sential.[11]

A fuller report of this work is being submitted for publication elsewhere. The authors would like to thank T. C. Lubensky for several comments on the general aspects of this work, P. Kubik and W. N. Hardy for many useful discussions and for allowing us to quote their experimental results prior to publication, and W. Opechowski for helpful comments on the manuscript. This work was supported in part by the National Science Foundation under Grant No. DMR76-21703 and Material Research Laboratory Grant No. DMR76-00678 and by the U. S. Office of Naval Research under Grant No. N00014-76-C-0106.

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Ultrasonic Observation of a Strong Pretransitional Anomaly near a Nematic–Smectic-*A* Phase Transition

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Strong anomalies in the velocity and attenuation of longitudinal ultrasound in the megahertz range were observed for the first time in the vicinity of the nematic–smectic-*A* phase transition in a liquid crystal (terephthal-*bis*-*p*-*p'*-butylaniline). Results are in strong contradiction with theoretical predictions and are qualitatively consistent with a picture involving both critical fluctuations and relaxation of the smectic order parameter, similar to that observed near the λ transition in liquid helium.

In recent years the nematic–smectic-*A* phase transition in liquid crystals has undergone extensive studies, both theoretical and experimental. The possibility of a second-order transition (either mean-field–like[1] or λ-like[2]) was predicted theoretically. Experimental evidence, though somewhat contradictory in nature, has been obtained on the pretransitional behavior of the Frank elastic constants, twist viscosity, etc., in N-*p*-cyanobenzylidene-*p*-octyloxyaniline (hereafter referred to as CBOOA) which is known to have an almost second-order nematic–smectic-*A* phase transition.[3] Sound propagation in CBOOA in the megahertz range of frequency, however, did not exhibit any anomaly near the transition.[4] Experiments performed at lower frequencies[5]

showed a trend towards a critical rise in the relaxation times, but nothing in the way of an anomaly in the attenuation or the velocity has ever been reported.

In this Letter we report the first observation of a strong anomaly in both the attenuation and velocity of longitudinal ultrasound near the nematic–smectic-*A* transition in a liquid crystal. The material chosen was terephthal-*bis*-*p*-*p'*-butylaniline (hereafter referred to as TBBA) which has the following transition temperatures:

$$\text{Solid} \xrightarrow{113^\circ\text{C}} \text{smectic-}B \xleftarrow{144^\circ\text{C}} \text{smectic-}C \xleftarrow{172^\circ\text{C}} \text{smectic-}A \xleftarrow{200^\circ\text{C}} \text{nematic} \xleftarrow{236^\circ\text{C}} \text{isotropic}.$$

In spite of the obvious problem associated with the high transition temperatures and the not-so-obvious problem of material stability at elevated temperatures, it was chosen for the following reasons. Firstly, calorimetric data[6] showed a small latent heat (about 0.29 kJ/mole) at the *N*-*A* transition accompanied by large pretransitional effects in the heat capacity. This prompted the authors to speculate about the possibility of an almost second-order *N*-*A* transition. Secondly, it has a wide nematic temperature range implying the possibility of a high degree of saturation of nematic ordering ($T_{NA}/T_{NI} = 0.92$ as opposed to 0.93 for CBOOA), a criterion regarded as necessary for a second-order transition to take place from theoretical considerations.[7] An attendant advantage of the wide nematic temperature range is the reduction of the interference of the *I*-*N* transition with the *N*-*A* transition. Finally, as we shall discuss later, the shifts in the velocity occurring at the *N*-*A* transition are much larger in TBBA than in CBOOA (because of the much stronger smectic ordering) which, in turn, leads to a siginficantly large dispersive anomaly.

The material was obtained from CPAC Organic Specialties Group,[8] and recrystallized from ethanol. Traces of solvent were removed by simultaneously heating and pumping on the sample. The temperature of the cell was regulated automatically to better than $\pm 0.03^\circ$C. The sample was heated to the nematic phase and slowly cooled down with the field, $\vec{H}$, at a particular orientation, θ, with respect to $\hat{q}$, the sound propagation direction; the field strength was ~ 20 kG. The sample inside the cell was kept in a helium gas environment in order to prevent oxidation. New sample material was used for each run. We tried to maintain a uniform thermal history in order to have a controlled sample deterioration, which could not be eliminated with the best precautions. The deterioration was evidence by a lowering of the transition temperature and a widening of the transition region. Without the aforementioned precautions the data were found to be much less reproducible.

