tion length and $u_2 \cong 4628t^{0.387}$ cm/sec for the second-sound velocity one obtains $D_2^{RGT} \cong D_0^{RGT} t^{-0.288}$ with $D_0^{RGT} \cong (0.3 \text{ or } 0.5) \times 10^{-4}$ cm^2/sec from the two values of R_2. The dashed lines in Fig. 4 correspond to these two theoretical estimates. For $t \lesssim 5 \times 10^{-4}$ they are consistent with the new measurements. For larger t, background contributions to D_2 presumably dominate and are expected to explain the difference between the theoretical asymptotic result and the data of Ref. 9.

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High-Resolution Calorimetric Study of the Nematic–Smectic-A Transition in Octyloxycyanobiphenyl (8OCB)

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An ac technique has been used to measure the heat capacity of 8OCB at 1 atm along several high-pressure isobars. The C_p data near the essentially second-order nematic–smectic-A (N-SmA) transition are inconsistent with the logarithmic singularity expected from the $d=3$, $n=2$ model of de Gennes but agree with a power-law divergence with $\alpha = \alpha'$ in the range 0.2–0.3. This behavior and an unexpected exponential decrease in the magnitude of the critical N-SmA heat capacity with increasing pressure are also confirmed in octylcyanobiphenyl (8CB).

The character of the nematic (N) to smectic-A (SmA) transition in liquid crystals is not yet fully understood. On the basis of the nature of the complex SmA order parameter, de Gennes[1] developed a model in which the N-SmA transition is analogous to the lambda transition in ^{4}He ($d=3$, $n=2$ universality class). If this is correct, the critical exponents should be the same in the two systems; in particular there should be a nearly logarithmic divergence in the heat capacity ($\alpha' = \alpha \simeq 0$). We have tested this prediction with a high-resolution ac calorimetric study of 4-n-octyloxy-4′-cyanobiphenyl (8OCB) at 1 atm and along several high-pressure isobars. This material has a bilayer smectic structure[2] and exhibits a reentrant nematic phase at high pressures.[3] Earlier C_p measurements at 1 atm were reported to be consistent with a logarithmic peak, but there were some difficulties due to impurities that caused a 40-mK-wide two-phase region at the transition.[4] In the pure material, there is strong evidence that first-order discontinuities are either absent or very small.[5,6] 8OCB is an attractive system since the chemical stability is excellent and high-purity samples are now available from BDH Chemicals.

The major conclusions of our work are as follows: (1) *The heat-capacity data are not consistent with $\alpha = \alpha' = 0$ but require a fairly large positive exponent*; (2) the C_p peak associated with the

N-SmA transition decreases markedly in magnitude without change in shape as the pressure is increased. These conclusions are confirmed by work in progress on 4-n-octyl-4′-cyanobiphenyl (8CB).

The measurements were carried out on a computer-controlled ac calorimeter using temperature oscillations with a 30-sec period and ~10-mK peak-to-peak amplitude. An 8OCB sample of 0.074 g was sealed in a silver/gold cell weighing ~0.5 g to prevent contact with the Ar pressure gas. Corrections for the contribution of the pressure gas are discussed in Baloga and Garland.[7] Thermodynamic equilibrium is ensured by long equilibration times: at least 30 min for each point (even when the temperature change was only 2–3 mK), 21 days for the 1-atm run from 50 to 90 °C. Details of our experimental procedure will be given elsewhere.[8] We wish to point out here that complications caused by a possible small latent heat and/or the finite amplitude of our temperature oscillations can only affect data within ±10 mK of the transition. Phase coexistence gives rise to abnormally high heat capacities and anomalous phase shifts; and these effects were observed at the nematic-isotropic (N-I) transition. No such effects were seen at the N-SmA transition, but we cannot rule out a very small latent heat (say a few J mol^{-1}).

