Specific-Heat Critical Exponents near the Nematic–Smectic-*A* Phase Transition

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We have applied a recently developed method for sensitive calorimetric measurements to investigate the nematic–smectic-*A* phase transition in pure N-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline. The results indicate a very weak first-order transition with a transition entropy of $(0.017\pm 0.002)R_0$. The critical exponents of the specific-heat anomaly have nonclassical values $\alpha = 0.16\pm 0.01$ and $\alpha' = 0.14\pm 0.02$.

Recent molecular-field calculations[1,2] and an observation of the analogy between smectic-*A* liquid crystals and superconductors[3] have greatly stimulated the interest in the nematic–smectic-*A* (*N*-*A*) phase transition. According to the molecular-field theory, the *N*-*A* transition is second order for a suitable choice of parameters. On the basis of measurements by differential scanning calorimetry[4] and nuclear magnetic resonance[5] a second-order *N*-*A* transition has been reported to occur in CBOOA (N-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline).

However, the latest calorimetric measurements[6] indicated that the *N*-*A* transition is probably a weak first-order phase transition. At the same time, a theoretical argument,[7] based on the analogy between smectic-*A* liquid crystals and superconductors, showed a presence of a small cubic term in the Landau expansion of the free energy, resulting in a weak first-order transition.

The analogy between *N*-*A* and superconducting transitions can be used to predict[3] the critical behavior of elastic constants near the phase transition. However, different experiments measuring the critical exponent ν have yielded the classical value[6] $\nu = 0.5$ as well as the value[8,9] $\nu = 0.66$ predicted on the basis of Wilson's calculations.

Here we report high-precision calorimetric measurements on refined CBOOA. The experiments prove that the *N*-*A* transition is indeed first order and that the exponents of the specific-heat anomaly have nonclassical values within a narrow interval from the phase transition. The reported experiments also represent the first successful use of the newly developed technique[10,11] for high-precision specific-heat measurements on materials with low thermal conductivity.

The samples of CBOOA (Eastman Organic Chemicals) were purified by a number of recrystallizations from *n*-heptane. Unrefined samples are characterized by a dark yellow color, which vanishes upon purification.[6] After several recrystallizations the sample was dissolved in *n*-heptane and sedimented over one month. The solution was then distilled without heating under reduced pressure, until only about 1% of the original amount of material remained. Our best sample subjected to this procedure had an ivory color and, depending on purity, $T_{N\text{-}A}$ of different samples ranged from 82°C to 84°C. The purest CBOOA with $T_{N\text{-}A} = 84.05°\text{C}$ has been used for specific-heat measurements. This is the highest value for $T_{N\text{-}A}$ in CBOOA reported until now. Upon cooling and heating T_0 exhibits a hysteresis effect of about 0.02 K.

The samples were sealed in a glass container as shown in Fig. 1 and the specimen was connected to the thermal sink by the thermal resistance of the thermocouple and heater leads, R_t. A step-function current input is applied to the 14-Ω Manganin heater (*H*) and the corresponding temperature-time response measured by the thermocouple (*T*) is detected by a Hewlett Packard 919A dc null voltmeter connected to a chart recorder.

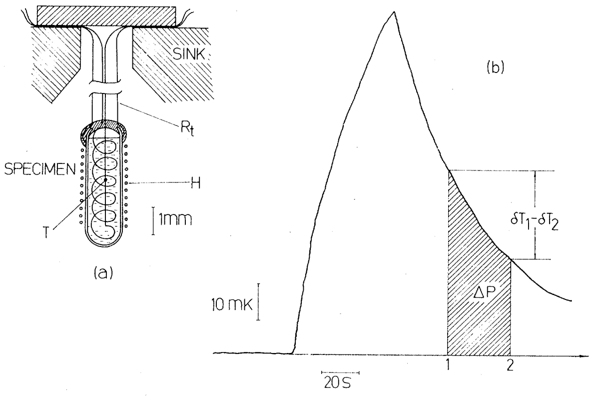

FIG. 1. (a) Specimen arrangement with thermocouple (*T*), thermal resistance (R_t), and heater (*H*). (b) Experimental heating-cooling curve used for evaluating the time constant τ_p.

