique known as Marquardt's compromise,[24] and the results are shown in Table II. The error bars are standard errors in the parameters and include the effects of all parameter correlations.[24]

The results shown in Table II reveal several points. (a) The data below the transition cannot be fitted well by Eq. 4(a) for $\lvert t'\rvert_{\max}\geq 6.12\times10^{-3}$ but a good fit is obtained for $\lvert t'\rvert_{\max}=3.15\times10^{-3}$. The data above the transition fit Eq. (4b) for all three values of $\lvert t\rvert_{\max}$ with remarkably little variation of A, α, B, and T_c. These results were additionally supported by an examination of deviation plots. (b) Scaling is statistically allowed by the data in that $\alpha=\alpha'$ is easily true within the combined standard errors. Furthermore, $\alpha=\alpha'=0$ is allowed as is $A=A'$. Thus a logarithmic divergence is consistent with the data. (c) $T_c=T_c'$ is statistically allowed. (d) $B=B'$ is easily consistent with the data, however $E=E'$ is not. B and B' have very reasonable values as can be seen by examination of Fig. 2.

The failure of the $E=E'$ hypothesis strongly suggests that the E and E' terms in Eqs. (4a) and (4b) cannot be understood in the present context as regular terms. A recourse is to replace them by correction to scaling terms.[25] Since the data for $T>T_c$ are consistent with $E=0$ over a wide range of $\lvert t\rvert_{\max}$, deleting both Et and $E't'$ is valid and consistent. Tables III and IV give the results of fits to equations of the form

$$C_p^- = -A'\ln\lvert t'\rvert(1+D'\lvert t'\rvert^{x'})+B', \tag{5a}$$

$$C_p^+ = -A\ln\lvert t\rvert(1+D)\lvert t\rvert^{x})+B, \tag{5b}$$

subject to the constraint $T_c=T_c'$. We have assumed that $336.571<T_c<336.581$ °K. D and D' are the coefficients of the correction to scaling terms. Table III shows that for $T<T_c$, and T_c in the given range, we must have $0.749\pm0.073<x'<1.07\pm0.172$. Therefore $x'=0.5$, which is predicted by theory for three dimensions,[26] is not allowed by the data. However $x'=1$, which is predicted theoretically for two dimensions,[26] is allowed by the data. For $T>T_c$ we found (not shown) that the data allow either $x=0.5$ or $x=1$ because $D\ll D'$. In Table IV we have taken $x=x'=1$. The results in Table IV are interesting for several reasons. First, we find that only for $T_c=T_c'=336.576$ °K is the scaling requirement[27] of equal amplitude ($A=A'$) consistent with the data. Second, for $T_c=336.571$ °K the data above T_c show substantial systematic deviations, whereas for $T_c=336.581$ °K the data below T_c show substantial systematic deviations; this justifies our assumption $336.571<T_c<336.581$ °K given $x=x'=1$. Furthermore, we find that $B\neq B'$ and that $P\equiv(B'-B)/A\sim1$ compared to the value $P\sim4$ predicted theoretically[28] for three dimensions. Finally, we found that removal of the several points near T_c having deviations in excess of two standard deviations resulted in a substantial improvement of the fit below T_c but had no effect on the previous conclusions. The results of these fits are given at the bottom of Table IV.[29]

TABLE III. Results of fitting the specific-heat data for $\overline{8}S5$ below the nematic–smectic-A transition to Eq. (5a). The first two columns give the range of reduced temperatures included in each fit and the third column gives the standard deviation of the data from the best fit. The fourth column gives the critical temperature which was fixed and the last four columns give the best-fit parameter values and their standard errors. The standard errors do not include correlations with T_c.