Figure 1 shows the variation in C_p with temperature in the smectic-A, nematic, and isotropic liquid phases at 1 atm and 500 bars. The N-I peak will not be analyzed or discussed here, but it is important to note that the size and shape of this peak are essentially identical at both pressures. As the pressure is increased, both T_{NI} and T_{NA} increase (in good agreement with Ref. 3) and the separation of the peaks (T_{NI}-T_{NA}) also increases. It can be established[8] that the best background for the N-SmA peak is a smooth extension of the N-I peak, as shown in Fig. 1. However, any reasonable choice of background will yield a critical N-SmA heat capacity $\Delta C_p(NA) = C_p(\text{obs}) - C_p(\text{back})$ that decreases drastically with increasing pressure. This trend is confirmed by measurements at 1000 bars, and $\Delta C_p(NA)$ values near the N-SmA transition are shown in Fig. 2 for these three isobars. At 1500 and 2000 bars, we searched carefully over the entire range where N-SmA transitions are observed visually[3] and found very little indication of thermal anomalies. Attempts to study the region of the smectic-A–reentrant-nematic transition at 1500 and 2000 bars were not successful since the metastable SmA liquid froze before reaching the reported reentrant temperature.

It should be stressed that our data are not consistent with a logarithmic singularity [see Fig. 3(a)]. Indeed, these data cannot be forced to

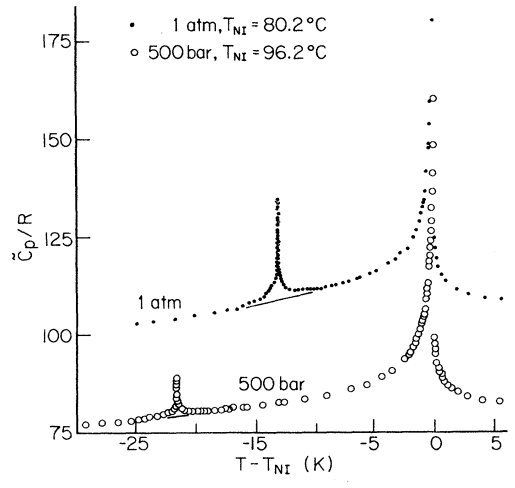

FIG. 1. Heat capacity of 8OCB at 1 atm (shifted up 25 units for clarity) and 500 bars. Background curves used to obtain ΔC_p at the N-SmA transition are shown.

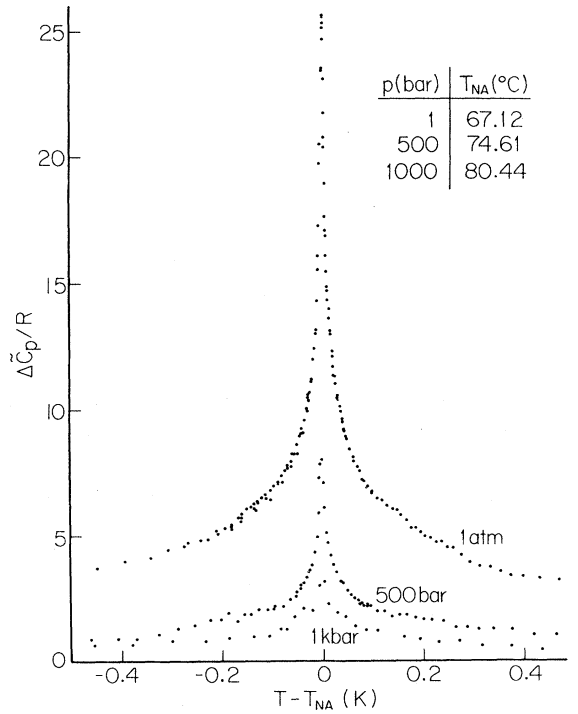

FIG. 2. Critical heat capacity $\Delta C_p(NA)$ near the nematic–smectic-A transition in 8OCB.

