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High-Resolution Heat-Capacity Studies near the Nematic-Smectic-*A* Transition in Octyloxycyanobiphenyl (8OCB)

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High-resolution ac calorimetry measurements on two different samples of 8OCB whose transition temperatures differ by less than 0.1 K show different critical behavior at the nematic-smectic-*A* transition. $\alpha^+ = \alpha^-$ is near zero on one sample, agreeing with Johnson's measurements, while $\alpha^+ = \alpha^-$ equals 0.25 on the second sample which agrees with Garland's measurements on 8OCB. These results suggest the possibility that the nematic-smectic-*A* transition on 8OCB is near a tricritical point or crossover between two types of critical behavior.

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In recent years there has been much theoretical and experimental work aimed toward the understanding of the nematic-smectic-*A* phase transition. The mean-field theories of McMillan[1] and Kobayashi[2] describe the smectic-*A* order parameter as a complex scalar, $\psi = |\psi| e^{i\varphi}$, where $|\psi|^2$ is the amplitude of the smectic layers and $\varphi = 2\pi z/d$, where d is the interlayer spacing. McMillan has predicted that the nematic-smectic-*A* transition can be second order and that the tricritical point, where the transition changes from second to first order, would occur at some critical value of the ratio of the nematic-smectic-*A* transition temperature to the nematic-isotropic transition temperature, T_{na}/T_{ni}. Since then there has been extensive work on pure compound which exhibit this transition in the effort to determine the order of the transition and to measure the critical exponents when it is a second- or slightly first-order transition. de Gennes[3] has predicted heliumlike exponents based on the expression for the Landau free energy of the smectic-*A* phase. Several experiments have been done to measure the exponents and compare them to the helium values of $\nu = 0.66$ and $\alpha = 0$. Johnson *et al.* have measured α in pentylphenylthiol-octyloxybenzoate ($\bar{8}$S5)[4] and in 8OCB[5] and have found $\alpha^+ = \alpha^-$ near zero. In their 8OCB measurements they observe a 40-mK-wide flattened region at the transition. Birgeneau, Litster, and co-workers[6] have done light-scattering and x-ray-scattering measurements and have found perpendicular and parallel correlation lengths which diverge at different rates. In the case of different $\nu_\parallel$ and $\nu_\perp$, an anisotropic scaling law can be written

$$2\nu_\perp + \nu_\parallel = 2 - \alpha.$$

Using anisotropic scaling with results of Ref. 6 on 8OCB, $\nu_\parallel = 0.71$, $\nu_\perp = 0.58$, we obtain $\alpha = +0.12$. In another ac heat-capacity experiment on 8OCB, Garland *et al.*[7] has measured α between 0.2 and 0.3 which does not agree with the value of Ref. 5 or with the value which emerges from Ref. 6. The sample used by Garland *et al.* is from the newer of two batches made by British Drug Houses (BDH).

We chose 8OCB for measurement because of its chemical stability. We decided to do measurements on samples from the two different batches of 8OCB because there existed such varying results for the exponent α found by the other groups. The samples of 8OCB were given to us by P. E. Cladis of Bell Laboratories and D. Johnson of Kent State University. Both samples originated from BKH but were reportedly from different stock. Cladis had vacuum sublimated the 8OCB from the earlier stock, while Johnson's sample

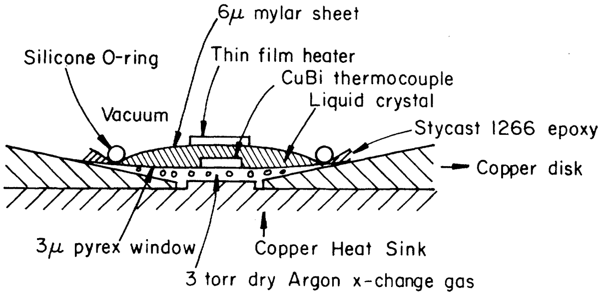

FIG. 1. The experimental cell for the ac heat-capacity measurements of liquid crystals. A Pyrex window with a thin-film thermocouple junction in its center is epoxied over a hole in a copper disk. The liquid crystal lies between the Pyrex window and a sheet of Mylar with a thin-film heater on its top. Several Torrs of exchange gas behind the window ensures perpendicular heat flow from the thin-film heater.

