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Volumetric Study of the Nematic–Smectic-*A* Transition of N-*p*-Cyanobenzylidene-*p*-Octyloxyaniline

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(Received 25 March 1974)

We have measured a change in specific volume of $(0.5 \pm 0.2)\times 10^{-4}$ cm^3/g at the nematic–smectic-*A* transition of N-*p*-cyanobenzylidene-*p*-octyloxyaniline. The order of this transition has recently been subject to dispute. On the basis of our data, we conclude unambiguously that it is of first order as is expected from theoretical analysis.

We report here conclusive evidence that the nematic–smectic-*A* transition of N-*p*-cyanobenzylidene-*p*-octyloxyaniline (CBOOA) is first order. We have deduced this by measuring the temperature dependence of the density of CBOOA. The measurements were performed on a variety of amounts (35 g to a few hundred micrograms) and a variety of purities (the nematic–smectic-*A* transition temperature T_{SN} ranging from 81 to 83.4°C). We have found that the transition is always of first order, even in the case of rather impure samples.

This transition has been believed to be of second order [1-3] since early differential-scanning-calorimeter (DSC) measurements[1] did not show the transition. Subsequent DSC measurements[4] in purified samples did show a small "bump" at the nematic–smectic-*A* transition. This "bump" appeared to be a latent heat; its magnitude (0.06 cal/g) did not contradict theoretical estimates expected for this compound[5] and it became broader and ill-defined with increasing sample impurity. Unfortunately, DSC measurements cannot distinguish unambiguously between a latent heat and a specific-heat anomaly, so that further experimental evidence was required to define the order of this transition for CBOOA.

The unambiguous determination of the order of the nematic–smectic-*A* transition for this compound is currently of great theoretical and experimental interest. Stimulated by de Gennes's[6] analogy between the smectic-*A*–nematic transition and the superconductor–normal-metal transition and the theoretical result predicting the possibility of a second-order transition,[5,7,8] a great deal of experimental effort has been expended[2,4] studying pretransitional effects near the smectic-*A* transition of this reputedly second-order compound. Briefly, these experiments show that in the case of *pure* CBOOA the transition behaves "classically"[4] (in the sense of the Ginzburg criterion) whereas in the case of "*dirty*" CBOOA, "nonclassical" behavior has been observed.[1,2,4] The nonclassical behavior of CBOOA was analyzed[1,2] by assuming *a priori* that the smectic-*A*–nematic transition was second order, and on this basis it has been argued[2] that this nonclassical behavior is similar to that which occurs at the superfluid-helium transition. However, the observed "classical" behavior for pure CBOOA does not exclude the possibility that this transition is second order, because, as Alben[9] has pointed out, classical behavior is expected for helium-like systems when the transition is only barely second order, i.e., in the vicinity of a tricritical point.[10] More recently, Halperin and Lubensky[11] have predicted that the smectic-*A*–nematic as well as the superconductor–normal-metal transition must always be at least weakly first order, and that for type-I materials[12] the transition must occur outside the critical region.

Samples of CBOOA (Kodak No. 11963) were introduced in glass test tubes of about 1 to 3 cm i.d. and 5 to 10 cm length. These tubes were previously treated with a silane coupling agent (Dow Corning XZ-2300) in order to align the molecules of CBOOA perpendicular to the glass surface[13] and hence minimize the effect of bend deformations which tend to suppress the smectic-A phase and diffuse the transition.[6] The bend deformations are expected to be very small when they occur over a macroscopic length such as ours.[14] The samples were kept for several hours at 100°C and at pressures below 1 mm of mercury to eliminate traces of solvents. Recrystallization of the sample did not substantially change the specific-volume jump at the transition. The test tubes were fused to U tubes which ended in capillaries with 1.5 to 0.4 mm i.d. (±1%). The samples were then evacuated, filled with triple-distilled mercury, and immersed in a large oil bath the temperature of which could be controlled to ±0.02°C. The volume change was calculated from the measurement of the change in height of the mercury column measured to ±0.01 mm at equilibrium.[15] The purpose of the mercury was to (1) isolate CBOOA from water vapor, which can destroy it, and from other gases that can become entrapped in it, particularly in the smectic phase; (2) provide a large, flat, liquid-crystal–mercury meniscus (see Fig. 1) so that the surface-energy changes at the liquid-crystal–glass interface at the transition would not contribute significantly in its observed volume change; and (3) induce a favorable configuration to the smectic phase, as also shown in Fig. 1 where one sees a very fine disclination line along the axis of the tube.[16]