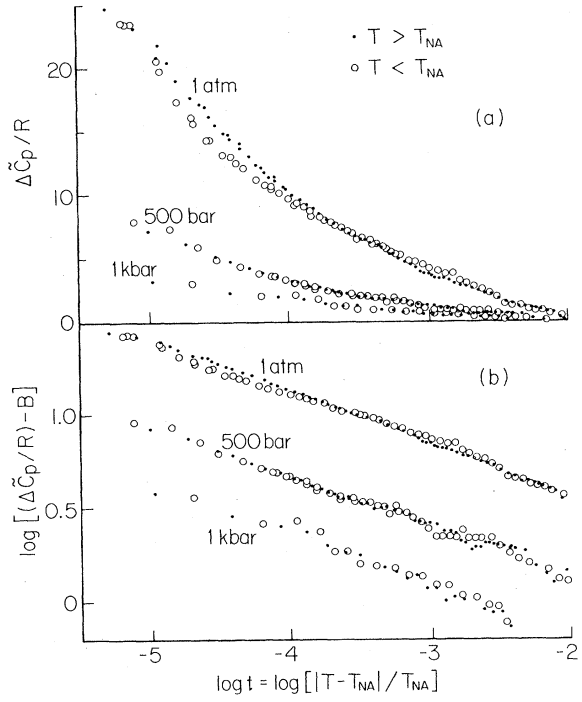

FIG. 3. (a) $\Delta\tilde{C}_p/R$ vs $\log_{10}t$; (b) $\log_{10}[(\Delta\tilde{C}_p/R)-B]$ vs $\log_{10}t$. See text for values of $B=B'$.

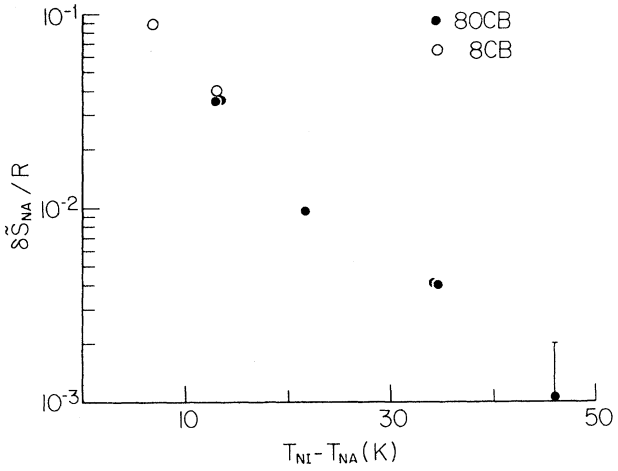

FIG. 4. Dependence of N-SmA transition entropy δS_{NA} on $T_{NI}-T_{NA}$ for 8OCB and 8CB at various pressures.

yield a good fit to the form $A\log_{10}t+B$, where $t=|T-T_{NA}|/T_{NA}$, with any physically reasonable choice of T_{NA} and background. A full discussion of fitting procedures will be given later,[8] but we wish to report two fits that indicate that our data require fairly large positive α values. The simple power-law form

$$\Delta\tilde{C}_p/R=At^{-\alpha}+B \quad \text{for } T>T_{NA},$$
$$\Delta\tilde{C}_p/R=A't^{-\alpha'}+B' \quad \text{for } T<T_{NA} \tag{1}$$

was tested for the full data set ($10^{-5}<t<10^{-2}$) with T_{NA} fixed at T_m, the temperature of maximum C_p, and $\alpha=\alpha'$, $B=B'$. Figure 3(b) shows the fit when $\alpha=\alpha'$ is taken to have the fixed value 0.27 at all pressures. The resulting least-squares values of A and B are $A=1.124$, $A'/A=0.955$, and $B=-3.22$ at 1 atm; $A=0.387$, $A'/A=1.005$, and $B=-1.35$ at 500 bars; and $A=0.185$, $A'/A=1.067$, and $B=-0.60$ at 1000 bar. The fits above T_{NA} are excellent, and the least-squares value of α is stable to range shrinking and the introduction of a corrections-to-scaling term. The 1-atm fit below T_{NA} is the least good, and this α' does vary somewhat with range shrinking. In order to avoid the influence of any systematic errors that might occur in ΔC_p at very small or large t, we also fitted a truncated 1-atm data set (10 mK $<|\Delta T|<$ 1 K; $3\times10^{-5}<t<3\times10^{-3}$) with T_{NA} treated as an adjustable parameter. The best fit gave $T_{NA}=T_m+3.5$ mK, $\alpha=\alpha'=0.20$, $A=2.446$, $A'/A=1.016$, and $B=B'=-6.04$. Thus we conclude that the effective α exponents for our data lie in the range 0.2 to 0.27. It should be noted that the data reported in Ref. 4 are compatible with our 1-atm data except for the range $|t|<7\times10^{-5}$ over which the earlier data were influenced by impurities. The different conclusions in Ref. 4 are largely the result of greater ambiguity in the choice of T_{NA}.

