the plasma wave and backscattered EM wave are approximately equal, half the energy leaving the pump will go directly into the unstable plasma wave. All of the energy in this electrostatic wave will eventually be locally absorbed by the plasma near the cutoff of the EM wave since the plasma wave is nonpropagating. When the density gradient is weak, most of the energy in the scattered EM wave is trapped in the resonant region of the plasma wave, and therefore a large fraction of this energy will eventually be locally absorbed by the plasma. In stronger density gradients most of the energy in the scattered EM wave will escape from the plasma.

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Study of the Bend Elastic Constant near a Smectic-A—Nematic Phase Transition

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The temperature dependence of the bend elastic constant of N-p-cyanobenzilidene-p-n-octyloxyaniline near the smectic-A—nematic transition temperature T_c is found to obey the power law $(T - T_c^*)^{-\gamma_3}$ with classical values for γ_3 in purer samples. Deviations from this value are discussed. Scanning calorimetry indicates that for purer samples the transition is either weakly first order or a λ transition.

Recently, de Gennes[1] has formulated an analogy between the superconducting-normal metal transition and the second-order nematic—smectic-A transition. In the former case, the fluctuations of temporal Cooper pairs in the normal state lead to an increase in the normal-state diamagnetic susceptibility near T_c.[2] In the latter, the density fluctuations in the nematic phase (which may be described by an order parameter, ψ), due to the continual production of evanescent, submicroscopic smectic regions, lead to an increase in the nematic elastic constants[3] of bend (K_3) and twist (K_2) so that

$$\delta K_i = K_i(T) - (K_i)_0 = (\text{const})_i (T - T_c)^{-\gamma_i}, \quad (1)$$

where T_c is the nematic-smectic transition temperature, $(K_i)_0$ is the value without the enhancement due to the order-parameter fluctuations, $i = 2, 3$. Here measurements are presented on the temperature dependence of $K_3(T)$ for CBOOA (N-

p-cyanobenzilidene-p-n-octyloxyaniline). Fitting the data with the functional form of Eq. (1), one determines the four parameters $(K_i)_0$, $(\text{const})_i$, γ_i, and T_c which best fit the data. This is done by the well-known technique of minimizing the weighted sum of the squares of the difference between the measured and computed values (i.e., χ^2) for $K_i(T)$ with respect to the four parameters. In the case of a second-order transition, T_c may be measured independently and so does not enter as a parameter in the fit. In the case of a first-order transition the T_c in Eq. (1) should be replaced by $T_c^* < T_{c,\text{meas}}$ which is to be found.

CBOOA was chosen because McMillan[4] recently indicated that he was unable to observe a latent heat associated with the smectic-A—nematic transition and that the transition was presumably second order. Figure 1 shows a differential thermal analysis of the transition made on 9.1 mg of purified CBOOA at constant pressure. An apparent
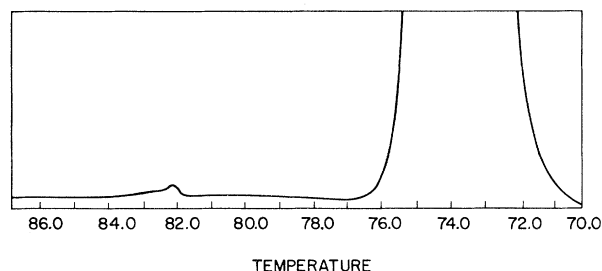
TEMPERATURE

FIG. 1. A differential thermal analysis of purified CBOOA. The sign of the peak changes sign with ΔT indicating that the transition is not pure second order. It may be a small first-order transition or a λ transition. The absolute temperature calibration is $\pm 1°C$. The temperature scale is in degrees Celsius.

