Anisotropic ultrasound propagation in a smectic-A liquid crystal

S. Bhattacharya* and S. Y. Shen†
Department of Physics and Astronomy and Materials Research Center, Northwestern University, Evanston, Illinois 60201

J. B. Ketterson
Department of Physics and Astronomy and Materials Research Center, Northwestern University, Evanston, Illinois 60201 and Argonne National Laboratory, Argonne, Illinois 60439

(Received 7 August 1978)

Anisotropic ultrasound propagation was studied in a magnetically aligned monodomain smectic-A liquid crystal (di-n-decyl azoxy methyl cinnamate). A large attenuation was observed near the isotropic-smectic-A phase transition. The anisotropy in the sound velocity was found to be in agreement with the predictions of hydrodynamic theory, and no dispersion was found in the frequency range used (4–12 MHz). The temperature dependence of the physically meaningful elastic constants was determined. The anisotropy in the attenuation was also measured. Unlike the velocity anisotropy, no intermediate minimum was observed.

Hydrodynamics describes the low-frequency long-wavelength behavior of a system. Longitudinal ultrasound, by virtue of its low frequency, is ideally suited to test the predictions of generalized hydrodynamic theories for various liquid-crystalline symmetries. In addition, ultrasound serves as a very effective tool for studying the dynamics of phase transitions between the various liquid-crystalline symmetries.

In contrast with the nematics, which have been quite widely studied, the smectics have received significantly less attention. To date only a few studies have been reported on the anisotropic propagation of sound in a smectic-A liquid crystal.[1-3] The magnitude of the velocity anisotropy varied by as much as three orders of magnitude from one material to another.[3,4] The complete velocity anisotropy by ultrasound propagation[2,3] has so far been reported on only two materials, namely, diethyl-p, p′-azoxybenzoate (DEAB) and ethyl-p-[(p-methoxybenzylidene)amino]cinnamate (EMBAC); Brillouin scattering[4] has been studied only in β-methyl-butyl-methoxy benzylidene amino cinnamate (MBMBAC). The attenuation anisotropy has been measured in DEAB[1,3] but some amount of controversy exists in terms of the relative magnitudes of the various viscosity terms that contribute to the attenuation anisotropy.[5]

Furthermore, the isotropic–smectic-A transition has received very little attention compared to the isotropic-nematic transition, which has been studied in great detail.

We report here results on the anisotropic ultrasound propagation in a smectic-A liquid crystal di-n-decyl-azoxy methyl cinnamate, hereafter referred to as DDAMC, which has the following transition temperatures[6]:

$$\text{crystal} \overset{65.6^{\circ}C}{\longleftrightarrow} \text{smectic C} \overset{72^{\circ}C}{\longleftrightarrow} \text{smectic A} \overset{87.5^{\circ}C}{\longleftrightarrow} \text{isotropic}.$$

The paper is arranged as follows: In Sec. I we shall briefly describe the phenomenological parametrization of the sound-propagation problem, followed by a brief description of the hydrodynamics of a smectic-A liquid crystal, making the connection between the phenomenological parameters and those appearing in the hydrodynamic description of sound propagation. Section II contains the experimental details, results, and discussion.

I. SOUND-PROPAGATION THEORY

A. Phenomenological theory of sound propagation

In this section we briefly describe the sound-propagation problem. For details, we refer the reader to Ref. 7.