The present C_p data seem to rule out the possibility that all the critical exponents correspond to those of the $d=3$, $n=2$ universality class (He analogy). The large α values lead one to consider the Lubensky-Chen model,[9] which involves an anisotropic fixed point that is important near the N-SmA transition. Their modified version of hyperscaling ($2-\alpha=\nu_{\parallel}+2\nu_{\perp}$) associated with this fixed point provides a link between our heat-capacity exponent and the critical exponents for the longitudinal and transverse correlation lengths. The present scattering data on 8OCB leads to an inconclusive result ($\nu_{\parallel}+2\nu_{\perp}=1.84$, yielding $\alpha=0.16\pm0.12$), but the better-characterized 8CB data are encouraging ($\nu_{\parallel}+2\nu_{\perp}=1.69$, which gives $\alpha=0.31\pm0.10$).[10] The general pattern in three bilayer smectics [8CB, 8OCB, and CBOOA (N-p-cyanobenzylidene-p-octyloxyaniline)] seems to be $\nu_{\perp}<\nu_{\parallel}\simeq\nu_{\mathrm{He}}$, and such anisotropy in the correlation-length exponents also indicates deviations from the simple helium analogy. In

the Lubensky-Chen model one would expect crossover from quasicritical anisotropic to isotropic behavior and then to first order, but our data suggest that this crossover must occur very close to T_{NA}.

The decrease in the magnitude of the N-SmA peak shows a systematic trend with pressure and with the difference $\Delta T \equiv T_{NI} - T_{NA}$, which is almost linear in p for 8OCB. Figure 4 shows that the excess entropy $\delta S_{NA} \equiv \int [\Delta C_p(NA)/T]\, dT$ varies like $\exp(-\Delta T)$ for 8OCB and for 8CB, a bilayer smectic without a reentrant nematic phase.[3] Our data on 8CB will be presented later, but it is worthwhile noting that it also gives a large positive α value in 0.25–0.4 range. For the present purposes, the 8CB results are cited to show a second case where the N-SmA peak shrinks with pressure while the N-I peak is essentially unchanged. The superposition of 8OCB and 8CB points in Fig. 4 suggests that $(T_{NI} - T_{NA})$ is a more appropriate variable than absolute pressure. This is also supported by the decrease in δS_{NA} observed at 1 atm in mixtures of 8OCB with 6OCB (see Lushington and Kasting[11]) and with 7CB (see Karat and Madhusudana[12]). It is clear that the energy fluctuations that give rise to $\Delta C_p(NA)$ must be very sensitive to the extent of saturation in the nematic ordering at T_{NA}.

Another way to consider the magnitude of the N-SmA heat capacity peaks in 8OCB and 8CB is in terms of two-scale-factor universality.[13] For these liquid crystals, we used $X \equiv (\Delta C_p - B)\xi_{\parallel}\xi_{\perp}^2 t^2 / k_B$ to reduce complications associated with the choice of individual critical exponents and their effect on the amplitude coefficients. The quantity X should be a universal constant. Although the uncertainties in this quantity due to the choice of B and experimental errors in ΔC_p, $\xi_{\parallel}$, and $\xi_{\perp}$ are fairly large, values of $100X = 9 \pm 3$ describe both 8OCB and 8CB over the range $10^{-4} < t < 10^{-2}$. The similarity in X values for 8OCB and 8CB demonstrates that large C_p peaks are associated with short correlation lengths. This strongly suggests that the correlation-length coefficient ξ_0 should increase with pressure for both materials, which seems physically reasonable and worth testing experimentally.

As a final suggestion for new experimental work on the cyanobiphenyl liquid crystals, measments of the critical exponent β associated with SmA ordering would be desirable, although this determination is complicated by the Landau-Peierls nature of the SmA phase of 8OCB.[14]

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