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Absolute Measurement of the Critical Properties of Second Sound at the Smectic-\(A\)–to–Nematic Phase Transition in 8OCB

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Light scattered from the driven free surface of the smectic-\(A\) phase of octyloxy cyanobiphenyl (8OCB) provides a low-frequency measurement of second sound. This yields an absolute measurement of the smectic elastic constant, \(B\). There is no dispersion in either the angular or frequency dependence of \(B\) for angles 35°–85° from the normal and for frequencies from 10–100 kHz. Near the smectic-\(A\)–to–nematic phase transition the smectic elastic constant can be described by \(B = (6.03 \pm 0.05) \times 10^7 (T - T_{NA})^{0.32 \pm 0.05}\) dyn/cm².

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A principal result of the theory that de Gennes proposed in 1972¹ to describe second-order smectic-\(A\)–to–nematic phase transitions was that the elastic constant \(B\) that describes resistance to changes in the smectic layer spacing should go to zero continuously, \(B = (T_{NA} - T)^6\). Almost all previous measurements⁶–⁷ of the temperature dependence of \(B\) have been indirect in that the quantity actually measured was \(\lambda = (K/B)^{1/2}\). Although in many materials the Frank elastic constant, \(K\), is believed to be relatively independent of temperature, direct measurements of \(K\) in the smectic-\(A\) phase are very difficult. In contrast, second sound provides a direct measurement of the temperature dependence of \(B\). There has been only one previous study of \(B\) which makes use of the second sound.⁸

In this Letter we present the first simultaneous measurement of the frequency, wave-vector, and critical-temperature dependence of second sound near the smectic-\(A\)–nematic phase transition.⁹ From these measurements we have determined the absolute value of the smectic elastic constant, \(B\).¹⁰ By using thin samples (~150–450 \(\mu m\) thick) of octyloxy cyanobiphenyl (8OCB), in which the top surface was a free liquid–crystal–air interface, low-frequency second sound was observed through light scattered by driven deformations of the free surface. The measurements all yield the same value of \(B\) indicating the absence of any dispersion effects over a wide range of wave vectors (varying in angle by 35°–85° from the normal and in magnitude from 100–400 cm⁻¹), and ranging in frequency from 10–100 kHz. The material studied, 8OCB, was chosen because of its chemical stability; it was obtained from British Drug House and used without further purification.

The experimental apparatus, shown schematically in Fig. 1, employs several techniques that were developed in other laboratories.¹¹,¹² An argon-ion laser (~30 mW, 5145 Å) is weakly focused onto the free surface of the sample. The surface is driven by an alternating potential that is applied between a knife edge approximately 25 \(\mu m\) above the sample and a conducting substrate that makes up the bottom surface of the liquid-crystal cell. This surface was treated with the surfactant hexadecyltrimethylammonium bromide (HTAB) so that the 8OCB molecules stand normal to the glass. To obtain a flat free surface the slope of the side walls of the sample cell were adjusted to equal the contact angle, \(\alpha\). The motion of the free liquid-crystal surface, in re-

FIG. 1. Schematic of the experimental arrangement and sample cell.
Heterodyne detection at a specific diffraction maximum of the grating selects a single known component of the wave vector, \( q_s \), parallel to the surface. The induced motion is kept small (< 0.05 \text{ Å}) in order to minimize perturbations to the smectic layers.

The frequency and wave-vector response \( \chi(q_s, \omega) \) of the free surface to the applied force can be obtained by solving the hydrodynamic equations with the appropriate boundary conditions. To a first approximation, \( \chi(q_s, \omega) \) is simply given by a linear superposition of simple harmonic-oscillator responses in which the characteristic frequencies are obtained from the hydrodynamics of second sound. Specifically, for modes of the form \( u(x, z) = u(z) \exp[i(\omega t - q_s x)] \), with \( \omega \ll \nu_0 q_s \) (where \( \nu_0 \) is the longitudinal sound speed), the dispersion relation becomes

\[
i \omega \nu_{\text{eff}} (q_s^4 + q_s^4)
\]

\[
+ [(B/\rho)q_s^2 - \omega^2 + i \omega \nu_{\text{eff}} q_s^2] q_s^2 - \omega^2 q_s^2 \approx 0,
\]

where \( q_s \) and \( q_s \) are the components of the wave vector in the smectic planes and normal to them, and \( \nu_{\text{eff}} \) is the kinematic viscosity which is a function of the angle \( \psi = \tan^{-1}(q_s/q_s) \). Further, the modes are wave-guide-like with

\[
q_s = (\pi/2h)(2m + 1), \quad m = 0, 1, 2, \ldots.
\]

