Rayleigh Scattering at a Second-Order Nematic to Smectic-A Phase Transition*

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(Received 25 June 1973)

We observe a second-order nematic to smectic-A phase transition in p-nitrilebenzylidene-p-octyloxyaniline using the Rayleigh scattering technique. The twist elastic constant K_{22} diverges at the transition, with the critical exponent $\nu = 0.66 \pm 0.05$ in agreement with de Gennes's prediction. For large-angle scattering we observe the onset of the critical regime.

Since the McMillan prediction[1] of the possibility of a second-order phase transition between the nematic and smectic-A liquid crystalline states, a growing effort has been devoted to this problem. De Gennes[2] has shown that, as a consequence of the conservation of the number of layers, distortions having nonzero curl are forbidden in the smectic-A phase; the associated Frank elastic constants K_{22} and K_{33} in the nematic phase at the temperature T are then expected to diverge close to the nematic to smectic-A transition temperature T_c, as $(T - T_c)^{-\nu}$ with $\nu = 0.66$. Since the first observation of this divergence by Gruler,[3] recent measurements of K_{33} have been made on various materials, using the Freedericksz critical-field technique and the parallel determination of the field coupling constant (anisotropy of the diamagnetic or dielectric susceptibility). The observed critical exponent ν started from 1,[4] decreased down to 0.5,[5] and is now stabilizing close to the theoretical prediction 0.66.[6,7] In this Letter, we report the observation of the K_{22} divergence at a second-order nematic to smectic-A phase transition using an entirely different technique, the observation of the Rayleigh scattering from the thermally excited angular fluctuations of the director in the nematic phase.

The interest in the Rayleigh scattering for observing this transition is obvious:

(a) For a given scattering wave vector $\vec{q}$, the scattered light intensity I is proportional[8] to $T \times \epsilon_a^2(T)/K(T)$, where $\epsilon_a(T)$ is the anisotropy of the optical susceptibility and $K(T)$ the angular average of the Frank constants defined by the scattering geometry. T is here expressed in °K. In the mean-field theory K is expected to be proportional to S^2, the square of the nematic order parameter; ϵ_a varies as S so that I should be invariant in temperature. Any pretransitional effect close to T_c should induce a strong temperature dependence on I.

(b) One can look at fluctuations of various scattering wave vectors, allowing the possibility of observing the critical regime $q\xi > 1$, where ξ is the coherence length defined in Ref. 2.

(c) Analyzing the time dependence of the scattered intensity, one can measure the damping time τ of the angular fluctuations[9] and obtain information on the singularity of the viscosities close to T_c.

Our experimental setup is the same as that of Ref. 9; the sample is CBOOA (p-nitrilebenzylidene-p-octyloxyaniline) previously studied by McMillan,[10] Cladis,[5] and Cabane.[11] It has a nematic phase from 109°C down to $T_c = 83$°C. We use the homeotropic alignment by coating the glass plates with hexadecyltrimethyl ammonium bromide. Our oven allows a temperature control better than 10^{-2} °C, and the peak-to-peak extension of the temperature inhomogeneity, observed by the light-scattering technique itself, is 4×10^{-2} °C. This value is independent of the rate of temperature sweeping of the sample (less than 0.1°C/min) and of the power of our light source, a He-Ne 6328-Å laser (kept under 0.5 mW). This incoming laser beam is tilted 26° away from the normal to the plates and can have extraordinary or ordinary polarization (wave vectors $\vec{k}_e$ or $\vec{k}_o$). The wave vector $\vec{k}^s$ of the scattered beam is chosen such that $\vec{q} \equiv \vec{k} - \vec{k}^s$ is normal to the director. As sketched in the inset of Fig. 1, we have chosen the two combinations, $(\vec{k}_e, \vec{k}_o{}^s)$ and $(\vec{k}_o{}', \vec{k}_e{}'^s)$, which for the same direction of the incoming laser beam select the scattering by a mode of pure twist[12] of small ($q = 0.18 \times 10^5$ cm^{-1}) or large ($q' = 1.0 \times 10^5$ cm^{-1}) wave vectors. The choice of these geometries guarantees that we observe the same part of the sample under the same conditions, and minimizes the number of apertures of the oven. The choice of the depolarized scattering from the twist mode simplifies the elimination of stray light. The light scattered intensity averaged over many coherence areas is measured by photon counting using a cooled photomul-