We start by introducing elastic-stiffness constants c_{ij} that connect a six-component vector formed out of the strain tensor u_{kl} to a similar vector formed from the stress tensor σ_{ij} via the generalized Hooke's law. For a crystal with hexagonal symmetry, which includes the uniaxial symmetry, there are five independent nonzero elements, namely, $c_{11}=c_{22}$, c_{13}, c_{33}, $c_{44}=c_{55}$, and $c_{66}=\frac{1}{2}(c_{11}-c_{12})$ (where the 3 axis is the symmetry direction). For the uniaxial smectic-A case only three elastic constants survive, namely, c_{11}, c_{13}, and c_{33}. Because the smectic planes can glide freely over one another, there is no restoring force for 1-2 and 2-3 shear, i.e., $c_{44}=0$. In order to account for dissipation we substitute c_{ij}/ρ by $C_{ij}-i\omega D_{ij}$, where $\omega D_{ij}/C_{kl} \ll 1$ so that the wave propagates through many wavelengths before being excessively attenuated. We obtain (to

lowest order in $\omega D_{ij}/C_{kl}$) the following expressions for the velocity and attenuation of longitudinal sound propagating at an angle θ with respect to the symmetry direction (i.e., the 3 axis):

$$2V^2(\theta) = C_{11}\sin^2\theta + C_{33}\cos^2\theta + [(C_{11}\sin^2\theta + C_{33}\cos^2\theta)^2 + 4(C_{13}^2 - C_{11}C_{33})\sin^2\theta\cos^2\theta]^{1/2}, \quad (1)$$

$$\alpha(\theta) = [\omega^2/2V^3(\theta)][D_{11}\sin^2\theta + D_{33}\cos^2\theta + (2D_{13} + 4D_{44} - D_{11} - D_{33}) \times \sin^2\theta\cos^2\theta]. \quad (2)$$

If we assume that the anisotropy in the velocity is small, i.e., $C_{11} \approx C_{13} \approx C_{33}$, then Eq. (1) can be written

$$V^2(\theta) \simeq C_{11} - 2(C_{11} - C_{13})\cos^2\theta + (C_{11} + C_{33} - 2C_{13})\cos^4\theta, \quad (1')$$

and the attenuation can be written

$$\alpha(\theta) = (\omega^2/2\overline{V}^3)[D_{11}\sin^2\theta + D_{33}\cos^2\theta + (2D_{13} + 4D_{44} - D_{11} - D_{33}) \times \sin^2\theta\cos^2\theta], \quad (2')$$

where $\overline{V}$ is the average velocity. The condition of elastic stability requires that $C_{11}C_{33} > C_{13}^2$.

B. Hydrodynamics of a smectic-A liquid crystal

The Martin-Parodi-Pershan (hereafter referred to as MPP) formalism[8] of the hydrodynamics of liquid crystals recognizes two sources of hydrodynamic modes: (i) the conservation equations, where a generalized density is proportional to the divergence of an associated current and (ii) the existence of broken symmetries in an ordered system. Modes arising from the first source occur in ordinary liquids, while modes originating from the second source exist only in liquid crystals (or superfluids). For a detailed account, we refer to the original paper[8] and a recent review article.[7] Here we shall only briefly mention the results.

The theory is generalized by incorporating a proper hydrodynamic variable u_α corresponding to a particular broken symmetry that results in the addition of a term of the form $\Sigma_\alpha \varphi_{\alpha i} d\nabla_i u_\alpha$ (where $\phi_{\alpha i}$ is the generalized stress conjugate to u_α) in the free-energy expression.

For a smectic-A liquid crystal, the proper hydrodynamic variable is u_3, the deformation of the smectic layers, the plane normals being parallel to the 3 axis. The associated stress is given by φ_3. The complete set of equations are then

$$\dot{\rho} = \rho_0 \nabla_i v_i, \quad (3)$$

$$\dot{u}_3 = v_3 + (\xi_3/T)\nabla_3 T + \xi \nabla_i \varphi_{3i}, \quad (4)$$

$$\dot{\epsilon} = -(\epsilon + p)\nabla_i v_i + \kappa_\perp(\nabla_1^2 + \nabla_2^2)T + \kappa_\parallel \nabla_3^2 T + \xi \nabla_3 \nabla_i \varphi_{3i}, \quad (5)$$

$$\dot{\rho} v_i = -\nabla_i p + \delta_{3i}\nabla_j \varphi_{3j} + \eta_{ijkl}\nabla_j \nabla_l v_k, \quad (6)$$

with usual notations (see Ref. 7). Solving these equations we obtain six modes: one viscous shear mode, one temperature diffusion mode and two pairs of propagating modes, with one pair corresponding to the longitudinal sound mode and the other to a propagating shearlike mode (corresponding to the deformation of the smectic layers, but involving only a very small volume change). The shear modes become diffusive for propagation parallel to the 1 or 3 direction.