Attenuation measurements were made by the pulse comparison technique, where the reference and signal pulses were derived from the same oscillator; velocity measurements were made with the pulse interference method. The acoustic spacer length and bore were 0.82 and 0.96 cm, respectively. All measurements were presumably in the linear response regime, since no amplitude-dependent effects were observable.

Figure 1 shows the temperature dependence of the velocity and attenuation of longitudinal ultrasound of frequency 2 MHz for θ equal to 0°, 45°, and 90°. As discussed above, it was not possible to control the deterioration completely. This

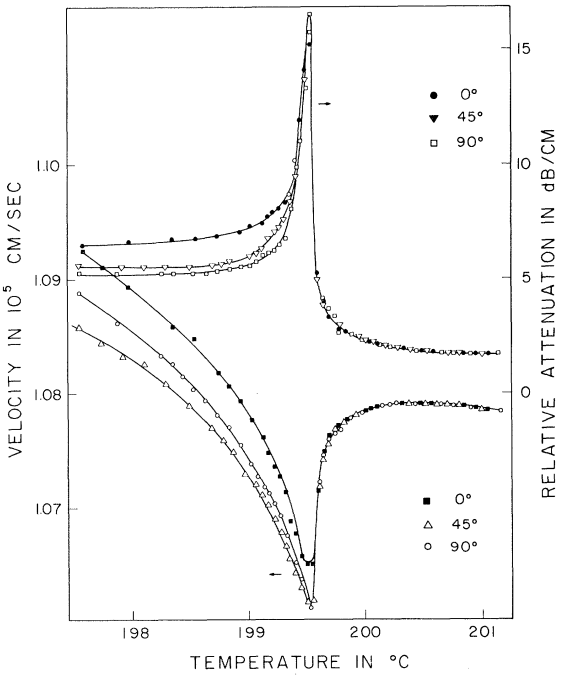

FIG. 1. Temperature dependence of the ultrasonic velocity and attenuation in the vicinity of the nematic–smectic-*A* phase transition. Frequency is 2 MHz and the angles between the sound propagation direction and the symmetry axis are 0°, 45°, and 90°.

resulted in shifts in the transition temperature, T_c, from one run to another of as much as a 0.3°. Hence the normalization of the data for various angles at one frequency was done in the following way. It was clear from the data that the anomaly existed at all orientations and the magnitudes of the anomalies were roughly isotropic. Hence, the peaks of the attenuation were assumed to occur at the same temperature for all angles at a given frequency, i.e., the relaxation time was assumed isotropic. The same procedure was followed for other frequencies.

Normalization of the data for different frequencies presents a more serious problem in that simultaneous measurements at different frequencies for a given angle must be performed. At this point in the experiments, however, a new rf spectrometer became available which is described elsewhere[9]; this instrument is suitable for such measurements. Using 2-MHz transducers we were able to measure simultaneously the velocity and attenuation across the transition at the fundamental and higher harmonics, i.e., 6 and 10 MHz. Figure 2 shows the temperature dependence of the velocity and attenuation at 2, 4, 6, and 10 MHz for $\theta = 0°$. The attenuation was plottted relative to its value at 203°C,

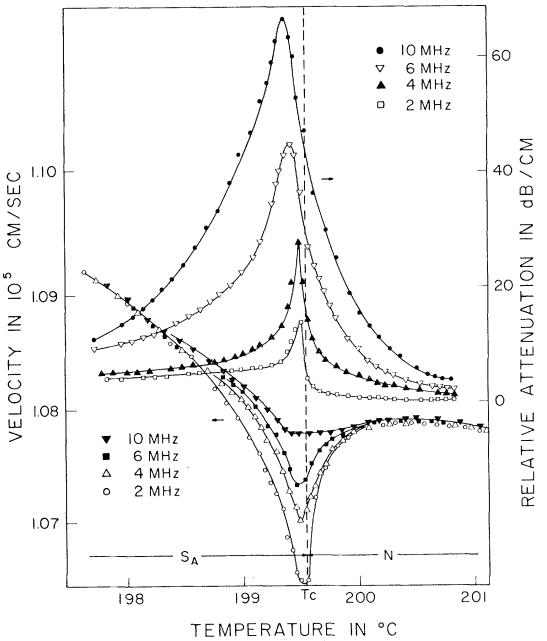

FIG. 2. Temperature dependence of the velocity and attenuation of longitudinal ultrasound at 2, 4, 6, and 10 MHz in the vicinity of the nematic–smectic-A phase transition for sound propagation parallel to the symmetry direction.

where it was found to be dispersionless within the accuracy of a pulse-echo measurement. The position of the peak of the attenuation shifts to lower temperature with increasing frequency. For 2, 6, and 10 MHz the shift was found to be linear with frequency. The data at 4 MHz were then interpolated accordingly.