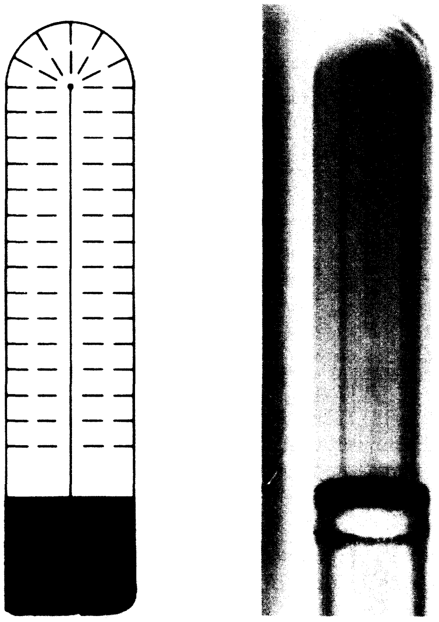

FIG. 1. The experimental configuration. The tube has been treated with a silane coupling agent (Ref. 13) to induce the homoeotropic alignment at the liquid-crystal–glass interface. The tube here is at 78°C ($T_{SN} \sim 83.3$°C). In the center we see a very thin line. The interface with mercury seems not to distort the disposition of the smectic layers. The alignment of the molecules in the layers is shown schematically on the left of the figure.

Microscope observations of very small tubes (80–100 μm i.d.) have verified that in the smectic-A phase the sample configuration is as shown in Fig. 1. This "melts" in the nematic phase into two disclinations of strength $S=\frac{1}{2}$ of the planar type.[17] With the mercury interface, these planar disclinations seem to be very stable. The orientation of CBOOA at this interface seems to be nearly parallel to the surface. The transition temperatures of CBOOA as prepared in this manner do not appear to change from day to day.

Table I summarizes our results and Fig. 2 shows typical sets of data obtained at the nematic-isotropic, smectic-A–nematic, and crystal–smectic-A transitions. In one of our experiments [Fig. 2(b)] we measured the variation of the expansion coefficients in the small range of temperature (1–2°C) about the transition but outside

TABLE I. Summary of results. The values for $\Delta\bar{V}$ were measured at the transition temperature as the distance between the two extrapolated lines which define the temperature dependence of the density of the two phases (see Fig. 2). To calculate dT/dP we used the Clapeyron equation and the latent-heat values ΔH found in Refs. 1, 4, and 18.

Phase transitions	T (°C)	ΔT (°C)	ΔH (cal/g)	$10^4\Delta\bar{V}$ (cm^3/g)	$10^3 dT/dP$ (°K/bar)
Crystal–smectic-A	73.8	0.30 ±0.1	18.7 [a]	540 ±10	23.9
Smectic-A–nematic	83.4	0.08 ±0.04	0.06 [b]; 0.04 [c]	0.5 ±0.2	7.1; 10.7
Nematic-isotropic	108.5	0.5 ±0.2	0.59 [a]; 0.50 [c]	16.0 ±2.0	24.8; 29.3

[a] Ref. 1.
[b] Ref. 4.
[c] Ref. 18.

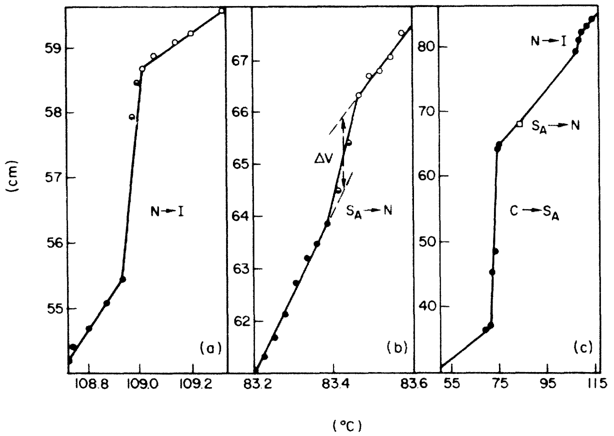

FIG. 2. The height of the mercury column in centimeters versus temperature (°C) for the three transitions (a) nematic to isotropic, (b) smectic-*A* to nematic, and (c) crystal to smectic-*A*. The three graphs are for three different samples and thus the ordinate is arbitrary. The half-filled circles indicate where the two phases were visually observed to coexist. The coexistence of the two phases or the existence of an "intermediate phase" (Ref. 19) was observed in both large and small samples. The size of the experimental points represents typical experimental reproducibility for a given sample. The measurements were made at equilibrium, i.e., when the height of the mercury column remained unchanged. Thermocouple measurements were taken with a Keithley 171 digital multimeter. The thermocouple was calibrated in a separate experiment against a platinum resistance thermometer.