The velocity of sound is anisotropic and is given by Eq. (1) with the following substitutions:

$$C_{11} = \left(\frac{\partial p}{\partial \rho}\right)_{s, \nabla_3 u_3}, \quad (7)$$

$$C_{13} = \left(\frac{\partial p}{\partial \rho}\right)_{s, \nabla_3 u_3} - \frac{1}{\rho}\left(\frac{\partial \varphi_3}{\partial \rho}\right)_{s, \nabla_3 u_3}, \quad (8)$$

$$C_{33} = \left(\frac{\partial p}{\partial \rho}\right)_{s, \nabla_3 u_3} - \frac{2}{\rho}\left(\frac{\partial \varphi_3}{\partial \rho}\right)_{s, \nabla_3 u_3} + \frac{1}{\rho}\left(\frac{\partial \varphi_3}{\partial \nabla_3 u_3}\right)_{s, \rho}. \quad (9)$$

The absorption of sound is also anisotropic and contains (in the small-anisotropy limit) five viscosity coefficients $\eta_1 - \eta_5$ and two thermal conductivity coefficients $\kappa_\parallel$ and $\kappa_\perp$. The final expression is given by Eq. (2) with the following substitutions:

$$D_{11} = (1/\rho)[\eta_2 + \eta_4 + \kappa_\perp(\gamma - 1)/c_p], \quad (10)$$

$$D_{33} = (1/\rho)[\eta_1 + \kappa_\parallel(\gamma - 1)/c_p], \quad (11)$$

$$2D_{13} + 4D_{44} - D_{11} - D_{33} = (1/\rho)[2\eta_5 + 4\eta_3 - \eta_1 - \eta_2 - \eta_4]. \quad (12)$$

For liquid crystals, the contribution of the thermal-conductivity terms is small compared with that of the viscosity terms. Hence the former can be neglected.

A phenomenological elastic theory of the smectic-A phase proposed by de Gennes[8] contains phenomenological constants A_0, B_0, and C_0, which in our notation are as follows:

$$A_0 = \rho C_{11} = \rho\left(\frac{\partial p}{\partial \rho}\right)_{s, \nabla_3 u_3}, \quad (7')$$

$$B_0 = \rho(C_{11} + C_{33} - 2C_{13}) = \left(\frac{\partial \varphi_3}{\partial \nabla_3 u_3}\right)_{s, \rho}, \quad (8')$$

$$C_0 = \rho(C_{11} - C_{13}) = \left(\frac{\partial p}{\partial \nabla_3 u_3}\right)_{s, \rho}. \quad (9')$$