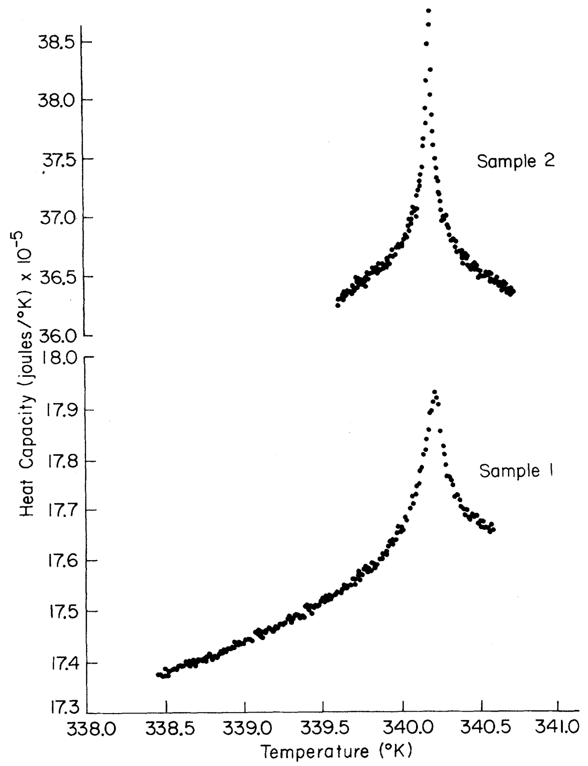

FIG. 2. The raw data on sample 1 is from run II. The different magnitudes of the heat capacity reflect the different amounts of sample used. The shapes of these curves illustrate the different behavior of the nematic-smectic-*A* transition in the two samples. The curves produce different specific-heat exponents and amplitude ratios in spite of the agreement between the transition temperatures.

was straight from the bottle. His sample was from the second batch and not the same as the earlier sample which he measured.

Our measurements are done in an ac calorimeter[8] operated between 1.0 and 10.0 Hz. The operating frequency must lie in the flat part of the heat capacity versus frequency curve. In this region the sample reaches thermal equilibrium in less time than the period of the temperature oscillation. The overall change in heat capacity is small enough so that this is still true near T_c. The experimental assembly is shown in Fig. 1. First a thin Pyrex window is epoxied onto a copper mount with Stycast 1266.[9] The temperature oscillations of the liquid crystal are measured with a copper-bismuth thermocouple evaporated on the window. Attached to the glass is a 6-μm-thick, 0.5-in.-diam Mylar disk on which is evaporated a Chromel-*A* heater and its leads. The sample sits between the Cu-Bi thermocouple junction and the heater-Mylar combination. A silicone *O* ring is pressed against the Mylar under vacuum to seal the sample. If necessary, a drop of Stycast 1266 epoxy is added around the edge of the Mylar to seal off any places where the liquid crystal could still be leaking from underneath the Mylar. Because we seal an unknown amount of liquid crystal, our measurements are of the changes in heat capacity and not of absolute values of specific heat. A microcomputer is used to control and measure the temperature and oscillations of the sample. The size of the temperature oscillations is varied from 1 to 10 mK depending on the resolution desired. After the data are taken the temperature oscillation at each point is converted to heat capacity and a χ^2 analysis is done.

The heat-capacity data for the two samples appears in Fig. 2 where Sample 1 is the earlier sample vacuum sublimated by Cladis. Two independent runs have been done on this sample, at 1.96 and 9 Hz, with reproducible results for background slope, α, and the critical amplitude ratio. These runs (I and II) have been done six months apart on two different speciments from the earlier batch of 8OCB. The data for sample 1 in Fig. 2 is from run II. The rms value of the temperature oscillation is 5 mK. The heater power for the two runs shown is on the order of 10^{-4} W. Sample 2 in Fig. 2 is the later BDH sample. The rms temperature oscillation is 1–2 mK enabling us to fit the data closer to T_c. The frequency of the heater voltage is also 9 Hz. The difference in the T_c's of the two samples is 32

± 35 mK. This is calculated with use of the average of the two runs on Sample 1. T_c is stable in both samples through repetitions of the experiment. The transition appears to be second order with a sharp symmetric peak for both samples within our temperature resolution. Neither flattening of the peak nor a two-phase region is observed in either sample. No hysteresis between heating and cooling sweeps, which would indicate first-order behavior, is observed. Although Halperin, Lubensky, and Ma[10] predict that this transition is always at least slightly first order, critical behavior is still observed close to T_c.

