

Anisotropic Ultrasound Propagation in a Smectic-A Liquid Crystal*

K. Miyano

Department of Physics, Northwestern University, Evanston, Illinois 60201

and

J. B. Ketterson

Argonne National Laboratory, Argonne, Illinois 60439

(Received 12 July 1973)

An anisotropic ultrasonic velocity in smectic-A diethyl 4,4'-azoxydibenzoate was measured at 2, 5, 12, and 20 MHz. The material was aligned by slowly cooling through the phase transition point in a magnetic field of 12.4 kOe. An accuracy of $\pm 0.08\%$ in the relative velocity was provided by the phase-matching technique, and three elastic constants were calculated.

The propagation of sound in liquid crystals has been discussed in terms of elastohydrodynamic theories.^{1,2} A unique prediction of these theories is that the minimum in the angular dependence of the longitudinal sound velocity of a smectic liquid crystal does *not* occur at a symmetry axis, as is the case for a nematic material; also, shearlike modes can propagate in smectics. Preliminary ultrasonic measurements³ on a smectic material showed a larger anisotropy than is typical for nematics, but did not establish the unique angular dependence. Brillouin-scattering studies⁴ on smectics showed clear evidence for the new shear modes; however, the anisotropy of the longitudinal mode was only slightly larger than experimental error. The light-scattering measurements probe hypersonic frequencies where viscoelastic effects may dominate.

We report here a detailed study of the propagation of longitudinal ultrasound in the smectic-A liquid crystal diethyl 4,4'-azoxydibenzoate, which clearly shows the unique anisotropy of the longitudinal mode in a bulk sample at low frequencies. The phase-matching technique⁵ was employed, which is very suitable for highly attenuative substances such as liquid crystals; the typical resolution was 0.02%. The copper sonic cell and electronics have been described elsewhere,⁶ with the exception that an Arenberg gated amplifier was used to increase the power output. The sound spacers, which contained the specimens, were gold-plated brass cylinders (9 mm i.d. by 7.8, 15.9, and 23.7 mm long for 20 and 12, 5, and 2 MHz, respectively). A thermocouple and two heaters were attached to the sonic cell which was, in turn, located in an evacuated chamber. The temperature of the cell was automatically regulated to better than $\pm 0.07^\circ\text{C}$.

Considering the resettability of the temperature, the error in the velocity was increased to $\pm 10^2$ cm/sec ($\pm 0.08\%$). The material was obtained from Eastman Organic, and recrystallization did not affect the experimental results other than to shift the isotropic-smectic transition point slightly ($\sim 1^\circ$). A transition from smectic-A to isotropic occurred at 122.6°C in the recrystallized sample; after a 10–20-h run at high temperatures it decreased to 121.6°C . The sample was first heated to the isotropic phase and then was cooled through the phase transition point in a magnetic field of 12.4 kOe.⁷ The absolute value of the velocity (1.18×10^5 cm/sec) was found at 131.8°C (where the material is in an isotropic phase and has a low attenuation) by measuring the time of flight of echoes at 2 MHz, and all measurements were done relative to this velocity. Because of the limited accuracy of this method, the error in the absolute value of the velocity is estimated to be $\pm 5\%$. The attenuation maximum was between 122.0 and 121.5°C . Between 122.4 and 120.4°C , the temperature was lowered by 0.2–0.4 deg, and at each step the sample was held at a constant temperature until equilibrium (as judged from the velocity shift and the attenuation change) was reached (5–10 min). Without this precaution, the sound velocity in the smectic phase was found to be slightly less anisotropic and less reproducible.

Figure 1 shows the temperature dependence of the sound velocity with the magnetic field parallel and perpendicular to the sound propagation direction. The velocity change is quite linear both in the isotropic and smectic-A phases; at the phase transition point it increases abruptly, indicating the first-order nature of the transition. In Fig. 2 we show the angular dependence of the