From these two figures we make the following observations:

(1) The pretransitional anomaly in both velocity and attenuation exists for all orientations, in particular for $\theta = 90°$, in clear contradiction with available theoretical predictions.[10,11]

(2) The critical dispersion causes the magnitude of the velocity dip to decrease sharply with increasing frequency because of a departure from the more pronounced zero-frequency velocity anomaly of the type described by the Pippard-Buckingham-Fairbank relations.[12]

(3) In the presence of a relaxation process characterized by a single relaxation time, τ, the velocity and attenuation of sound of frequency ω are given (to first order in the velocity shift) by

$$c(\omega) = c(0)\left[1 + \frac{\delta c}{c}\frac{(\omega\tau)^2}{1+(\omega\tau)^2}\right] \quad (1)$$

and

$$\alpha(\omega) = \frac{\delta c}{c^2}\frac{\omega^2\tau}{1+(\omega\tau)^2}, \quad (2)$$

where $\delta c \equiv c(\infty) - c(0)$ and $c(\infty)$ and $c(0)$ are the velocities of sound at infinite and zero frequencies, respectively. As a function of τ, the attenuation goes through a maximum at $\omega\tau = 1$, the peak of which scales as ω. As a function of T, the position and strength of the maximum will be shifted somewhat since τ and δc are both functions of temperature. From Fig. 2 we observe that the height of the attenuation peak above the dispersionless background scales very nearly as ω.

(4) The shift in the position of the attenuation maximum with changing frequency clearly demonstrates the presence of a strongly temperature dependent relaxation time. By fitting the positions of the peaks (assumed to occur at $\omega\tau = 1$) by a τ of the form

$$\frac{1}{\tau} = a\frac{(T_c - T)^n}{T} = \frac{a\Delta T^n}{T},$$

we obtained $n \simeq 1$ (which is the original Landau-

Khalatnikov form), $a \sim 10^{11}$/sec, and the T_c indicated in Fig. 2. We attribute the relaxation phenomena to a critical slowing down of the smectic order parameter, a process which is present only below T_c.

(5) The anisortropy in the velocity and attenuation in the smectic phase are consistent with the known anisotropy curves with the velocity showing an intermediate minimum as expected. The peak value of the attenuation for $\theta = 90°$ was found to be consistently higher than that for $\theta = 0°$. This could be interpreted to result from the fact that the N-A velocity shift at $\theta = 90°$ is larger than that at $\theta = 0°$ and thus, by Eq. (2), would produce a larger attenuation. Deep in the smectic phase the situation reverses because of the dominance of the normal viscosity effects.

(6) The attenuation anomaly is strongly asymmetric about T_c, in a way reminiscent of the λ transition in helium. This could be understood in the following way: Two separate mechanisms may be present, the Landau-Khalatnikov mechanism below T_c (as discussed above), and a second one, both above and below the transition, connected with the critical fluctuations presumably of the Kawasaki-Hohenberg type.[13] In addition to the above two mechanisms, far below T_c, a finite dispersion is clearly present presumably due to the relaxation of the molecular alkyl chains; this relaxation appears to be significantly modified by the smectic ordering[5] as, judged by the difference in the residual dispersion in N and A far from T_c.

If we now restrict our attention to the region above T_c, we notice a pretransitional rise in attenuation for all angles. From the hydrodynamic theory of nematics we obtain the following for the attenuation at different angles:

$$\alpha(\theta = 0) = \omega^2 \eta_1 / 2\rho c^3 ,$$

$$\alpha(\theta = 45) = \omega^2 [\eta_1 + \eta_2 + \eta_4 - 2\eta_5 - 4\eta_3] / 8\rho c^3 ,$$

$$\alpha(\theta = 90) = \omega^2 (\eta_2 + \eta_4) / 2\rho c^3 ,$$

where η_i are viscosity parameters.[14] Thus we can determine the temperature dependence of certain combinations of bulk and shear viscosities. With this analysis, it follows from the data that the bulk viscosities diverge much faster than the shear viscosities.