latent heat is observed; however, the curve is not symmetric as a usual latent heat curve is, e.g., the solid-smectic transition shown to the right. Furthermore, there is a suggestion that one can amplify this bump by scanning the temperature faster. The peak begins to look like a specific heat jump when scanned rapidly; however, upon cooling, the bump becomes a dip which is evidence that the transition is not of pure second order. As purity deteriorated, the peak became smaller and smaller. In the impure limit it is virtually impossible to detect. The area shown in Fig. 1 would correspond to a latent heat of about 0.06 cal/g. The variation of this number from one curve to another is within the overall experimental error ($\pm 20\%$). The lack of symmetry of the transition, the switching of the effect with ΔT, and the apparent dependence of the effect on scanning rate suggest that it may be fruitful to investigate the possibility that the transition is a λ transition using more refined techniques. In very clean samples, however, $T_c > 83.4°C$, we have observed a hysteresis effect in T_c, ~ 0.2–$0.4°C$. This would seem to indicate that the transition is first order.

The CBOOA used in the bend measurements was always recrystallized. The method[5] used was to dissolve 10% CBOOA in heptane, filter out a first small crop, reboil the liquid, filter out a second small crop, reboil, then finally reap the third crop $\sim 50\%$ of the original amount. The original crystals were dark yellow. The yellow color fades in successive crops so that in the absolutely pure limit, the crystals should be white.[5] So far, the crystals have never been pure white but were considerably less yellow than the original crystals.

The methods used to measure the elastic constant of bend have been discussed elsewhere.[6] The technique consists of measuring the critical field of the well-known Freedericksz[7] transition by conoscopic observation of distortions induced by a magnetic field on monocrystalline samples at constant temperature. Thus, actually, one measures a threshold field whose square is proportional to K_3/χ_a, χ_a being the anisotropy in the diamagnetic susceptibility. While measuring K_3/χ_a one also finds[8] K_1/χ_a (the splay constant which does not diverge) and the birefringence. In the following, the results for K_1/χ_a are not presented, and I have not taken into account the temperature dependence of $\chi_a(T)$. A measure of the temperature dependence of χ_a is given by the change in birefringence with temperature. This was found to be rather small ($\sim 0.002/°C$). A nonmagnetic Mettler hot stage was used to control the temperature.

Good monocrystalline samples are required for these measurements. The homeotropic alignment required for the K_3 (bend) measurement was fabricated by coating the microscope slide and cover slip with a suitable surfactant.[9] Some of the samples were made by sealing the glass plates together with double bonding Mylar. This ensured that the sample thickness remained constant —even upon crystallization. Others were made by separating the glass plates with ordinary Mylar and the cell was sealed completely with rapid bonding epoxy. The Mylar samples showed no change in T_c even though the samples were kept several weeks. The measured values of $K_3(T)$ were also highly reproducible from day to day and even from month to month.

The results for the bend measurements are shown in Fig. 2(a). Two runs are shown. $T_c{}^*$ was determined by finding the best fit for several fixed values of T_c. χ^2 versus T_c is shown in Fig. 2(b). The $T_c{}^*$ that best fits the data was chosen to be where the minimum occurred in the χ^2. Thus the error shown for γ_3 is a standard error based on a three-parameter fit $[\gamma_3, (K_3)_0,$ and $(\text{const})_3]$ but the fit is a four-parameter fit. The main result is that for the "clean" sample $\gamma_3 = 0.52 \pm 0.03$. This is a classical result. For the "dirty" sample, $\gamma_3 = 0.60 \pm 0.01$. The trend is is that the lower the T_c, the more the exponent deviates from the classical value of 0.5.