The response is that of a driven harmonic oscillator with a resonant frequency that is only slightly shifted from \( \omega_0 = (B/\rho)^{1/2} q_s q_s (q_s^2 + q_s^2)^{-1/2} \) because of viscous effects, and a full width at half maximum \( \Delta \omega = 2 \nu_{\text{eff}} (q_s^4 + q_s^4) \). The measured and predicted signals as a function of frequency are

\[
B \times 10^5 \text{ dyn/cm}^2
\]

\[
\Delta T (\text{K})
\]

FIG. 3. \( B(\Delta T) \) for different thickness samples and different scattering wave vectors. The symbols represent the different measurements: squares, \( q_s = 112 \text{ cm}^{-1} \); triangles, \( q_s = 55 \text{ cm}^{-1} \); diamonds, \( q_s = 250 \text{ cm}^{-1} \); hexagons, \( q_s = 33.4 \text{ cm}^{-1} \); circles, \( q_s = 38.9 \text{ cm}^{-1} \); inverted triangles, \( q_s = 125 \text{ cm}^{-1} \). The solid line represents the least-squares fit to the data for \( \Delta T < 1.24 \text{ K} \); its continuation is the broken line.
shown in Fig. 2.

The measured $B(\Delta T = T_{NA} - T)$ for all the samples versus the respective $\Delta T$ for each of the samples are shown in Fig. 3. Although the transition temperature, $T_{NA}$, was not the same for all the samples, the $B(\Delta T)$ curve is universal. The asymptotic region, corresponding to $\Delta T \leq 1.24$ K, was least-squares fitted to a simple power law of the form $B = B_0(\Delta T)^\phi$ yielding $B_0 = (6.03 \pm 0.05) \times 10^7$ dyn/cm$^2$ and $\phi = 0.32 \pm 0.015$ with $\chi^2 = 1.06$. Nelson and Toner$^{15}$ recently proposed a model in which $B$ is not zero but a constant at the transition temperature. This could be described by $B = B_0 + B_1(\Delta T)^\phi$. A least-squares fit of the data in Fig. 3 to this form yields $B_0 = (0.15 \pm 0.43) \times 10^7$ dyn/cm$^2$, $B_1 = (5.9 \pm 0.45) \times 10^7$ dyn/cm$^2$, and $\phi = 0.33 \pm 0.04$, with $\chi^2 = 1.0$. Thus our data are consistent with either a simple power law or the Nelson-Toner form in which $B_0 \approx 5 \times 10^6$ dyn/cm$^2$.

A comparison between the wave-vector dependence of the results at two different temperatures and the hydrodynamic prediction is shown in Fig. 4(a). To reduce all of the data to a dimensionless form that is independent of temperature the figure shows $\Omega(\psi) = \omega_0/|q|(B_{\text{fit}})^{1/2}$, where $\omega_0$ is the resonant frequency of the response, $|q|$ is the magnitude of the wave vector, and $B_{\text{fit}}$ is the value of $B(\Delta T)$ that is obtained from the best fit to the data in Fig. 3. It is clear that there are no observable systematic deviations from the hydrodynamic form. For the same two temperatures, Fig. 4(b) shows the frequency dependence of $B/B_{\text{fit}}$. Once again there are no apparent systematic deviations from the hydrodynamic prediction. There is no evidence for the angle- and frequency-dependent corrections to the second sound speed proposed by Liu$^{16}$ and Jähng$^{17}$ in the frequency range of the present experiment (10–100 kHz).