$\lvert t_{min}\rvert$	$\lvert t_{max}\rvert$	σ' (R_0)	T_c	A'	B'	D'	x'
5.94×10^{-5}	6.12×10^{-3}	0.301	336.571	3.770 ±0.269	138.441 ±2.912	−30.031 ±6.15	0.749 ±0.073
5.94×10^{-5}	6.12×10^{-3}	0.331[a]	336.576	4.676 ±0.237	130.235 ±2.40	−37.64 ±16.32	0.901 ±0.115
5.94×10^{-5}	6.12×10^{-3}	0.363[b]	336.581	5.360 ±0.209	124.487 ±2.00	−58.01 ±43	1.07 ±0.172

[a] Deviation plot shows systematic deviation of data from best-fit curve by an amount approximately equal to the random scatter.

[b] Data show systematic deviation from the fit curve of approximately two to three times the random scatter.

It is of interest to compare our results with the predictions of Halperin and Lubensky[4] (HL). They predict that the smallest supercooling limit of the NA transition is given by

$$\Delta T_{min} = T_c - T_c^* = \frac{\Delta S_{min}\, T_c}{2\Delta C} \gtrsim 0.005\,^{\circ}\mathrm{K}\,, \tag{6}$$

where ΔS_{min} is the minimum estimated entropy

TABLE IV. Results of fitting the specific-heat data for $\overline{8}S5$ near the nematic–smectic-A transition to Eqs. (5a) and (5b) with T_c (T_c') and X (X') held fixed as shown in columns 4 and 8. The first two columns give the range of reduced temperatures included in each fit and the third column gives the standard deviation of the data from the best fit. Columns 5, 6, and 7 give the best-fit parameter values and their standard errors.

$\lvert t'\rvert_{min}$ ($\lvert t\rvert_{min}$)	$\lvert t'\rvert_{max}$ ($\lvert t\rvert_{max}$)	σ' (σ)	$T_c = T_c'$	A' (A)	B' (B)	D' (D)	$x \equiv x'$	$\bar{\sigma}$[b]
5.94×10^{-5}	6.12×10^{-3}	0.325		4.377 ±0.059[c]	132.049 ±0.518	−71.82 ±3.56		
(6.83×10^{-5})	(5.76×10^{-3})	(0.285)[a]	336.571	(5.254 ±0.102)	(120.856 ±0.866)	(23.309 ±2.52)	1	0.311
5.94×10^{-5}	6.12×10^{-3}	0.331[a]		4.845 ±0.066	128.518 ±0.575	−55.37 ±3.26		
(6.83×10^{-5})	(5.76×10^{-3})	(0.251)	336.576	(4.908 ±0.084)	(123.439 ±0.718)	(18.814 ±2.37)	1	0.304
5.94×10^{-5}	6.12×10^{-3}	0.361[a]		5.275 ±0.078	125.33 ±0.675	−43.34 ±3.27		
(6.83×10^{-5})	(5.76×10^{-3})	(0.229)	336.581	(4.543 ±0.071)	(126.199 ±0.613)	(12.293 ±2.342)	1	0.319
6.83×10^{-5}	4.93×10^{-3}	0.222		4.702 ±0.055	129.720 ±0.481	−62.55 ±3.05		
(1.28×10^{-4})	(5.76×10^{-3})	(0.211)	336.576	(4.698 ±0.094)	(125.143 ±0.792)	(14.488 ±2.54)	1	0.217
6.83×10^{-5}	4.93×10^{-3}	0.226	336.578	4.860 ±0.058	128.535 ±0.503	−57.219 ±3.00	1	

[a] These fits show small systematic deviations near T_c, but removing eight points below T_c having deviations in excess of two standard deviations and five such points above T_c resulted in the last three fits which show no apparent systematic deviations.

[b] $\bar{\sigma} \equiv [(N^-\sigma'^2 + N^+\sigma^2)/(N^+ + N^-)]^{1/2}$, where N^+ and N^- are the number of data points above and below T_c, respectively.