The best fit gave $T_c{}^* \sim T_{c, \text{meas}}$. In fact, $T_c{}^*$ differs from the measured T_c (when cooling the sample) by $\lesssim 0.02°C$. When fitting only points within $3°C$ of T_c, γ_3 is not sensitive to the value
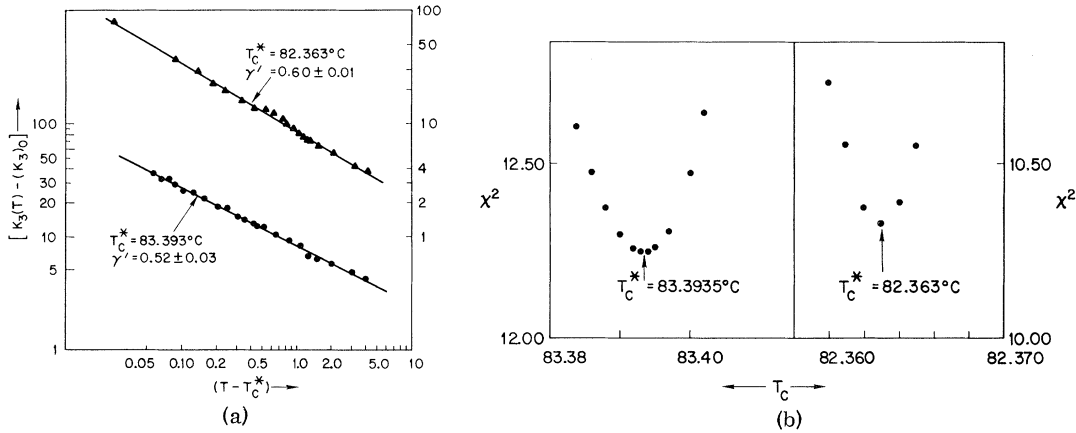
FIG. 2. (a) Plot of $K_3(T) - (K_3)_0$ in arbitrary units versus $T - T_c^*$. The criterion for picking T_c^* is shown in (b) For clarity, the dirtier sample (right-hand scale) is shown one decade above the cleaner one (left-hand scale). For the dirty sample $(K_3)_0 = 0.3067 \pm 0.406$ and for the cleaner sample $(K_3)_0 = 0.196 \pm 0.942$ in arbitrary units. The lines drawn are the calculated best fits. (b) χ^2 versus T_c showing minimum for the definition of T_c^* for the curves shown in (a). T_c shown in degrees Celsius. The χ^2 shown is the χ^2 which resulted when T_c was fixed and γ_3, $(K_3)_0$, and (const)$_i$ were found which best fit the data for that particular value of T_c.

of $(K_3)_0$. This can be seen from their respective computed standard errors [Fig. 2(a)]. As more points are added to the fit the standard error for $(K_3)_0$ decreases. It is, in fact, possible to continue the fit for the cleaner samples to very close to the nematic-isotropic transition, i.e., ~100°C, without changing γ_3 [10] or the minimum in χ^2 versus T_c^* (Fig. 2).

The crucial point in evaluating errors for this kind of an experiment is the uncertainty in T_c^*. The errors quoted above assume that T_c^* is defined infinitely precisely. Assuming an uncertainty in T_c^* of ±0.01°C, $\gamma_3(\text{clean}) = 0.52 \pm 0.05$. For an uncertainty of ±0.02°C, $\gamma_3(\text{clean}) = 0.52 \pm 0.1$. The χ^2 at $T_c^* \pm 0.02$°C is somewhat more than twice its value at T_c^*. This tells us that T_c^*, determined in this way, can be relied upon to better than ±0.02°C but not as close as ±0.01°C. In order to define T_c^* better we require points closer to T_c^*. We are unable to continue these measurements indefinitely because very close to T_c^* the low-numbered birefringence fringes are not well defined.

Critical exponents are hypothesized to be universal functions of two parameters,[11] the dimensionality, d, of the system and the number, n, of components of the order parameter. Recently, Wilson[12] has calculated in the vicinity of small $\delta = 4 - d$ an expansion for the exponents γ and η in terms of n and d. The exponent for the correlation length, ξ, is deduced from these two using

the Fisher equality, $\nu = \gamma/(2 - \eta)$, i.e.,

$$\xi = \xi_0(T_c/|T - T_c|)^\nu, \qquad (2)$$

where ξ_0 is the zero-temperature correlation length. It is expected[1] that $\delta K_3 \sim \xi_{\parallel}$, where $\xi_{\parallel}$ is the coherence length along the molecule as measured by McMillan using x rays.[4] $\xi_\perp$ is the coherence length perpendicular to the molecule. Thus $\gamma_3 \equiv \nu_{\parallel}$, where $\nu_{\parallel}$ is the exponent for $\xi_{\parallel}$.