After the Joule heating is stopped the cooling curve obeys the exponential law with time constant $\tau_p = R_t(C_p + C_0)$. C_p is the heat capacity of the sample itself and C_0 measures the contribution of the glass container, bonding agent, and wires. The initial part of the recorded curve must be excluded. It is affected by internal relaxation within the specimen, due to thermal resistance between the heater and the sample, thermal resistance of the sample itself, and parasitic capacity contributions to C_0.[12]

The time constant τ_p is simply related to the area ΔP under the exponential part of the curve between two arbitrary points (1, 2) (Fig. 1) by the relation

$$R_t(C_p + C_0) = \Delta P/(\delta T_1 - \delta T_2). \tag{1}$$

It is important to note that this evaluation of the time constant is also possible in the case of strong temperature dependence of the specific heat of the sample. The exponential law is then distorted on a large time scale, but a time constant $R_t(C_p + C_0)$ can be associated with the temperature corresponding to a small part of the curve with the area ΔP as shown in Fig. 1. This type of analysis is valid in the limit where the temperature inhomogeneity in the sample is small compared to the temperature interval $\delta T_1 - \delta T_2$. The areas have been measured for time intervals 10 sec or greater which correspond to a temperature inhomogeneity across the whole sample of less than 10% of $\delta T_1 - \delta T_2$. Since the time constant of the specimen to the sink is about 60 sec the most important condition for a good recording of temperature-time curves is a good temperature stability of the sink. The best results are obtained with an instability of a few millikelvins per hour. The temperature of the sample was monitored by a copper-Constantan thermocouple connected between the sample and an ice bath. The maximum amplitude δT_{max} of the heating steps was about 80 mK and typical values of $\delta T_1 - \delta T_2$ close to the transition temperature ranged from 10 to 20 mK. The heat capacity C_0 of the glass container, the bonding agent, and the wires was subtracted by making additional blank temperature-time recordings. The controlled amount of silicone rubber on the upper side of the container was carefully removed and the sample dissolved from the glass. The rubber was then put back on the empty container with a wire configuration as similar as possible to that during the measurement of the specimen.

In a latent-heat run the sink is heated in such a way as to obtain a linear temperature rise in time. The recorded sweep of the N-A transition (Fig. 2) shows a small peak, typical of a first-order phase transition.[11] The peak observed at the nematic-isotropic phase transition (transition entropy $0.22R_0$) is also shown for comparison. The initial slope of the curve in Fig. 2 corresponds to an ideal isothermal first-order transition during which the absorbed heat from the thermal sink would be all consumed by latent heat of the sample. The flat portion in both peaks is caused by the small thermal diffusivity of the material, and its extent is a measure of the partial heating of the specimen during the phase change.[11] Finally after the transition the specimen heats exponentially to equilibrium. The latent heat is distinguished from the specific-heat anomaly because of the very slow scanning rate used in these measurements. With a heating rate of 0.25 K/min (Fig. 2) the latent heat is absorbed in about 10 sec, while the specific-heat anomaly is covered in about 20 min. At this scanning rate the specific-heat anomaly is not visible. The transition entropy of the N-A transition (obtained by cooling the specimen) is $(0.017 \pm 0.002)R_0$. The value estimated by Cladis[6] was somewhat larger probably because the peak was relatively smeared. In such a case, part of the specific-heat anomaly is not resolved, resulting in an overestimate of the latent heat. The first-order phase transition in CBOOA is also confirmed by a recent volumetric measurement.[13]

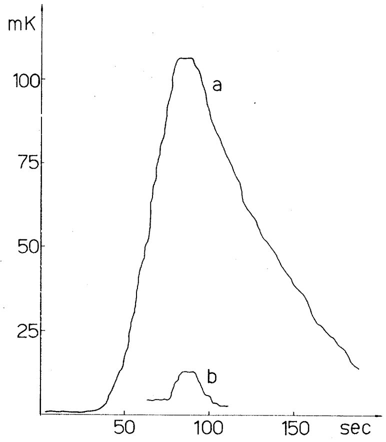

FIG. 2. Recorder sweep of latent heat in the temperature–excess-time dependence for isotropic-nematic (curve a) and nematic–smectic-A (curve b) transitions of CBOOA.

