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Anisotropic Ultrasound Propagation in a Smectic-C Liquid Crystal†

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We report here the results of longitudinal ultrasound propagation in a magnetically aligned smectic-C liquid crystal (*p-p'* Heptyloxyazoxy benezene). In the smectic-C phase the plane normals can lie anywhere on a cone with the axis along the magnetic field direction in which the sample was cooled. The effects of the layer normal direction and the molecular orientation within the planes on the velocity anisotropy were separated by cooling the sample into the smectic-C phase at particular orientations of the magnetic field and subsequently rotating the magnetic field. The results were analyzed on the basis of a multidomain model where the azimuthal angle of the plane normal around the field direction was averaged over.

INTRODUCTION

In recent years a considerable effort has gone into the formulation of hydrodynamic theories of liquid crystals. Martin and co-workers[1–4] have sought to treat liquid crystals as having additional internal degrees of freedom over normal liquids. Similarities have been noted[5,6] between liquid crystals and systems like superfluids, superconductors, and ferromagnets—particularly in terms of phase-transitions in those systems.

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Various different points of view have arisen in attempting constructing a suitable theory of liquid crystals. However, in the hydrodynamic limit ($\omega, \mathbf{q} \to 0$) most theories agree. Ultrasound, as a low frequency probe, is ideally suited to test the various predictions of the different theories.

Of the various crystalline mesophases, nematics have been most extensively studied.[7,8] Some ultrasonic experiments were done in smectic-A liquid crystals.[9-11] Smectic-C liquid crystals, however, have been very sparsely studied. Compared to the nematic-smectic-A phase transition, the nematic-smectic-C phase-transition has received very little attention.

In this paper we present some data on the anisotropic longitudinal ultrasound propagation in a magnetically aligned smectic-C liquid crystal. The material chosen for this experiment was *p-p'* Heptyloxyazoxybenezene (hereafter referred to as HAB) which has the following transition temperatures:

$$\text{Crystal} \xleftrightarrow{74.4^\circ\text{C}} \text{Smectic-C} \xleftrightarrow{95.9^\circ\text{C}} \text{Nematic} \xleftrightarrow{124.0^\circ\text{C}} \text{Isotropic}$$

It was shown by optical[12] and NMR[13,14] experiments that HAB has a tilt angle close to 45°. However, when it is prepared by cooling from the nematic phase in a magnetic field, a polycrystalline arrangement may result. The molecules themselves will tend to lie parallel to the field cooling direction. The normals to the smectic planes will then have a polar angle of $\sim 45^\circ$ but their azimuthal angle will be unspecified; it will be assumed that a polycrystal consisting of a near random distribution of azimuthal angles is formed on cooling. It is therefore necessary to modify the problem of sound propagation in a smectic-C liquid crystal in order to account for this polycrystalline arrangement.

In Section I we describe briefly the sound propagation problem in a smectic-C liquid crystal and derive an expression for the anisotropic velocity of sound in terms of the so-called "titled smectic-A" model.

Section II contains the experimental results for sound propagation at frequencies of 7 and 12 MHz.

SECTION I

A Theory of sound propagation

In this section we briefly describe the theory of sound propagation in a liquid crystal. For details, the reader is referred to Ref. 11; we give only the final results.

We introduce elastic stiffness constants c_{ij} which connect a six component vector formed from the strain tensor u_{ij} to a similar vector formed from the

stress tensor σ_{kl}. For a crystal with hexagonal symmetry, which includes uniaxial symmetry as well, there are five independent non-zero elements: $c_{11} = c_{22}$; $c_{13} = c_{33}$, $c_{44} = c_{55}$ and $c_{66} = \frac{1}{2}(c_{11} - c_{12})$. For the uniaxial smectic-A case there will be three independent constants: $c_{11} = c_{22} = c_{12}$, c_{13} and c_{33}. Because the smectic planes can glide freely over one another, the shear component in the 1-3 and 2-3 planes i.e., c_{44} has been put equal to zero. With the substitution $c_{ij}/\rho = C_{ij} - i\omega D_{ij}$ [where we require $\omega D_{ij} \ll C_{kl}$ in order that the mode propagates many wavelengths without excessive attenuation] we obtain the following expression for the velocity of longitudinal ultrasound in a smectic-A liquid crystal.

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

Here θ is the angle between the sound propagation direction and the 3-axis which is parallel to the layer normal for smectic-A. A corresponding equation exists for the attenuation.

B Theory

According to the theory of Martin *et al*[3] hydrodynamic modes originate from two sources:

1) conservation laws, where a generalized density is proportional to the divergence of a corresponding current,

2) the existence of broken symmetries in an ordered system.

The theory recognizes that in liquid crystals hydrodynamic modes having the second origin exist.