The heat-capacity data are fitted with the following equations:

$$C_p^{\,+} = (A^+/\alpha)(|t|^{-\alpha} - 1) + B^+ + Dt,$$

$$C_p^{\,-} = (A^-/\alpha)(|t|^{-\alpha} - 1) + B^- + Dt,$$

where $t = (T - T_c)/T_c$. The transition temperature, linear background slope, and α are assumed to be the same on both sides of the transition. Even with these assumptions the fit involves seven parameters with which we minimize the χ^2. We have adapted a program from Bevington[11] which uses a standard nonlinear least-squares technique known as Marquadt's compromise. Before doing the nonlinear fit we subtract off the background slope and do a linear fit for $C_p^{\,+}$ as a function of $C_p^{\,-}$. This is possible as long as $\alpha^+ = \alpha^-$. We choose values for T_c, the slope, and the range of data which optimize the linear fit based on the condition that $\alpha^+ = \alpha^-$. The data are then folded with use of the linear relationship between $C_p^{\,+}$ and $C_p^{\,-}$ and a three-parameter nonlinear fit is done. This gives values for α, A^+, and B^+. The slope and intercept from the linear fit contain all the coefficients so that A^- and B^- can be calculated. Although we do not assume $B^+ = B^-$ it comes out of the fits that they are the same. The results for the various parameters for the two samples appear in Table I. The fits are done for different ranges of reduced temperature. The experimental rounding is observed by making a plot of $\log C'$ versus $\log|t|$ where C' is the divergent part of the heat capacity. Such a plot indicates the range of data which could be fitted without rounding affecting the value of the exponent. In the linear range we can peel off the data closest to T_c without the value of α changing.

Our results clearly indicate that there are different values of the exponent α for the two samples of 8OCB. The fact that the transition temperatures are in agreement is evidence that we have two samples of the same compound. High-pressure liquid chromatography has shown that each has three overlaping peaks with a slight difference in the height of one of the peaks.[12] This

TABLE I. Runs I and II on sample 1 were done on different liquid crystal from batch 1 and at different frequencies. We obtain A^+/A^- between 1.3 and 1.39 and α lying between − 0.02 and + 0.06 for both runs on sample 1. This result agrees with the experiment of Johnson *et al.* (Ref. 5) on the earlier batch of 8OCB and with de Gennes (Ref. 3) prediction of $\alpha \sim 0$. The best fit for sample 2 shows A^+/A^- to be about 1.2 and α lies between 0.23 and 0.27. The exponent agrees with the recent measurement of Garland *et al.* (Ref. 7) on the later batch of 8OCB. His value of A^+/A^-, however, was approximately 1.0.

Experiment	Reduced temperature range	T_c	α	A^+/A^-	10^6A^+	10^6A^-	10^3B^+, 10^3B^-	10^3D
Sample 1, run I (Early batch)	$5.0\times10^{-3} - 6.0\times10^{-5}$	340.107 ± 3 mK,[a] ± 40 mK[b]	0.025 ± 0.04	1.39	1.2	0.86	0.17	0.45
Sample 1, run II (Early batch)	$1.3\times10^{-3} - 9.8\times10^{-5}$	340.215 ± 7 mK,[a] ± 50 mK[b]	0.034 ± 0.03	1.3	0.92	0.7	0.17	0.47
Sample 2, run II (Late batch)	$1.3\times10^{-3} - 2.5\times10^{-5}$	340.193 ± 2 mK,[a] ± 15 mK[b]	0.25 ± 0.02	1.2	0.64	0.52	0.35	0.4

[a] The error bars represent the uncertainty in the value of T_c obtained in the data-fitting procedure.

[b] These error bars represent the uncertainty in the absolute value of T_c due to the dc temperature rise and in the Pt-thermometer reading.

indicates the presence of impurities similar to the main compound which may be positional isomers. Homologous impurities may be ruled out as pure octylbromide would be used in the alkylation of the molecule. 220-MHz NMR has indicated the presence of only one component in each sample. These analyses indicate that both samples may contain small but differing amounts of positional isomeric impurities. It is essential that future measurements of liquid crystals be combined with better chemical characterization.

We conclude that small compositional differences can drastically affect critical behavior. Perhaps these compounds are on different sides of a special critical point such as a tricritical point or a crossover between two kinds of critical behavior. We do not have evidence for a tricritical point as we have not observed first-order behavior in either sample within the temperature resolution. The values for the exponent and amplitude ratios do not agree quantitatively with any of the values coming out of the n-vector model. However, the shift of α away from zero and the accompanying decrease in A^+/A^- might indicate a crossover to critical behavior where the number of fluctuating components in the order parameter has decreased from $n=2$ to $n=1$.

We have measured α on several other compounds and have a found a dependence on the T_{na}/T_{ni} ratio where the exponent shifts at T_{na}/T_{ni} equal to 0.96, the value for 8OCB. $\bar{8}$S5 and CBOOA, whose T_{na}/T_{ni} ratio is 0.94, behave as sample 1 of 8OCB with α less than or equal to zero. 8CB, whose value of T_{na}/T_{ni} equals 0.98, however, behaves as sample 2 of 8OCB with α near 0.3. The results on these samples, which will appear in a more complete article, indicate further that 8OCB lies at a crossover between two types of critical behavior.

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