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Measurements of Nematic Elastic Constants near a Second Order Nematic–Smectic-*A* Phase Change*

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The splay and bend elastic constants of nematic *p*-cyanobenzylidene-*p'*-octyloxyaniline have been measured as a function of temperature. The bend constant diverges near the nematic–smectic-*A* phase change, with the temperature dependence predicted by de Gennes. The splay constant shows no anomaly, as expected.

We report here the first measurements of the temperature dependence of elastic constants of a nematic liquid crystal (*p*-cyanobenzylidene-*p'*-octyloxyaniline, or CBOOA) near a second order nematic–smectic-*A* phase change. Similar pretransition effects have been reported near a nematic–smectic-*C* transition,[1] and a first order nematic–smectic-*A* transition.[2] The bend elastic constant K_{33} exhibits the theoretically predicted rapid increase near the critical temperature T_{NA}, while the splay elastic constant K_{11} has only a weak temperature dependence, as expected. We find that the fluctuation-dependent part of K_{33} varies as $(T-T_{NA})^{-\nu}$, with $\nu=0.65\pm0.05$ in agreement with de Gennes's[3] prediction. In the course of the experiments a new magnetic-field-induced instability was observed in the nematic near T_{NA}, which is described briefly below.

The nematic phase is characterized by long-range orientational ordering of rodlike molecules. The smectic-*A* phase has, in addition, one-dimensional periodic ordering; the molecules are arranged in layers, with their long axes parallel, on the average, to the layer normal. An appropriate order parameter for the nematic–smectic-*A* transition is the amplitude of the lowest Fourier component of the periodic smectic-*A* structure.

Using this order parameter in mean-field calculations, Kobayashi[4] and McMillan[5] predicted the possibility of a second order phase change. de Gennes[3] developed an analogy between this phase change and the normal metal-superconductor transition, on the basis of which he calculated pretransition fluctuation phenomena in the nematic phase near T_{NA}.

The fluctuations involved are localized regions of dimension ξ, a coherence length, in which the smectic layers appear temporarily. These can be studied directly by x-ray diffraction, which McMillan has done for this material.[6] His results are compared to ours below.

de Gennes showed that the fluctuations are also manifested as anomalous increases in the bend and twist elastic constants of the nematic, which are analogous to pretransition diamagnetism in the normal-metal–superconductor transition.[7] The expression for the bend elastic constant is

$$K_{33}=K_{33}^{N}+\frac{\pi\sqrt{2}}{6}\frac{kT}{d^2}\xi_{\parallel},$$

in which K_{33}^{N} is the ordinary nematic contribution, d is the smectic layer thickness, and $\xi_{\parallel}$ is the coherence length parallel to the molecular axis. In contrast to the superconducting case, the low-temperature coherence length ξ_0 should be only a molecular dimension, so that the critical exponents are those for the λ transition in He^4, rather than for the superconductor.

In that case, ξ varies as $(T-T_{NA})^{-\nu}$ with $\nu=\gamma/(2-\eta)$. de Gennes estimates the critical exponents, via the Wilson calculations, as $\gamma=1.3$ and $\eta=0.04$, yielding $\nu=0.66$. The splay elastic constant K_{11} should be independent of the coherence length, but may have a slight pretransition anomaly due to nearest-neighbor rearrangements as

the layers appear.

We chose to measure K_{33} and K_{11} by optical observation of the magnetic-field-induced Freedericksz transition in a homeotropically aligned planar sample.[8-10] In this experiment, a thin film of sample is contained between glass slides, the surfaces of which have been treated with silane surfactants[11] producing alignment of the molecules normal to the glass, in the absence of a field. The magnetic field is applied in the plane of the sample, and above a critical field H_c, the nematic alignment axis begins to tilt toward the field direction. The birefringence $\Delta\psi$ produced by the tilting increases linearly with field, just above H_c. From H_c and $\partial\Delta\psi/\partial(H^{-1})$ one can deduce the ratio of the elastic constants to the anisotropy of the magnetic susceptibility $\Delta\chi$:

$$K_{33}/\Delta\chi = (H_c t/\pi)^2,$$

$$\frac{K_{11}}{\Delta\chi} = \frac{(H_c t)^3}{\pi^2\lambda}\left[\frac{n_o(n_e^2 - n_o^2)}{n_e^2}\right]\left[\frac{\partial\Delta\psi}{\partial(H^{-1})}\right]^{-1}.$$

The wavelength of the light used is $\lambda = 6328$ Å. The sample thickness is $t = 145$ μm. The ordinary and extraordinary indices of refraction, n_o and n_e, were measured, as a function of temperature, in a Pulfrich refractometer.