The theory is generalized by incorporating a proper hydrodynamic variable x_α (corresponding to the particular order associated with a given liquid crystalline symmetry) and incorporating a term of the form $\sum_\alpha \Phi_i^\alpha \mathrm{d}\nabla_i x^\alpha$ in the expression for the free energy [where Φ^α is the generalized force field conjugate to x_α].

For a smectic-A liquid crystal, the proper variable is x_3, the deformation of the smectic planes, the normal to the planes being parallel to the 3-axis. The necessary equations are then

$$\begin{aligned} \dot{\rho} + \rho\nabla_i v_i &= 0 \\ \dot{x} - v_3 &= \zeta\nabla_i\Phi_i + \xi T^{-1}\nabla_3 T \\ \dot{Q} &= \xi\nabla_3\nabla_i\Phi_i + K_\perp(\nabla_1^2 + \nabla_2^2)T + K_\parallel\nabla_3^2 T \\ \rho v_i &= -\nabla_i p + \delta_{i3}\nabla_j\Phi_j + \eta_{ijkl}\nabla_j\nabla_l\nabla_k \end{aligned} \quad (2)$$

where ζ, ξ and η_{ikjl} are the diffusion constant, diffusion-temperature gradient coupling coefficient, and viscosity tensor respectively. Neglecting all dissipative processes, the velocity of longitudinal ultra-sound is given by equation (1) with the following substitutions

$$\begin{aligned} C_{11} &= \left(\frac{\partial p}{\partial \rho}\right)_{sx} \\ C_{33} &= \left(\frac{\partial p}{\partial \rho}\right)_{sx} - \frac{2}{\rho}\left(\frac{\partial p}{\partial \nabla_3 x}\right)_{s\rho} + \frac{1}{\rho}\left(\frac{\partial \Phi_3}{\partial \nabla_3 x}\right)_{s\rho} \\ C_{13} &= \left(\frac{\partial p}{\partial \rho}\right)_{sx} - \frac{1}{\rho}\left(\frac{\partial p}{\partial \nabla_3 x}\right)_{s\rho}. \end{aligned} \tag{3}$$

The smectic-C and smectic-A cases differ in that for the former the molecules are perpendicular to the layers. The effect of this on the reactive part of the stress-tensor is of higher order in $\mathbf{q}$ than that of other variables. Therefore the real part of the elastic constant matrix of a smectic-C material is the same as a smectic-A. Thus for a monodomain sample of smectic-C, the expression for sound velocity is the same as Eq. (1) with the 3-direction along the layer normal.

The conditions for static stability (i.e. that the free energy of the system is minimal) implies for smectic-A:

$$\left(\frac{\partial p}{\partial \rho}\right)_x > 0 \quad \text{and} \quad \left(\frac{\partial T}{\partial s}\right)_\rho > 0$$

$$\left(\frac{\partial \Phi_3}{\partial \nabla_3 x}\right)_{sp} > 0$$

$$\frac{1}{\rho}\left(\frac{\partial p}{\partial \rho}\right)_{sx}\left(\frac{\partial \Phi_3}{\partial \nabla_3 x}\right)_{sp} - \left(\frac{\partial \Phi_3}{\partial \rho}\right)_{sx}^2 > 0$$

In terms of the C's the conditions are

$$C_{11} > 0$$
$$C_{33} + C_{11} - 2C_{13} > 0$$
$$C_{11}C_{33} - C_{13}^2 > 0$$

These conditions would be the same for the smectic-C case also.

C The multi-domain smectic-C model

Figure 1 shows the molecular arrangement in the smectic-C phase in a magnetic field. Here **H** is the magnetic field and **N** is the plane normal. The plane normals are assumed to be distributed evenly on a cone with an apex angle equal to 90° the axis of which is along the magnetic field.