[c] All uncertainties are standard parameter errors (Ref. 24). Correlations with T_c and x are not included.

discontinuity and ΔC is the underlying mean-field specific-heat discontinuity. Since our instrumental resolution is $\delta T = 0.02\,^\circ$K, we cannot make a direct test of such a small supercooling limit. On the other hand, if in Eq. (6) we may correctly take $\Delta C = B' - B$, then experimentally we have $\Delta C \sim 5R_0$ and taking $\Delta S \sim 0.002R_0$, our experimental upper limit on ΔS, gives $\Delta T = 0.07\,^\circ$K which is certainly greater than any experimentally allowable value of $T_c - T_c^*$, giving reason to suspect that in fact $\Delta S \ll 0.002R_0$. Furthermore, given $A = A'$, $x = x' = 1$, $\alpha = \alpha' = 0$ we may conclude[29] that $T_c - T_c^* < 0.002\,^\circ$C which is smaller than the HL estimate of the lower limit of supercooling.

We may use our experimental value of $\Delta C = B' - B$, along with estimates of the zero-temperature longitudinal and transverse coherence lengths $(\xi_0)_\parallel$ and $(\xi_0)_\perp$, to estimate the width of the critical region δT_c using the Ginzburg criterion[30] as calculated for the smectic A by HL. They give

$$\delta T_c = \epsilon_c T_c = \frac{k_B^2 T_c}{32\pi^2 \Delta C^2 (\xi_0)_\parallel^2 (\xi_0)_\perp^4}\ , \qquad (7)$$

where k_B is the Boltzmann constant. For $(\xi_0)_\parallel = 10$ Å and $(\xi_0)_\perp = 3$ Å and $\Delta C = 5R_0$, we get $\delta T_c \sim 2.5\,^\circ$K, a reasonable value, though probably somewhat small. One must note, however, the very strong dependence of δT_c on $(\xi_0)_\parallel$ and $(\xi_0)_\perp$ which have not been measured for this compound as yet. For CBOOA, a molecule with approximately the same size and shape as $\bar{8}S5$, x-ray scattering measurements yield $(\epsilon_0)_\parallel = 27.9$ Å and $(\epsilon_0)_\perp = 4.82$ Å which would give $\delta T_c \sim 0.05\,^\circ$K, certainly an unreasonable result for $\bar{8}S5$. Assuming that 27.9 Å represents approximately twice the $\bar{8}S5$ longitudinal coherence length due to double layering in CBOOA helps but not enough since then $\delta T_c \sim 0.4\,^\circ$K which is probably an order of magnitude or more too small. We conclude that zero-temperature coherence lengths *significantly smaller than the extended length and width of the molecule* are required if Eq. (7) is to give a reasonable estimate of the critical region for $\bar{8}S5$, given the present measured value of ΔC. Since $\delta T_c/T_c$ is small, one expects the Ginzburg criterion, which is based on mean-field calculations, to give a reasonable estimate of the width of the critical region.

B. Smectic-A–smectic-C transition

Equation (4a) was used to fit the data below T_c. The results are given in Table V. No attempt was made to fit the data above T_c because of strong residual temperature dependence of the smectic-A phase.

It appears that the data determine the exponent α' quite well and that the value of α' is remarkably independent of the range of data used in the fit, as is $B' - A'/\alpha' = C_p(T_c)$. The best fit occurs for the range $325.068 < T < 329.198\,^\circ$K. It gives $T_c = 329.30 \pm 0.10\,^\circ$K and $\alpha' = -0.54 \pm 0.07$. This value of α' is

TABLE V. Results of fitting the specific-heat data for $\bar{8}S5$ below the smectic-A–smectic-C transition to Eq. (4a). The first two columns give the range of temperatures included in each fit and the last two give the range of reduced temperatures. The third column gives the standard deviation of the data from the best fit. Columns 4–8 give the best-fit parameter values and their standard errors. Column 9 gives the best-fit value of $C_p(T_c)$.