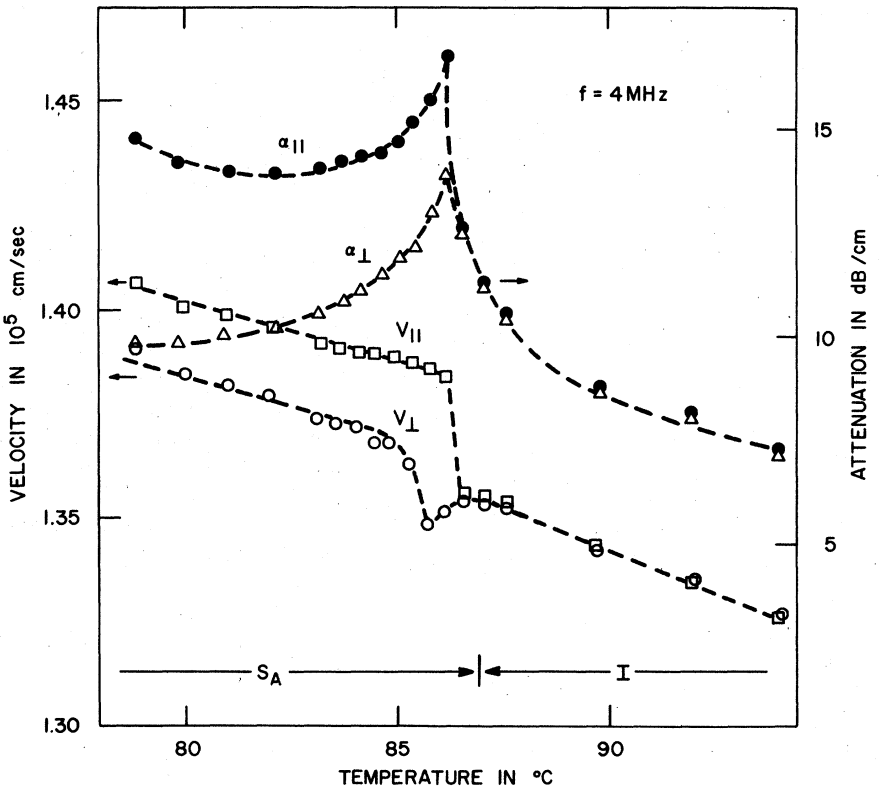

FIG. 1. Temperature dependence of the velocity and attenuation in DDAMC for $\theta = 0°$ and 90° at 4 MHz.

II. EXPERIMENTAL RESULTS

The material used in these experiments was obtained from CPAC Organic Specialities Group and used without recrystallization. A phase-sensitive technique was used for accurate velocity measurements. The details of the method are described elsewhere.[3] An accuracy of better than one part in 5000 was routinely achieved in the relative velocity measurements. The acoustic path length was 8.2 mm. The temperature of the cell was controlled automatically to approximately ±0.02 °C. The cell was placed between the pole pieces of an Arthur D. Little electro magnet, the strength of which could be varied continuously up to 28 kG.

A monodomain sample was obtained by cooling from the isotropic phase in a field of 15 kG. Measurements performed at a higher field (~20 kG) gave nearly identical values of the velocity and the attenuation indicating no significant change of orientation. The rigidity of the smectic layers was evidenced by no change in the velocity or the attenuation when the field was rotated in the smectic-*A* phase.

The absolute values of the velocity and attenuation were determined by the standard time-of-flight technique at 91.9 °C in the isotropic phase, and were found to be 1.31×10^5 cm/sec and 7.5 dB/cm at a frequency of 4 MHz. Because of the limited accuracy of the method, the error was estimated to be ±5%. The relative changes of the velocity and attenuation were normalized to their values in the isotropic phase.

The temperature dependence of the velocity and the attenuation at 4 MHz, for propagation both parallel ($\theta = 0°$) and perpendicular ($\theta = 90°$) to the field $\vec{H}$ (i.e., the symmetry direction), is shown in Fig. 1. The isotropic–smectic-*A* transition is found to be accompanied by an anomaly in the attenuation. The peak value of the attenuation is higher for $\theta = 0°$ than for $\theta = 90°$. The velocity parallel to the symmetry direction rises very sharply following a pretransitional flattening. This is understood to result from the appearance of the smectic layers. The velocity for propagation perpendicular to the symmetry direction shows a dip near the transition, which is less marked at 12 MHz.