At this point we emphasize that the absence of an attenuation peak above T_c suggests that a mode-mode coupling theory of the Kawasaki-Hohenberg type is probably applicable very close to the transition where $\omega\tau \gtrsim 1$. Without a careful treatment of this type it is not useful, in our opinion, to try to fit the data to obtain exponents for viscosities or by a dynamic heat capacity theory of Imura-Okano type.[15]

Since it is not known *a priori* what part of the attenuation above T_c should be subtracted from that below T_c, and also since more than one relaxation mechanism seems to be present in the smectic phase, we have resisted the temptation to fit the subtracted attenuation below T_c by a relaxation model of the Landau-Khalatnikov type. We also did not attempt to fit the hydrodynamic velocity anisotropy below T_c to obtain an exponent for the order parameter. Without a detailed knowledge of the strengths of the various relaxation processes, which is not now available, it is not possible to fit the hydrodynamic velocity anisotropy.

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Origin of Saturation Effects in Electron Transport

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The diffraction model is generalized to incorporate a postulate on the electron-phonon interaction; viz., phonons with wavelength exceeding the electron mean free path are ineffective electron scatterers. This postulate leads to a limiting resistivity when the electron mean free path is of the order of the interatomic spacing. The generalized diffraction model is also shown to explain many anomalous features common to high-resistivity metals. Crsytalline Nb, *A*15's, and glassy metals are discussed.

High-resistivity amorphous and disordered-crystalline metals exhibit many anomalous transport properties. The variety of explanations for these anomalies reflects the complexity of high-resistivity systems. Examples of mechanisms invoked to explain the behavior of these systems include virtual-bound-state formation,[1] breakdown of the Boltzmann equation,[2] electron localization,[3] s-d scattering,[4] vacancy formation,[5] multiple-scattering effects,[6] and thermal excitation of nearly degenerate core configurations.[7]

Many of these anomalies can be understood within the framework of the diffraction model, i.e., Ziman theory[8] and its extensions.[9,10] We have shown[11-13] that this model explains the $+T^2$ low-temperature dependence of the resistivity ρ, the variations of the temperature coefficient of resistivity (TCR), and the small resistivity maxima seen in alloys at concentrations for which the crossover from positive to negative TCR occurs.

However, a number of anomalies have not been explained by the diffraction model, including the following: (1) Breakdown of Matthiessen's rule in high-resistivity metals (the occurrence of small or negative TCR for all high-resistivity metals[14]). (2) Low-temperature anomaly (very-high-resistance amorphous alloys exhibit $\rho \propto 1 - AT^2$ at low temperatures rather than the predicted positive T^2 dependence and concommitant small maximum[15]). (3) Saturation[16] (many intermetallic compounds, e.g., the *A*15 alloys,[17] exhibit a loss of temperature dependence of ρ at high temperatures. Saturation has also been suggested to occur in pure Nb.[2,18]). We shall show that these anomalies can be explained in the framework of the diffraction model if we invoke a plausible postulate concerning the electron-phonon interaction as follows:

Interaction postulate.—Phonons with wavelength exceeding the electron mean free path Λ *are ineffective electron scatters.*[19] The effect of the interaction postulate is to produce a low-wave-vector (or low-frequency) cutoff in the integrals over the phonon spectrum which occur in the diffraction model. In the following we shall consider a Debye spectrum so that the electron-phonon interaction will be turned off completely for $\Lambda = 2\pi/q_D$, where q_D is the Debye wave vector. The resistivity corresponding to $\Lambda = 2\pi/q_D$ is approximately 200 $\mu\Omega$ cm for a monovalent free-electron metal.

The temperature dependence of ρ is essentially determined by that of the resistivity structure factor $S^{\rho}(K)$.[20,21] Thus, consider the one-phonon resistivity structure factor neglecting the interaction postulate

$$S_1^{0}(K) \cong \frac{(hK)^2 e^{-2W(K)}}{2Mk_B T} \sum_q [a(\vec{K}+\vec{q}) + a(\vec{K}-\vec{q})] n(x)[n(x)+1], \tag{1}$$

where h is Planck's constant, k_B is Boltzmann's constant, $\vec{K}$ is the scattering vector, $e^{-2W(K)}$ is the