The birefringence was measured conoscopically by focusing a helium-neon laser beam on the sample placed between crossed linear polarizers oriented at $\pm 45°$ to the field. Below H_c, the usual uniaxial pattern is observed, the center of which locates the sample normal. Above H_c, the pattern shifts off center, and the birefringence is measured by counting the interference fringes crossing the sample normal position.

The CBOOA was obtained from Eastman Organic Chemicals, and was used without further purification. The sample cell was sealed under argon with solvent-free epoxy to isolate it from the atmosphere. This prevented degradation during the experiment; T_{NA} changed by only 0.015°C over a period of three weeks at high temperature.

The sample cell was held in an aluminum block heated by a Yellow Springs Instruments temperature controller providing long-term stability of ± 0.006°C. The magnetic field was measured by a Bell model 640 gaussmeter accurate to about 0.2%.

T_{NA} is easily determined visually, by the sudden disappearance of the characteristic nematic scintillation, which occurs in this sample at 82.93°C. This is a useful test, because the scintillation mode associated with K_{11} remains strong right up to T_{NA}.

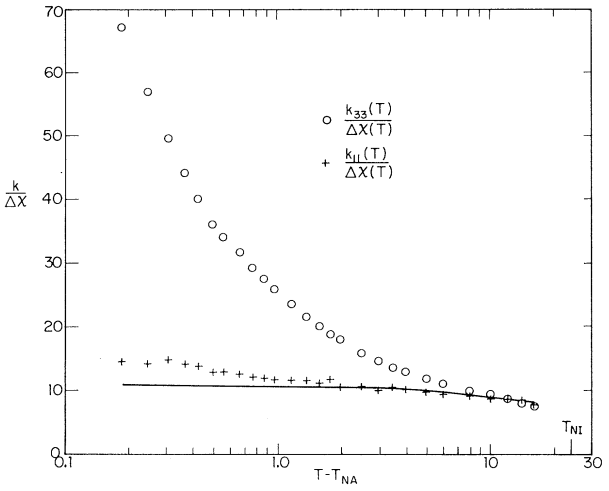

FIG. 1. The ratio of splay (K_{11}) and bend (K_{33}) elastic constants to the anisotropy of the magnetic susceptibility $\Delta\chi$. The line is the orientational order parameter, fitted to the splay curve at high temperature.

Data were taken between 83.12 and 98.90°C. The results are shown in Fig. 1. The overall accuracy for $K_{33}/\Delta\chi$ is $\pm 2\%$ and for $K_{11}/\Delta\chi$ is $\pm 10\%$.

The equipment was accurate enough to examine another decade in $T - T_{NA}$ closer to T_{NA}, but below 83.12°C, a new instability appeared which interfered with these measurements. In the presence of the magnetic field, we first observed a regular array of stripes, oriented parallel to the field. The period is of the order of the sample thickness. Examination with polarized light indicates a more or less constant tilt angle and periodic rotation of the optical axis out of the plane defined by the sample normal and the field; that is, a splay wave. A possible explanation of this phenomenon, involving the piezoelectric (flexoelectric) effect[12] is described elsewhere.[13]

To compare the data to de Gennes's prediction, one must account for the temperature dependence of $\Delta\chi$ and subtract $K_{33}{}^N$. We may assume $\Delta\chi(T) = \Delta\chi^0 S(T)$, with S being the orientational order parameter. Mean field theory also predicts $K_{ii}{}^N = K_{ii}{}^0 S^2$. Two measurements of $S(T)$ are available for this material: the index of refraction measurements done for this experiment and NMR measurements done by Cabane and Clark.[14] The two measurements are in close agreement. The solid line in Fig. 1 shows $S(T)$, normalized to fit $K_{11}/\Delta\chi$, far away from T_{NA}. Clearly, K_{11} deviates only slightly from the ordinary nematic behavior near T_{NA}, suggesting that the strong temperature dependence of K_{33} is due entirely to the