Near the critical point, the specific-heat data

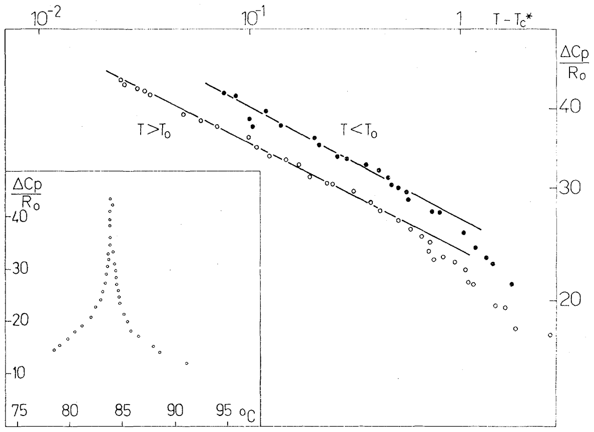

FIG. 3. Specific-heat data $\Delta C_p = C_p - C_{p0}$ near the nematic–smectic-A transition as a function of temperature.

are expected to follow the law

$$C_p - C_{p0} = A(T-T_c)^{-\alpha}, \quad T>T_c,$$
$$C_p - C_{p0} = A'(T_c'-T)^{-\alpha'}, \quad T<T_c'. \tag{2}$$

The value of C_{p0} was determined by fitting the specific heat in the isotropic liquid with the straight line $C_{p0}/R_0 = 0.3t + 166$ and extrapolating to the smectic-A–nematic temperature region. The best resolution in C_p was about 0.3% and the accuracy of C_{p0} was between 1 and 2%.

Since the transition is first order, the values of T_c and T_c' are not equal, and do not coincide with the measured transition temperature T_0. Therefore, both above and below T_0 the three constants A, α, and T_c must be determined from the best fit of the data by the functional form of Eq. (2). We have used a standard least-squares fitting program for this procedure and the results are shown in Fig. 3. With the use of only the data points within an interval of 1.5 K around the transition temperature, the critical exponents have the values $\alpha = 0.16 \pm 0.01$ and $\alpha' = 0.14 \pm 0.02$. As the temperature interval is expanded, the functional form of Eq. (2) becomes inappropriate and the quality of the fit decreases. When only data points for temperatures which satisfy $T - T_c \geqslant 10$ K are used, the critical exponent α obtained from the fit ($\alpha = 0.35$) approaches the Ornstein-Zernike value of $\alpha = 0.5$.

The values of $T_0 - T_c$ and $T_c' - T_0$ obtained from the fit by using a χ^2 test are 0.020 ± 0.001 K and zero, respectively. This agrees well with the results of Cladis,[6] who found $T_c \sim T_0$ (when cooling the sample $T_0 - T_c$ was less than 0.02 K). The fact that $T_c' - T_0$ is smaller than $T_0 - T_c$ is easily understood on the basis of the Landau theory of first-order phase transitions.[14] $T_0 - T_c$ is the difference between the phase-transition temperature and the temperature where the coefficent of the quadratic term in the free-energy expansion becomes zero. It is 8 times as large as the difference between the temperature where the fluctuations of the order parameter diverge (i.e., T_c') and T_0.

With the scaling relation $d\nu = 2 - \alpha$, our results near the critical temperature lead to the value $\nu = 0.62 \pm 0.01$. For temperatures of 10 deg and above from T_c, α is close to the value in the Ornstein-Zernike regime. This suggests the possibility that the two sets of reported experiments have determined ν in the classical[6] and the critical[8,9] region of the phase transition. We find that the critical behavior is obtained in the asymptotic region within about 1.5 K around the critical point.