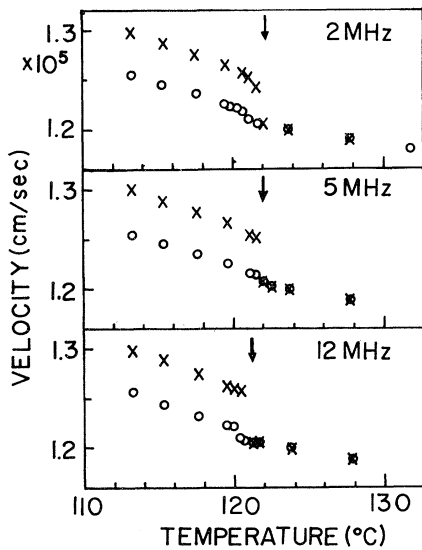


FIG. 1. Temperature dependence of the sound velocity at 2, 5, and 12 MHz. Crosses, magnetic field parallel to the sound propagation direction; circles, field perpendicular to the propagation direction. Arrows indicate the smectic-A-isotropic transition point.

sound velocity at several temperatures; θ is the angle between the direction of propagation and the magnetic field. A velocity minimum occurs at about 60° , and reflection symmetry of the pattern about 90° was observed.

The anisotropic velocity can be explained phenomenologically by simply using the symmetry of smectic-A liquid crystals.^{1,4} In a conventional theory of elasticity, stress and strain are related by a 6×6 matrix of elastic stiffness constants, c_{ij} ($i, j = 1, 2, \dots, 6$). By imposing the condition that the x and y directions (see inset, Fig. 2) are equivalent, it follows that $c_{11} = c_{22} = c_{12}$ and $c_{13} = c_{23}$; also, the fact that a liquid crystal cannot support a static shear requires $c_{44} = c_{55} = c_{66} = 0$; the remaining elastic constants vanish. Elastic stability requires that $c_{11}c_{33} - c_{13}^2 > 0$. The angular dependence of the anisotropic longitudinal sound velocity v is then easily calculated by solving an eigenvalue problem, and is given by the larger root of the equation

$$(\rho v^2)^2 - (c_{11} \sin^2 \theta + c_{33} \cos^2 \theta)(\rho v^2) + (c_{11}c_{33} - c_{13}^2) \sin^2 \theta \cos^2 \theta = 0, \quad (1)$$

where θ is the angle defined above and ρ is the density of the material; the smaller root corresponds to a shear wave. The data were fitted by least squares with Eq. (1) at each frequency, and the results are shown in Fig. 2. At 20 MHz

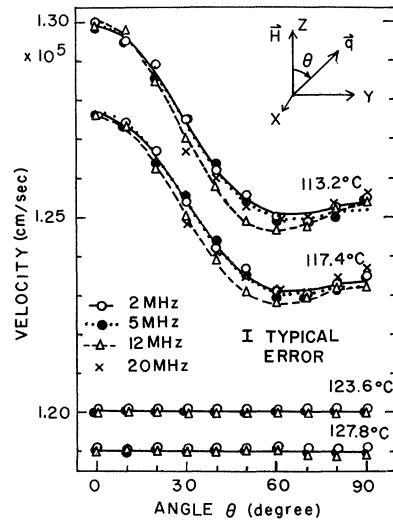


FIG. 2. Angular dependence of the velocity at several temperatures. Angle is between \vec{H} (magnetic field) and \vec{q} (sound propagation direction).

the attenuation was so high that no reliable measurements were possible at angles less than 30° ; however, the three parameters were calculated with the available data. The anisotropy at 12 MHz is significantly different from that at other frequencies. This was completely reproducible and, because the experiment at 20 MHz was done under exactly the same condition as that at 12 MHz, the possibility of a size effect (a perturbation on the properties of the bulk liquid by the surface of the spacer or transducer) was excluded. The parameters c_{11} , c_{13} , and c_{33} are related to de Gennes's phenomenological parameters (A_0 , B_0 , and C_0) and the thermodynamic derivatives of Martin, Parodi, and Pershan² as follows [Eq. (1) is identical to de Gennes's Eq. (III.7)]:

$$\begin{aligned} c_{11} &= A_0 = \rho (\partial p / \partial \rho)_{s, x}, \\ c_{11} - c_{13} &= -C_0 = (\partial p / \partial \nabla_3 x)_{x, \rho}, \\ c_{33} + c_{11} - 2c_{13} &= B_0 = (\partial \varphi_3 / \partial \nabla_3 x). \end{aligned}$$

The temperature dependence of these quantities is shown in Fig. 3. Quantities which involve the derivative with respect to $\nabla_3 x$ (compression and expansion of layer spacings) are less sensitive to the temperature change, which indicates that the "rigidity" of the layered structure sets in at the transition point and does not change significantly afterwards. Some dispersion is observed, however, which may be responsible for the anomalous anisotropy of the velocity at 12 MHz as was noted before. However, because the data at 20