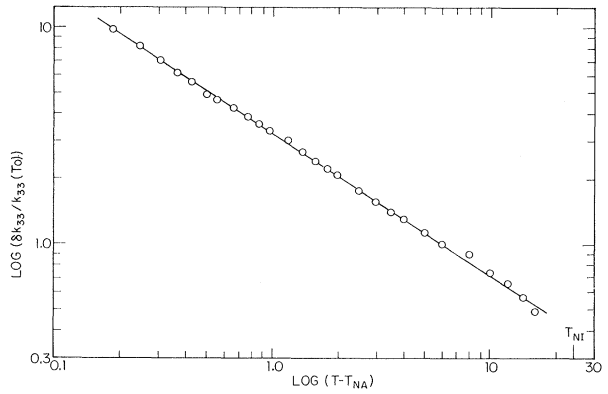

FIG. 2. Our best estimate of the temperature dependence of the fluctuation part of K_{33}, normalized to K_{33} (98.9°C).

pretransition fluctuations.

The fluctuation contribution to the elastic constant, δK_{33}, normalized to K_{33} at an arbitrary temperature $T_0 = 98.9°C$, can be written in terms of the measured $K_{33}(T)/\Delta\chi(T)$ and $\Delta\chi(T)/\Delta\chi(T_0)$ as

$$\frac{\delta K_{33}(T)}{K_{33}(T_0)} = \frac{K_{33}(T)}{\Delta\chi(T)} \frac{\Delta\chi(T)}{\Delta\chi(T_0)} \frac{\Delta\chi(T_0)}{K_{33}(T_0)} - \frac{K_{33}{}^0 S^2(T)}{K_{33}(T_0)}.$$

The second term is $K_{33}{}^N(T)/K_{33}(T_0)$.

Anticipating a power-law dependence on $T - T_{NA}$, a log-log plot of δK_{33} versus $T - T_{NA}$ was made, varying the constants T_{NA} and $K_{33}{}^N(T_0)/K_{33}(T_0)$ within reasonable ranges. Trusting our value of T_{NA}, we varied it by $\pm 0.01°C$. We varied the background level, $K_{33}{}^N(T_0)/K_{33}(T_0)$, from 0 to 1. With T_{NA} at its lower limit and the background at 0.6, one obtains a distinctly bent curve to which one can fit a straight line just passing through the error limits (about the diameter of the dots in Fig. 2) of the 23 lowest temperature points, with a slope of $\nu = 0.71$. Taking T_{NA} at its upper limit, and the background level at 0.4, one obtains a curve with the opposite bend, which is similarly fitted by a line of slope $\nu = 0.60$. For $T_{NA} = 82.935°$ C and the background level at 0.52, one obtains a remarkably straight curve (Fig. 2) with a slope of 0.653, in excellent agreement with de Gennes's prediction. We also tried the subtraction scheme $K_{33}{}^N \propto K_{11}$ which produced the best straight line fit with a slope $\nu = 0.670$.

Estimating $\Delta\chi(T_{NA}) = 1.3 \times 10^{-7}$ cgs units from measurements on structurally similar *p*-methoxybenzylidine-*p*-*n* butylaniline,[15] and $d = 35$ Å, from McMillan's measurements, the straight-line fit in Fig. 2 gives $\xi_{\parallel} = 2740$ Å at $T - T_{NA} = 0.185°C$, in excellent agreement with McMillan's x-ray measurements. At $T - T_{NA} = 5.965°C$, the last point fitting closely the straight line, $\xi_{\parallel} = 276$ Å. This is still probably large compared to the molecular interaction range, and therefore self-consistent with the observation of a scaling-law critical exponent over the entire range of the experiment.