T_{min}	T_{max}	σ (R_0)	T_c	A'	α'	B'	E'	$B' - A'/\alpha'$	$\lvert t\rvert_{min}$ [a]	$\lvert t\rvert_{max}$ [b]
327.018	329.311	0.141	329.308 ±0.003	27.35 ±3.98	−0.500 ±0.022	86.76 ±5.62	···	141.46	1.12×10^{-4}	7.07×10^{-3}
325.068	329.311	0.136	329.308 ±0.003	28.39 ±2.42	−0.505 ±0.014	85.28 ±3.30	···	141.50	1.12×10^{-4}	1.30×10^{-2}
325.068	329.286	0.138	329.279 ±0.003	33.96 ±2.92	−0.540 ±0.014	78.31 ±3.81	···	141.20	1.88×10^{-4}	1.30×10^{-2}
325.068	329.268	0.136	329.274 ±0.012	34.97 ±4.76	−0.546 ±0.024	77.08 ±6.00	···	141.13	2.43×10^{-4}	1.30×10^{-2}
325.068	329.249	0.132	329.271 ±0.028	35.90 ±6.27	−0.551 ±0.033	75.93 ±6.00	···	141.08	3.0×10^{-4}	1.30×10^{-2}
325.068	329.198	0.126	329.297 ±0.100	34.15 ±11.04	−0.540 ±0.066	77.96 ±13.36	···	141.20	4.55×10^{-4}	1.30×10^{-2}
325.068	329.311	0.137	329.317 ±0.013	17.03 ±14.66	−0.439 ±0.111	102.90 ±23.83	57.34 ±86.85	141.69	1.12×10^{-4}	1.30×10^{-2}
322.318	329.311	0.137	329.312 ±0.006	43.62 ±17.30	−0.551 ±0.050	62.30 ±24.32	−81.86 ±58.44	141.47	1.12×10^{-4}	2.13×10^{-2}

[a] $\lvert t\rvert_{min} \equiv \lvert T_{max}/T_0 - 1\rvert$, where $T_0 = 329.348$ is the temperature where dC_p/dT is maximum. T_0 is also the zero reference in Fig. 3, where it is called T_{AC}.

[b] $\lvert t\rvert_{max} \equiv \lvert T_{min}/T_0 - 1\rvert$ with T_0 defined above.

consistent[31] with the n-vector model for the cases $n \sim 5-8$, $d=3$ and $n=2$, $d=2$, where n is the number of components in the order parameter and d is the dimensionality of the critical fluctuations. For comparison, de Gennes' theory[1] of the AC transition predicts a logarithmic divergence ($\alpha'=0$), i.e., $n=2$, $d=3$. This theoretical result has been confirmed by others[13,14] and found to be unchanged by coupling to elastic degrees of freedom. *The data presented here are not consistent with a logarithmic divergence.* It appears that renewed theoretical effort is in order for the smectic-A–smectic-C transition. It may be argued that the nematic–smectic-A–like fluctuations are interfering and that the present results are not typical of a pure AC transition. We believe the cusplike AC transition is indeed typical of an isolated AC transition because we also observe it for 4-n-pentyloxy-benzylidene-4′-n-heptylanline which has a 10° smectic-A range above the AC transition and very little residual A-phase temperature dependence near T_{AC}.

V. CONCLUSION

The specific-heat data presented here are asymptotically consistent with the de Gennes superfluid analogy[1] for the NA transition ($\alpha=\alpha'=0$). However, the highest-order correction term has an exponent $x' \sim 1$ contrary to the prediction $x'=0.5$ for three-dimensional models. The experimentally determined correction exponent is in fact consistent with the prediction for two-dimensional models. We note that it has been shown that, due to divergent phase fluctuations, the smectic-A phase, in common with $n \geq 2$, $d=2$ systems, lacks conventional long-range order.[1,7] The effect of divergent phase fluctuations on critical fluctuations has not been studied theoretically. We conclude that in the asymptotic limit the present experimental results are consistent with de Gennes' prediction that the nematic–smectic-A transition is analogous with the superfluid transition in helium-4, but that a deviation may occur in the leading correction to scaling term. The close proximity of the AC transition prevents a firm conclusion concerning this latter point.

The smectic-A to smectic-C phase transition in 8S5 is consistent with the exponent $\alpha' = -0.54 \pm 0.07$ which, in turn, is consistent with the n-vector model for $n=d=2$ and $n \cong 5-8$, $d=3$. It is inconsistent with the superfluid analogy predicted originally by de Gennes[1] and subsequently by others.[13,14]

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