In order to show the transition behavior, the attenuation for $\theta = 90°$ at 4 and 12 MHz is plotted in Fig. 2. The attenuation is plotted relative to its value at 94 °C, where it is found to be dispersionless within the accuracy of a pulse-echo measurement. The peak of the anomalous attenuation

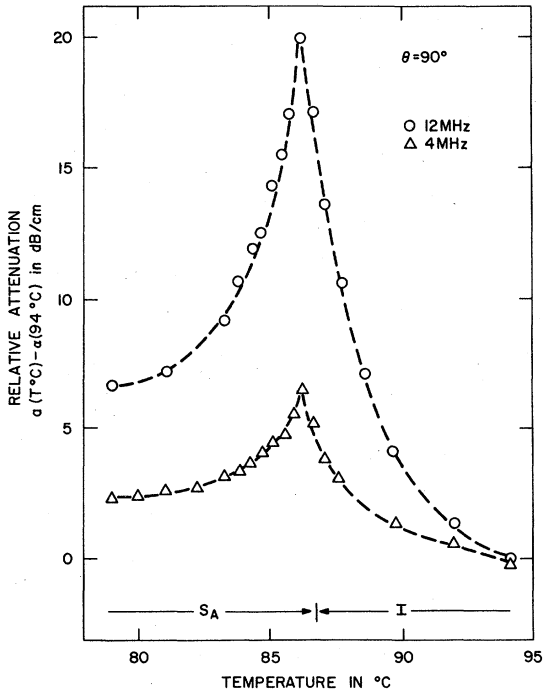

FIG. 2. Temperature dependence of the attenuation in DDAMC for $\theta = 90°$ at 4 and 12 MHz.

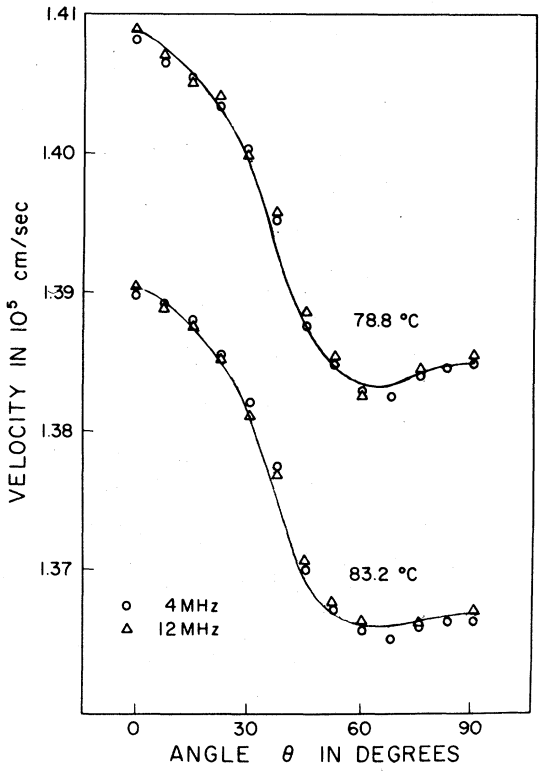

FIG. 3. Velocity anisotropy in the smectic-A phase in DDAMC at 4 and 12 MHz.

scales approximately as the frequency instead of the square of the frequency as is expected from dispersionless behavior.

From a phenomenological theory of dispersion, the attenuation is given by[9]

$$\alpha(\omega) = [\delta V / V^2(0)]\omega^2\tau/[1 + (\omega\tau)^2], \qquad (13)$$

where $\delta V = V(\infty) - V(0)$ and $V(\infty)$ and $V(0)$ are the velocities of sound at infinite and zero frequencies, respectively, and τ is the temperature-dependent relaxation time; Eq. (13) is valid in the limit $\delta V/V \ll 1$. The above expression has a maximum as a function of τ for $\omega\tau = 1$, where $[\alpha(\omega)]_{max} \propto \omega$. As a function of the temperature the position of the maximum can shift slightly from the point where $\omega\tau = 1$ since both δV and τ are temperature dependent. Our results appear to be consistent with this dispersive behavior. Unfortunately, however, no theory exists to the best of our knowledge, that deals with the sound-propagation problem near this transition. Even though the transition is known to be first order from calorimetric measurements, second-order-like behavior, though somewhat weaker than for the isotropic-nematic transition, seems to be present.