Taking $n = 2$ (for a complex order parameter) and $d = 3$, de Gennes estimates from the Wilson expansion that in the temperature region where the Landau theory fails, $\nu = 0.66$. However, McMillan finds[4] $\xi_{\parallel} \sim (T - T_c)^{-0.75 \pm 0.01}$ but $\xi_\perp \sim (T - T_c)^{-0.625 \pm 0.01}$ which indicates that either the simple Wilson model is inapplicable to the present system or the experimental errors are larger than have been stated. In fact, a recent calculation by Halperin, Lubensky, and Ma[13] indicates that there should always be a first-order nematic–smectic-A transition. The various exponents, therefore, would only have an approximate meaning and would depend upon the temperature range over which the fit is made.

De Gennes's calculation[1] is mean field. An estimate of the temperature range, $\epsilon = (T - T_c)/T_c$, where mean field theory fails, $\epsilon \ll \epsilon_c$, is given by the Ginzburg criterion,[14]

$$\epsilon_c = \frac{1}{32\pi^2} \left(\frac{k}{\Delta C_p} \frac{1}{(\xi_0)_\perp^2 (\xi_0)_{\parallel}} \right)^2, \qquad (3)$$

where k is Boltzmann's constant and ΔC_p is the specific heat jump at the transition. $(\xi_0)_\perp = 3$ Å, $(\xi_0)_\parallel = 10$ Å,[4] and from an extrapolation of Fig. 1, $\Delta C_p \sim 0.09$ cal/g °C. Interpreting Fig. 1 as a specific heat jump gives $\Delta C_p \sim 0.2$–0.3 cal/g °C. Using the smaller $\Delta C_p \sim 0.09$ cal/g °C, $\epsilon_c \sim 5 \times 10^{-4}$. Thus, only for $(T - T_c) \ll 0.2$°C is non-classical behavior expected. This estimate may be broadened by impurities for then the ξ_0's are smaller still. ΔC_p is hard to define for a first-order transition. We think our estimate is an underestimate. It may also be broadened when one includes the fluctuations in the director field.

We recall that the x-ray measurements of McMillan, by definition, measure $\xi_\parallel$ and $\xi_\perp$ always, even in the nonclassical region. It has been shown that $\delta K_3 \sim \xi_\parallel$ in the linearized, mean-field limit. It is to be noted that our dirtier sample does not exclude the possibility of 0.66, whereas our clean one does. We can broaden our nonclassical region by purposely adding controlled amounts of impurity to CBOOA. This results[10] in $\gamma_3 \to 1.0$ (independent of impurity concentration) in agreement with previous results of Cheung and Meyers[15] on a compound known to be first order.

Although we cannot exclude completely the possibility that the nematic–smectic-A transition is a λ transition, we have anticipated the eventuality that it is a small first-order transition. Our data have been subjected to a least-squares fit. It appears possible to use the data to define T_c^* to ±0.015°C. Our results are as follows: For the "clean" samples, γ_3 approaches classical values. For the "dirty" sample, $\gamma_3 = 0.6 \pm 0.08$. As impurity is added, and hence T_c^* lowered, $\gamma_3 \to 1$. The Ginzburg criterion indicates that classical values are expected for clean samples except within a rather narrow temperature range near T_c.

A more complete account of this work, including the $K_2(T)$ measurements and measurements on $K_3(T)$ in the dirty limit, is in preparation.

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[5]Taylor, Ref. 4. It appears that the art of recrystallization depends upon guessing at what the impurities might be (in this case an "azo-compound," whence the yellowness of the crystals), then choosing a solvent which one thinks dissolves the impurity better than the compound (CBOOA) so that the crystals that form will be less rich in this impurity. I thank G. N. Taylor for sharing with me his expertise on the homologous series of this compound and for his assistance on the differential thermal analysis of purified CBOOA.

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