the transition range ΔT_{SN}, and found that they did not depend substantially on the temperature, thus suggesting, moreover, that the transition was a *normal* first-order transition.[20] This result allowed us to establish the volume-temperature relationships for the smectic-*A* and the nematic phases as two least-squares lines, and hence to calculate (i) the expansion coefficients α of the two phases in the neighborhood of the transition, and (ii) the statistical significance of the volume jump $\Delta\bar{V} = (0.5 \pm 0.2)\times 10^{-4}$ cm^3/g. We found that α was 8.1×10^{-4} and 4.7×10^{-4} cm^3/g °C for the smectic-*A* and nematic phases, respectively, and that even if the measured volume jumps varied as much as 40% from sample to sample, they were always significant at least at the 95% level. Experiments on a small sample (9.0×10^{-5} g) in an 80-μm capillary contained in the Mettler FP5 hot stage, where we measured the variation of the CBOOA-mercury meniscus with temperature, confirmed the results for $\Delta\bar{V}$ obtained with the large samples.

Hysteresis of the volume-temperature relationship was always observed during our experiments. It appeared that the width of the transition ΔT_{SN} was not reproducible when cooling the sample, and was 2 or 3 times larger than the reproducible ΔT_{SN} measured when heating the sample. We think this is an experimental artifact caused by the different kinetics of the two processes as has been shown long ago by Maas.[21] He found that the time required for the establishment of equilibrium, when an ordered structure involving orientation is being formed, is much larger than the time required to disrupt it. It is therefore more difficult experimentally to judge the achievement of equilibrium for a slow-growing smectic-*A* phase than for a relatively fast-growing nematic phase. In Table I we have reported only transition widths ΔT_{SN} and volume jumps $\Delta\bar{V}$ measured by "melting" the smectic-*A* phase into the nematic phase. We also observed that the smectic-*A*–nematic transition was more easily detectable, i.e., larger $\Delta\bar{V}$ were measured, for "monocrystalline" samples (like that shown in Fig. 1) than for "polycrystalline" samples.[22] We discuss this problem in greater detail elsewhere.[19]

We also measured the volume jump at the nematic-isotropic and crystal–smectic-*A* transitions. Taking the values of the latent heats for the various transitions as measured by other authors,[1,4,18] we are able to compute the variation of the transition temperatures with pressure, dT/dP, at the transition temperatures from Clapeyron's equation. These are also shown in Table I. From the table, we see that although dT/dP is bigger for the nematic-isotropic transition than it is for the smectic-*A*–nematic, one still requires a pressure of about 1 kbar to drive this transition to the tricritical point, where the ratio of the transition temperatures $T_{\mathrm{SN}}/T_{\mathrm{NI}} \simeq 0.88$, as given by earlier theories.[5,7,8] From the theory of Halperin and Lubensky, one does not expect a pressure-induced tricritical point. Since this is an experimentally realizable pressure, it would be interesting to see if the tricritical point does in fact exist.

In conclusion, from our measurements of the volume change of CBOOA as a function of temperature we deduce that the nematic–smectic-*A* transition for CBOOA is weakly first order. These results are in keeping with the theoretical considerations of Halperin and Lubensky.[11] One would also expect this result even on the basis of earlier theories.[5,7,8] Further, they show that impurities do not change the nature of the transition even if one is no longer able to observe the transition on a DSC. On the basis of the theory of Halperin and Lubensky, then, we can expect this compound to exhibit "classical" pretransitional behavior. The "nonclassical" behavior found for dirty samples[1,2,4,23] may arise from a phase-separation effect.

We thank S. Marcelja for sending us the results of Djurek and Franulović for the latent heat at the nematic-smectic-*A* transition of CBOOA and B. Halperin for fruitful discussions.

We would also like to thank F. Hardouin, H. Gasparoux, and P. Delhaes for having sent us their results on the specific-heat measurements at the nematic-smectic-*A* transition for CBOOA. Their measurements confirm the first-order nature of the transition. Unfortunately, their letter arrived when this paper was already completed and therefore was not included in the discussion.

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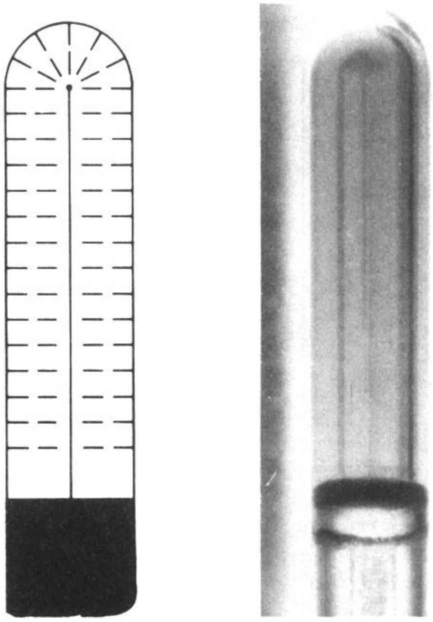

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