The result for the latent heat at the N-A transition reported here represents experimental support for the ideas about the superconducting and the N-A transitions developed by Halperin, Lubensky, and Ma.[7] The measured critical exponent for the specific-heat anomaly is in agreement with the earlier work by de Gennes.[3] Finally, we have shown that our new method for specific-heat measurement is capable of providing high-precision results in unfavorable conditions of materials with low thermal conductivity.

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Observation of the Anomalous Refractive Index of a Critical Binary Fluid*

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We report the first observation of the anomaly in the real part of the refractive index of a critical binary fluid (methanol-cyclohexane). A theoretical relation was obtained for the refractive index of a binary mixture in the vicinity of its critical point which agrees with the experimental results within the experimental error. More precise experiments are in progress.

A number of theoretical predictions have been made of an anomalous increase in the refractive index of a pure fluid near its critical point,[1-4] and preliminary evidence of such an anomaly has been found in xenon.[2,5] We wish to report the measurement of such an anomalous refractive index for the binary mixture methanol-cyclohexane in the single-phase region near its critical mixing point. We also report the results of a theoretical description of the anomaly based on a simple model for a critical binary mixture. The real part of the refractive index is described in terms of the critical parameters ν, ξ_0, and η. The theory together with the experimental results can provide values for these three parameters.

The measurement technique employs a Fabry-Perot etalon with the fluid under study contained between the interferometer flats. The flats are oriented vertically and an expanded and collimated horizontal beam from a 0.5-mW He-Ne laser illuminates the mirrors at normal incidence. The mirrors are adjusted to a slight tilt such that a series of three or four vertical "equal-thickness" fringes are observed from the opposite side of the flats by a measuring telescope. The change in refractive index with temperature is determined by measuring the lateral shift of the fringes at a fixed vertical position in the cell. The lateral fringe shift $\delta(x_N)$ of the Nth-order fringe is related to the change in refractive index δn by $\delta(x_N) \cong N(\lambda_0/2\tan\theta)\delta n/n^2 = (N\Delta x/n)\delta n$, where $N = d/(\lambda_0/2n) \simeq 2650$, d is the distance between the flats at the position of the Nth-order fringe ($d \approx 0.06$ cm), λ_0 is the free-space wavelength of the incident radiation ($\lambda_0 \cong 6328$ Å), n is the refractive index of the fluid ($n \approx 1.41$), Δx is the fringe spacing ($\Delta x \approx 0.4$ cm), and θ is the angle between the flats.

The fluid cell containing the mirrors is mounted inside an aluminum heat shield and the cell and shield are mounted inside a brass vacuum envelope. The cell, shield, and vacuum envelope are mutually isolated from heat conduction and heat is transferred principally through radiation. Corrections for the normal expansion of the cell with temperature change are made.

The cell temperature is controlled by a thermistor in a 33-Hz Kelvin bridge.[6] Temperature measurements were performed by use of a platinum resistance thermometer in a separate similar type bridge circuit. A third separate system controls the heat shield to ± 0.01 K. We could consistently measure the cell temperature with a *resolution* of 0.1 mK. Since the platinum thermometer was uncalibrated we could determine our *absolute* temperature only to ± 0.2 K. By monitoring the position of the fringes themselves at fixed control-bridge settings, we determined that our cell temperature was typically stable to about ± 0.1 mK/day. All temperatures were measured relative to the critical temperature ($T_C = 45.15$°C) which was measured *absolutely* only to ± 0.2 K. T_C is considered that temperature at which the fringes just disappear after becoming progressively dimmer, broader, and stippled as the temperature is decreased toward T_C. T_C was located before and after each set of measurements of the refractive index and was typically reproducible to ± 1 mK from one day to the next. However, T_C was located to within ± 0.2 mK for the measurements made in the range $0.3 \text{ mK} \leq T - T_C \leq 3$ mK.

The fluid composition of the mixture was (29.97 ± 0.03)% methanol compared with the reported