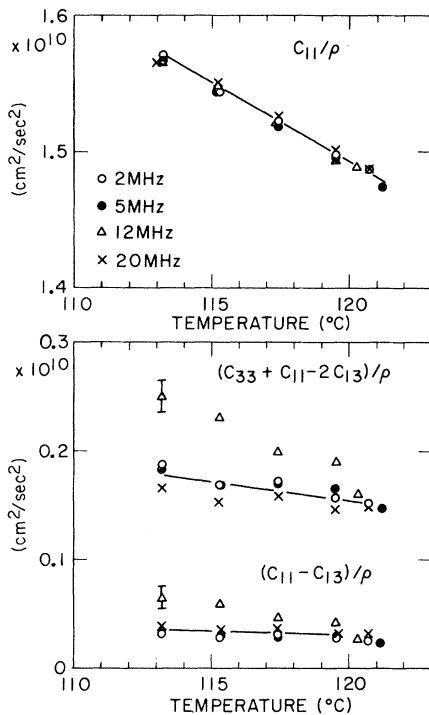


FIG. 3. Temperature dependence of some combinations of elastic constants.

MHz are in good agreement with those at 2 and 5 MHz, it is not understood if this effect is a truly dispersive one or not. There is, however, frequency dependence in the anisotropy of the absorption as is shown in Fig. 4, where the difference of attenuation at 0° and 90° is divided by the square of the frequency. A similar plot for the absolute values of the sound absorption of para-azoxyanisole was made by Hoyer and Nolle,⁸ suggesting that there is a relaxation process which has a time constant of 10^{-8} – 10^{-7} sec. Although the data points in Fig. 4 show that there may be a relaxation process with a time constant of the same order as in para-azoxyanisole, more accurate measurements over a wider range of frequencies are clearly required.

The rigidity of the smectic structure of diethyl 4, 4'-azoxydibenzoate was demonstrated by rotating the magnetic field to 0° after cooling the sample into a smectic phase through the transition temperature with the magnetic field at 90° . After 30 min no change of either the attenuation or velocity was noted within the resolution of our equipment, indicating that the field could not rotate the sample significantly. If there is a strong boundary effect⁹ at the surfaces of the transducers and the spacers, then there could

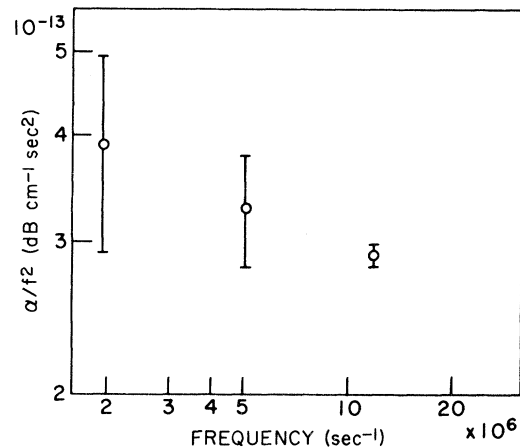


FIG. 4. Frequency dependence of attenuation α divided by the square of the frequency, f^2 . α is the difference between the attenuations at 0° and 90° .

be a variation of the molecular orientation over the sample; this would result in the measured velocity being less anisotropic. The consistency of data points in Fig. 2 obtained using a variety of sizes of samples suggests that the boundary effect was not large. This point was further checked by measuring the sound velocity without an external field. If the boundary effect is small, molecules or aggregates of molecules ("crystallites") are oriented randomly and the sound velocity v_0 will be the orientational average of the anisotropic velocity $v(\theta)$:

$$v_0 = (1/4\pi) \int_0^{2\pi} d\varphi \int_0^\pi v(\theta) \sin\theta d\theta. \quad (2)$$

The integration was done numerically using the parameters derived from the least-squares fit, and the calculated and measured velocities are in agreement within experimental error at each temperature.

We would like to acknowledge theoretical discussions with Professor C. W. Woo.

*Work supported by the U. S. Atomic Energy Commission, and by the National Science Foundation through Grant No. GP-29130 administered by Northwestern University.

¹P. G. de Gennes, J. Phys. (Paris), Colloq. **30**, C4-65 (1969).