The velocity anisotropy in the smectic-A phase at 4 and 12 MHz is shown in Fig. 3. The velocity shows a distinct intermediate minimum—in a way totally consistent with previous measurement in other smectic-A materials.[2-4] The anisotropy is of the same order of magnitude as that in DEAB and EMBAC, and about two orders of magnitude larger than that in p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA).[3] The magnitude of the velocity anisotropy does not differ significantly between the two frequencies, and thus may represent the anisotropy in the hydrodynamic limit. The curve in Fig. 3 is a least-squares fit.

The anisotropy of the attenuation in the smectic-A phase is shown in Fig. 4. Unlike the velocity anisotropy, no intermediate minimum was observed. On the basis of earlier data, it was speculated that the attenuation anisotropy in the smectic-A phase has a $\cos^4\theta$ dependence as opposed to $\cos^2\theta$ dependence in nematics. Our results are inconsistent with a predominant contribution coming from the coefficients of the $\cos^4\theta$ term in Eq. (2). A least-squares fit to the data using Eq. (2) yields the following values of the combinations of the viscosity coefficients at 78.8 °C: $\eta_1/\rho = 1.7$ P cm^3 g^{-1}, $(1/\rho)(\eta_2 + \eta_4) = 1.2$ P cm^3 g^{-1}, and $(1/\rho)(2\eta_5 + 4\eta_3) = 2.5$ P cm^3 g^{-1}. As stated earlier, for liquid crystals the contribution to the attenuation due to the thermal conductivities is very small

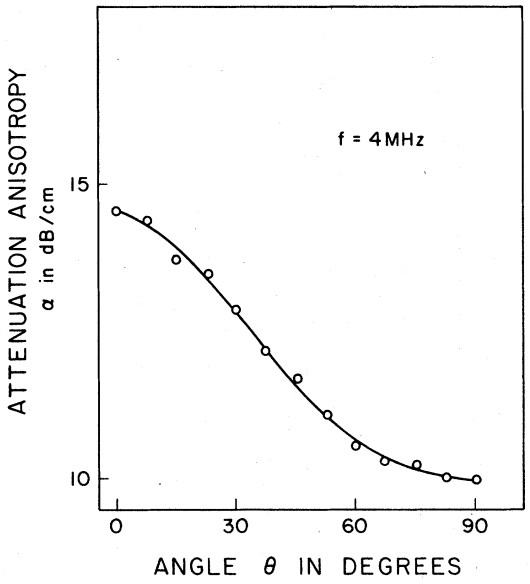

FIG. 4. Attenuation anisotropy in the smectic-A phase in DDAMC at 4 MHz.

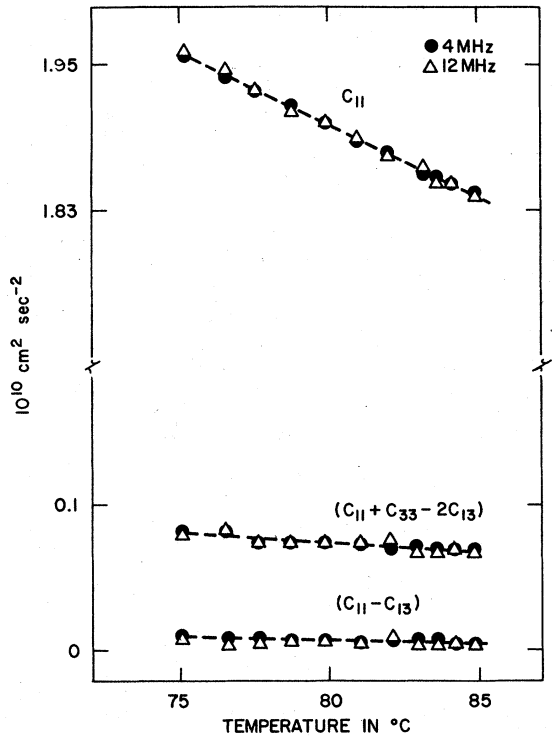

FIG. 5. Temperature dependence of elastic constants in the smectic-A phase in DDAMC at 4 and 12 MHz.

compared with that from the viscosities. Hence the former were ignored.