The main disagreement between our results and McMillan's x-ray results is that he finds $\gamma = 1.49$, so that $\nu \cong 0.75$. McMillan measured the x-ray intensity distribution in the diffuse peak, observed above T_c, centered at the location of the first Bragg reflection from the layers. One determines γ from the temperature dependence of the peak height, and $\xi_{\parallel}$ ($\xi_{\perp}$) from the linewidth parallel (transverse) to the nematic axis. A possible source of error in interpreting these measurements, pointed out by McMillan earlier,[16] is orientational fluctuations of the nematic axis, which reduce the peak height and increase the transverse linewidth. They may also account for the non-Lorentzian transverse line shape McMillan observed. These fluctuations are reduced as the elastic constants increase. The strong temperature dependence of K_{22} and K_{33} would therefore produce an apparently larger value of γ. Quantitative corrections for this effect, which will also require $K_{22}(T)$, may bring the x-ray data into agreement with our results.

In conclusion, our results are in agreement with the de Gennes theory. Our estimate of $\xi_{\parallel}$ agrees well with McMillan's measurements near T_{NA}, and an explanation for the remaining discrepancies between the x-ray measurements and our results is proposed. Measurements of $\Delta\chi(T)$ and $K_{22}(T)$ for this material would be very useful.

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Microscopic Theory of NMR in an Anisotropic Superfluid (^{3}He A)*

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Equations are derived for the motion of the magnetization and the "spin axes of the Cooper pairs," and solved for the case of unsaturated cw resonance. In general two discrete resonances are predicted, but if a special condition is met, only one occurs. The complete field dependence of the line(s) determines the gap configuration almost uniquely. The predictions are consistent with existing data and in strong conflict with Anderson's theory.

Several months after its original discovery,[1] the anomalous NMR shift in the "A phase" of liquid ^{3}He remains a source of controversy. In an earlier Letter[2] this author showed that the existence of the shift could be qualitatively understood if the system possessed the property of "broken spin-orbit symmetry"; in the presence of the nuclear dipole forces there would then be a strong correlation between the direction of total spin of any two particles and the direction of their relative orbital angular momentum.[2] If, as seems to widely believed, liquid ^{3}He A is an anisotropic BCS-type superfluid, then it is the Cooper pairs which have their spins and orbital angular momenta correlated in this way. This mechanism for the shift does not require that the total orbital angular momentum or total spin be finite, or that there be a preferred axis of quantization for the spins: The shift is therefore predicted to persist to zero field, and to occur even for the "isotropic" Balian-Werthamer[3] (BW) state. A resonance is also predicted to occur for "longitudinal" polarization of the rf field (i.e., parallel to the external field). However, this approach is clearly somewhat unsatisfactory in that the existence of a single shifted peak with the observed frequency dependence,

$$\omega^2 = \omega_L^2 + \omega_0^2(T), \tag{1}$$

and no appreciable background was taken from experiment rather than demonstrated explicitly.

A very different approach to the problem of this shift was developed by Anderson[4] under the assumption that ^{3}He A is indeed an anisotropic BCS superfluid. This approach rests fundamentally on the hypothesis of the existence of a macroscopic *total* orbital angular momentum which is coupled to the total spin and to the "reference system for the spins of the condensed pairs" (called $\hat{k}_\chi$ by Anderson) by some semiphenomenological energies. Among the predictions of this theory are that the shift $\omega^2 - \omega_L^2$ is a strong function of the external field and tends to zero in zero field; that there is no "longitudinal" resonance; and that the BW state shows no shift. If the last conclusion is correct, we could interpret the "B phase" of ^{3}He as a BW phase.[4]

In the present Letter I outline[5] a microscopic theory of NMR in an anisotropic BCS-type superfluid, based on a Born-Oppenheimer type of approximation. I derive general equations for the magnetization vector and a vector related to the spin of Cooper pairs at a particular point on the Fermi surface. The equations are applicable to quite general NMR situations in which field gradients can be neglected. They are solved explicitly for the case of unsaturated cw resonance, with some somewhat surprising results. The predictions of Ref. 2 are confirmed, in the sense that *if* a single resonance line (rather than two) is observed, then its frequency must satisfy Eq. (1), and that the existence of a shift is a consequence