²P. C. Martin, O. Parodi, and P. S. Pershan, Phys. Rev. A **6**, 2401 (1972).

³A. E. Lord, Phys. Rev. Lett. **29**, 1366 (1972).

⁴Y. Liao, N. A. Clark, and P. S. Pershan, Phys. Rev. Lett. **30**, 639 (1973).

⁵The same technique was used in the measurement of an anisotropic sound velocity in a nematic liquid crystal. M. E. Mullen, B. Lüthi, and M. J. Stephen, *Phys. Rev. Lett.* **28**, 799 (1972).

⁶B. M. Abraham, Y. Eckstein, J. B. Ketterson, and J. Vignos, *Cryogenics* **9**, 274 (1969).

⁷The aligning effect of a magnetic field seems to

saturate around 10 kOe. See Ref. 3 and also L. S. Chou and E. F. Carr, *Phys. Rev. A* **7**, 1639 (1973).

⁸W. A. Hoyer and A. W. Nolle, *J. Chem. Phys.* **24**, 803 (1956).

⁹The smectic planes of diethyl 4,4'-azoxydibenzoate tend to be parallel to a clear surface. E. Friedel, *C. R. Acad. Sci.* **180**, 269 (1925).

Densities of States and Calculated *K* X-Ray Spectra of TiFe

D. A. Papaconstantopoulos*

Naval Research Laboratory, Washington, D. C. 20375

(Received 20 August 1973)

Densities of states and *K* x-ray emission and absorption spectra from both components of a 50-50 intermetallic compound TiFe were calculated using results of self-consistent energy-band calculations. The calculated x-ray spectra agree well with experiment.

In recent years, self-consistent band calculations have been performed for many monatomic materials and some compounds in which only one component is a transition metal.¹ Several x-ray emission spectra and a few absorption spectra² have also been computed using the results of non-self-consistent band calculations.

In the present work the augmented plane-wave method (APW)³ of band theory was employed to calculate, self-consistently, the energy bands and wave functions of an intermetallic compound between the 3*d* transition elements Ti and Fe. Slater's *X α* method⁴ was used to approximate the exchange potential, with the α values calculated by Schwartz.⁵ The results were subsequently used to obtain the x-ray spectra involving the 1*s* (*K*) level.

This is the first time that emission and absorption spectra have been calculated for both sites in an alloy. Comparison of calculated and measured spectra provides a test of the theoretical, local, component densities of states over a wide energy range.

The APW calculation was carried out at 512 points in the simple cubic Brillouin zone. Eigenvalues and the electronic charges⁶ within the APW spheres were then interpolated⁷ by Monte Carlo sampling of 96 000 points in the zone, and the *s*-, *p*-, and *d*-like densities of states (DOS) were obtained for both the Ti and the Fe sites.

Figure 1 shows the total DOS and its two *d* components. We observe the low DOS at the Fermi level characteristic of a paramagnetic material⁸ and consistent with electronic specific heat mea-

surements.⁹ We also observe that, as one might have expected,¹⁰ the heavier element (Fe) has larger local DOS below the Fermi level, while the lighter element (Ti) yields larger local DOS above the Fermi level. Figure 2 shows the *s*- and *p*-like DOS which are, typically for transition metals, much smaller than the *d*-like DOS. (Note a factor of 10 difference in our scale for Figs. 1 and 2.)

In order to obtain x-ray spectra from the above component DOS we form their products with the

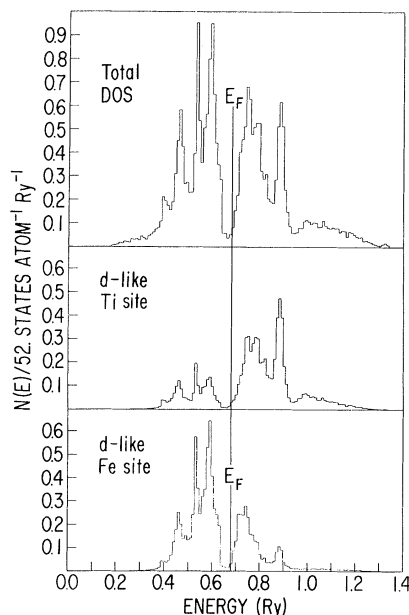


FIG. 1. Total and *d*-like densities of states of TiFe.