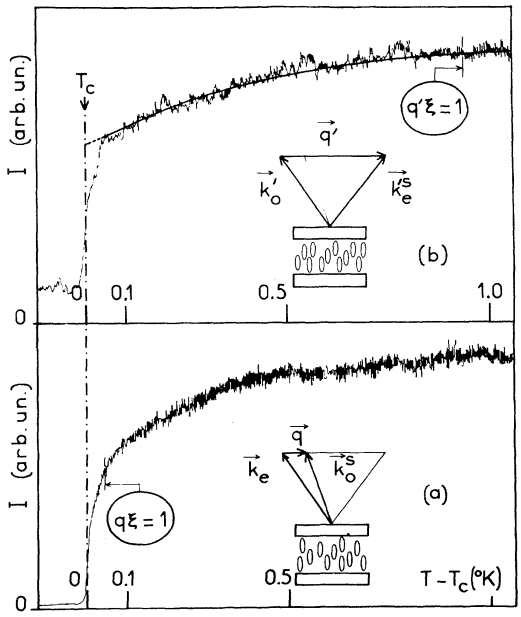

FIG. 1. Scattered light intensity versus temperature, for small- (a), or large-angle (b) scattering.

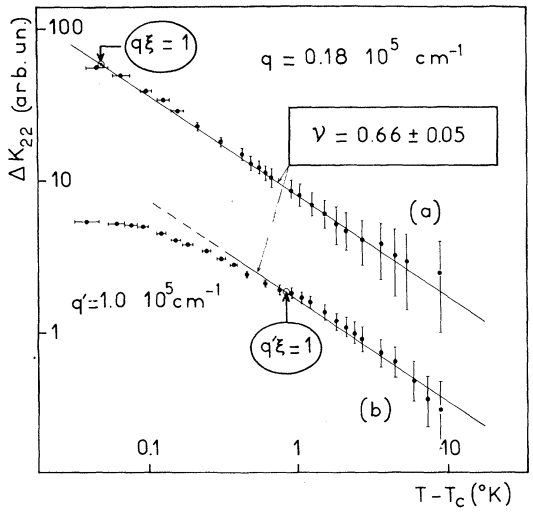

FIG. 2. Divergence of the elastic constant K_{22} versus temperature, for small- (curve *a*), or large-angle (curve *b*) scattering.

tiplier. At the same time, a digital single-clipped autocorrelator is used to measure the autocorrelation function of the photocurrent, from which we deduce the correlation function of the twist angular fluctuations.

The photon counting measurement of I is delicate in the presence of stray light originating from static twist defects, which are always present even in our best samples. The best technique would be to deduce the true intensity from the zero-delay value of the autocorrelation function. In the smectic phase, for example, we find a nonzero counting rate, due to stray light, but the true signal is found to be zero. Over the entire nematic range, we have measured the ratio R =[true signal intensity (from the autocorrelator)]/total photocounts by observing over less than one coherence area. R is typically $0.8 \pm 5\%$, independent of the temperature. This can be understood if we suppose that the amplitude of the static twist defects depends on K_{22} in the same way that the thermally excited twist fluctuations do. The fluctuations $\pm 5\%$ on R are mainly due to the sensitivity of our setup to mechanical vibrations when counting over less than one coherence area; we eliminate these fluctuations by observing the total I over many coherence areas. The temperature independence of R legitimizes the choice of photon counting for measuring I, with an estimated uncertainty of $\pm 3\%$.