The velocity anisotropy data were least-squares fitted using Eq. (1′), which gives the following three physically meaningful combinations:

$$C_{11}=\left(\frac{\partial p}{\partial \rho}\right)_{s,\nabla_3 u_3}=\frac{A_0}{\rho},$$

$$C_{11}+C_{33}-2C_{13}=\frac{1}{\rho}\left(\frac{\partial \varphi_3}{\partial \nabla_3 u_3}\right)_{s,\rho}=\frac{B_0}{\rho},$$

$$C_{11}-C_{13}=\frac{1}{\rho}\left(\frac{\partial p}{\partial \nabla_3 u_3}\right)_{s,\rho}=\frac{C_0}{\rho}.$$

The temperature dependence of these combinations is shown in Fig. 5. The latter two combinations involve the derivative with respect to $\nabla_3 u_3$, which corresponds to the compression and tension of the layer spacing. These are significantly less sensitive to the temperature change in the smectic phase compared to the isotropic compressibility. This suggests that once the rigidity of the smectic layers sets in at the transition, it does not change significantly. The values of C_{11}, C_{33}, and C_{13} obtained from these combinations satisfy the condition of elastic stability, i.e., $C_{11}C_{33}>C_{13}^2$.

In conclusion, we summarize our results. A strong dispersion is observed in the attenuation of sound near the isotropic–smectic-A phase transition. The results are qualitatively consistent with critical dispersion near the transition. The anisotropy in the velocity of sound is found to be consistent with previous measurements. The anisotropy in the attenuation does not show an intermediate minimum, and is not consistent with a $\cos^4\theta$ dependence, as was proposed earlier. We have also obtained the temperature dependence of the physically meaningful combinations of elastic constants.

Finally, we would like to point out that the velocity anisotropy in the smectic-A phase in the liquid crystals studied so far (DEAB, EMBAC, and now DDAMC) is two orders of magnitude larger than that in CBOOA. This indicates, admittedly from a rather small sample, that CBOOA has an unusually weak smectic ordering. In view of the recent observation of a reentrant nematic phase[10] and particularly the recent speculations[11] that the smectic-A phase may actually be better characterized by a strictly sinusoidal density wave along the symmetry direction, it would be interesting to study smectics with considerably stronger ordering. In these materials, the older concept of smectic layers appear to be physically quite reasonable.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under Grants No. DMR-74-12486, No. DMR-76-21370, and No. DMR-76-05181, by the NSF-MRL program under grant No. DMR-76-80847 through the Northwestern Materials Research Center and the U.S. Department of Energy.

*Present address: Department of Physics, University of Rhode Island, Kingston, R.I. 02881.
†Present address: Argonne National Laboratory, Argonne, Ill. 60439.

[1]A. E. Lord, Phys. Rev. Lett. 29, 1366 (1972).
[2]K. Miyano and J. B. Ketterson, Phys. Rev. Lett. 31, 1047 (1973).
[3]K. Miyano and J. B. Ketterson, Phys. Rev. A 6, 615 (1975).
[4]Y. Liao, N. A. Clark, and P. S. Pershan, Phys. Rev. Lett. 30, 639 (1973).
[5]F. Jahnig, J. Phys. (Paris) 36, 315 (1975).
[6]H. Arnold, E. B. El-Jazairi, and H. König, Z. Phys. Chem. 234, 401 (1966).
[7]K. Miyano and J. B. Ketterson, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1979).
[8]P. G. de Gennes, J. Phys. (Paris) Colloq. 30, C4-65 (1969).
[9]L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959).
[10]P. E. Cladis, Phys. Rev. Lett. 35, 48 (1975).
[11]J. D. Litster, paper presented at the American Physical Society Meeting, Washington, D.C., March 1978 (unpublished).