In conclusion, we have presented the first complete study of second sound near the smectic-$A$–nematic phase transition. There is no observable angle- or frequency-dependent dispersion in $B$ for the frequency region 10–100 kHz, and for wave vectors varying in angle $\psi$ from 35°–83°. Further, we have presented the first absolute measurement of the critical properties of $B$ at low frequencies. Finally, the critical exponent describing the smectic elastic constant $B$ has been directly measured for the first time. If we assume a simple–power-law form, we obtain a value $\phi = 0.32 \pm 0.015$. This can be compared with values obtained by other researchers by use of indirect techniques, which measure $\lambda = (K/B)^{1/2}$ rather than $B$.

In particular, for 8OCB, Listler$^{3}$ obtained $\phi = 0.26 \pm 0.08$. For 4-cyano-4′-octylbiphenyl (8CB), Davido$^{3}$ found $\phi = 0.26 \pm 0.06$, for N-p-cyanobenzylidene-p-octyloxyanilene (CBOOA), Birecki et al.$^{4}$ and Ribotta$^{5}$ measured $\phi = 0.33 \pm 0.05$ and Clark$^{6}$ found $\phi = 0.36 \pm 0.14$, and for butoxybenzilidene octyloxyanilene (40.8) von Känel and Litster$^{7}$ obtained $\phi = 0.32 \pm 0.03$. For all of these smectic-$A$–nematic transitions, $\phi$ is close to a value of $\frac{1}{3}$. Further measurements are required to determine whether there is a universal exponent for the smectic elastic constant.

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**FIG. 4.** (a) $\Omega(\psi) = \omega_0/|q|(B_{\text{fit}})^{1/2}$ for two temperatures. The solid line is the hydrodynamic prediction. (b) $B/B_{\text{fit}}$ vs $\omega_0/2\pi$ for the same two temperatures. The symbols represent the same measurements as Fig. 3. The open symbols are for $\Delta T \approx 0.54$ K and the closed symbols for $\Delta T \approx 0.17$ K.
Direct Nuclear-Magnetic-Resonance Measurements of Biaxiality in the Cholesteric Liquid Crystalline Phase

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We report what we believe is the first experimental measurement of biaxiality in a cholesteric phase. This observation is made in a selectively deuterated nematic that was twisted by the addition of a chiral compound. A theoretically predicted biaxial order parameter (measured in terms of an asymmetry in the time-averaged deuteron quadrupole interaction) was found to be $\sim 10^{-3}$ for a pitch $\sim 3 \mu m$ and to increase both with decreasing pitch and as the isotropic phase is approached.

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The possibility of observing biaxial molecular order in a twisted nematic has been a topic of discussion for several years. The nematic liquid crystal is normally uniaxial, but when it is twisted the cylindrical symmetry is broken by the helical twist defined by the pitch axis and biaxial ordering, though perhaps very weak, has been expected in such systems. Several theoretical investigations have regarded biaxiality as an important feature of cholesterics and of the blue phases which often intercede between the cholesteric and the isotropic phase. In an experiment on light scattering the data could be interpreted as a result of competing fluctuations of both uniaxial and biaxial order parameters, but no values of the biaxial order parameters were reported. On the other hand, other optical experiments have not revealed any observable biaxiality. Nevertheless, theory has been encouraging for further experimental study with some authors suggesting the use of NMR to observe this feature.

In this paper we report a direct deuteration NMR measurement of biaxial order in a nematic that has been twisted by an optically active compound added to the sample. The nematic material is a binary mixture of 75 wt.% 4-methoxybenzylidene-4′-n-butylaniline (MBBA) and 25 wt.% 4-n-butyloxybenzylidene-4′-n-heptyl-d6-aniline (4.O7-d6) selectively deuterated on one aromatic ring. To this material was added various concentrations of chiral 4-cyano-4′-(2-methyl)butylbiphenyl (CB-15) to yield the twisted structure.

In the untwisted material, the nematic aligns in the magnetic field yielding the typical deuteron spectrum illustrated in Fig. 1(a). Of interest in