We now sweep up the temperature, starting from the smectic phase, with the small scattering wave vector setup ($q = 0.18 \times 10^5$ cm^{-1}). A typical recording of I ($\Delta T = T - T_c$) is shown in Fig. 1(a). Above T_c, I rises continuously throughout the whole nematic range, showing a strong pretransitional effect. The effect of the temperature inhomogeneity is observed as the small rounding off at T_c; it becomes negligible for $\Delta T > 4 \times 10^{-2}$ °C. To deduce ν from this observation, we express K_{22} as $S^2 K_{22}^0 + \Delta K_{22}$; TI^{-1} can thus be written as $K_{22}^0 + \Delta K_{22}/S^2$ with

$$\Delta K_{22} = C(\Delta T/T_c)^{-\nu}, \quad (1)$$

where C is a constant of the same dimension as K. Up to now, we do not know if C itself should be proportional to S^2; we know S^2 from the measurement of Cabane and Clark.[11] This S^2 correction is negligible close to T_c, but can be important at large ΔT. Unfortunately, within our present accuracy a change in the adjustable K_{22}^0 can compensate for the absence of the S^2 correction at large ΔT, so that we cannot give an experimental answer on this point. A plot of $\Delta K_{22}(\Delta T)$ on a log-log scale with the best K_{22}^0 value is shown in Fig. 2, curve *a*. ΔK_{22} is found to follow the predicted law (1) over two decades of temperature; the slope of the straight line gives the value $\nu = 0.66 \pm 0.05$. We can estimate $\xi(T)$ using de Gennes's expression[2]

$$\xi(T) \simeq \xi_0(\Delta T/T_c)^{-\nu}, \quad (2)$$

where ξ_0 is an unknown molecular length. In the case of low-angle scattering, the critical regime ($q\xi > 1$) is entirely concealed within the temperature inhomogeneity, as shown in Fig. 1(a), and is unobservable.

We now measure $I(\Delta T)$ for the larger scattering wave vector $q' = 1.0 \times 10^5$ cm^{-1}. As shown in Fig. 1(b), close to T_c, I undergoes a large discontinuity; the dotted line shows what $I(\Delta T)$ would be in the absence of any temperature inhomogeneity. The corresponding log-log plot is shown in Fig. 2, curve b. (a) For the high-temperature limit ($q\xi < 1$) we observe a divergence of K_{22} with the same critical exponent. (b) Close to T_c ($q\xi > 1$) K_{22} stops its divergence and tends to a finite value at $T = T_c$. This behavior is typical of the critical regime. When $q\xi > 1$, the fluctuations of the smectic order parameter extend in space on a larger scale ξ than the one (q^{-1}) observed by the light scattering, and the system does not detect any subsequent increase of ξ. In that case, as shown by Brochard, K can be represented by the expression

$$K_{22} = K_{22}^{0} + (C\xi/d)(q^2\xi^2 + 1)^{-1/2}, \quad (3)$$

where d is an interlayer distance. A fit by this analytic form of the observed $I(\Delta T)$ is shown in Fig. 1(b) in the form of a solid line. The agreement is quite good with $\xi_0 = 8$ Å $\pm 10\%$ which corresponds to a molecular width; it would be interesting to measure ξ for a bend distortion to compare with the molecular length.

Finally, we have also measured $\tau(T)$. Our preliminary data show a critical behavior which can be analyzed using the previous measurement of $K_{22}(T)$, and the expression

$$\tau^{-1}(T) = K_{22}(T)q^2/\gamma_1(T), \quad (4)$$

where γ_1 is the temperature-dependent twist viscosity. A full account of this experiment will be published in a forthcoming paper.

In conclusion we have studied a second-order nematic to smectic-A phase transition using Rayleigh scattering. We have observed the divergence of the twist Frank elastic constant K_{22}, with a critical exponent $\nu = 0.66 \pm 0.05$. This confirms de Gennes's prediction[2] and some recent measurements on K_{33},[6,7] but is in contradiction with others.[4,5] We have also observed, at a large scattering angle, the critical regime where K_{22} stabilizes. This regime is almost impossible to observe with the usual Freedericksz technique.

We thank J. Dubois for the synthesis of very pure CBOOA, B. Cabane for a preprint of his data on S, P. G. de Gennes and F. Brochard for stimulating discussions, and I. W. Smith and Y. Galerne for their help in processing the data from the correlator.

*Work supported in part by Direction des Recherches et Moyens d'Essais, Ministère des Armées, under Contract No. 72/868.

†Associated with Centre National de la Recherche Scientifique.

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[12]In fact the temperature dependence of the indices of refraction tilts $\vec{q}$ slightly out of the plane of the sample and adds a weak bend distortion. The resultant relative change of I is less than 10^{-3} over all the nematic range and is thus negligible.

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