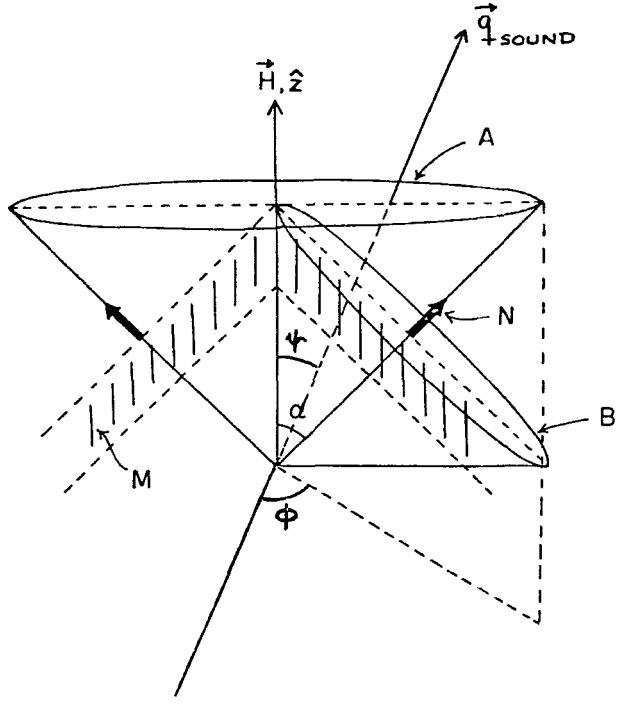

FIGURE 1 Geometry of sound propagation in a multi-domain smectic-C liquid crystal. **H** is the magnetic field, **N** is the normal to the smectic layer, M is the molecule, and $\mathbf{q}_{sound}$ is the sound wave-vector.

The magnetic field direction is chosen along the z axis; the spherical coordinates of the plane normal are specified by (α, Φ) where Φ is the azimuthal angle and α is the tilt or polar angle of $\sim 45°$. If the sound wave-vector is given by $(\psi, 0)$ where ψ is the angle between the magnetic field direction and the sound propagation direction, then the angle θ between the sound wave-vector and the plane normal is given by

$$\cos\theta = \cos\psi \cos\alpha + \sin\psi \cos\alpha \cos\Phi. \tag{4}$$

Substituting (4) in Eq. (1) for the sound velocity and averaging over the cone azimuthal angle Φ, we obtain in first order in the anisotropy

$$V^2(\psi) = \left[C_{11} + \frac{\Delta}{4} - \frac{5}{32}\frac{\beta}{C_{11}}\right] + \left(\frac{\Delta}{4} + \frac{5}{16}\frac{\beta}{C_{11}}\right)\cos^2\Psi - \frac{13}{32}\frac{\beta}{C_{11}}\cos^4\psi \tag{5}$$

where $\Delta = C_{33} - C_{11}$ and $\beta = C_{11}C_{33} - C_{13}^2$. Equation (5) was used to analyze the velocity data.

SECTION II

Experimental results

The material was obtained from Eastman Organic Chemicals, and was recrystallized from heptane. Traces of solvent change the transition temperature; therefore the recrystallized HAB was pumped on for 48 hours to remove the solvent. The material was placed in a fixed path sonic cell which is described elsewhere.[11]

A phase-sensitive technique was used for accurate measurements of the velocity change. Figure 2 shows a block-diagram of the electronics. The method is described in detail elsewhere.[15] We routinely obtained an accuracy of better than one part in a thousand for relative changes in velocity. The absolute values were obtained in the isotropic phase by the standard pulse-echo technique. The acoustic path length was 7.8 mm. The temperature of the cell was controlled electronically by a feed-back loop and the stability was better than $\pm 0.02°C$. Measurements were performed at frequencies of 7 and 12 MHz. The cell was placed between the pole-pieces of an ADL electromagnet (Bitter type), the strength of which can be varied continuously up to ~ 28 KG.

Figure 3 shows the variation of velocity and attenuation with temperature for a frequency of 7 MHz and with the field perpendicular to the propagation direction. The isotropic-nematic phase-transition showed the familiar features. The anisotropy in the nematic phase is shown in Figure 4. For a frequency of 7 MHz, the velocity anisotropy was too small to be measured. At a frequency of 12 MHz, however, the velocity anisotropy was larger, as expected.

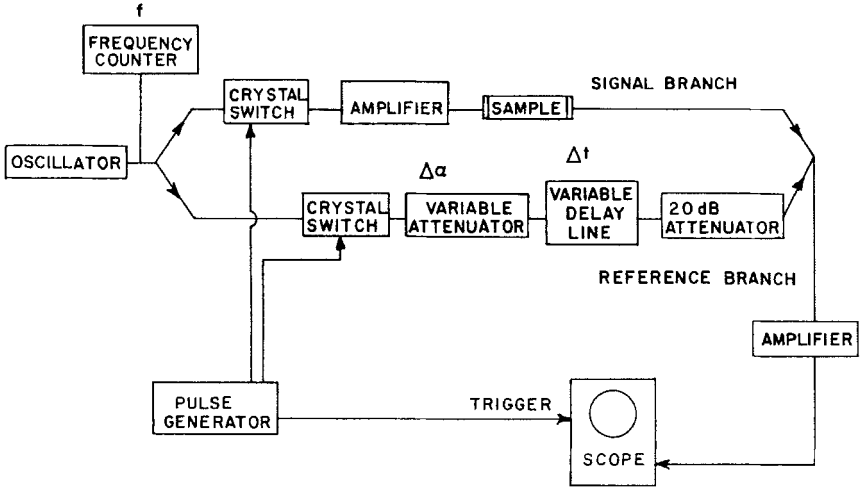

FIGURE 2 Block diagram of the electronics.

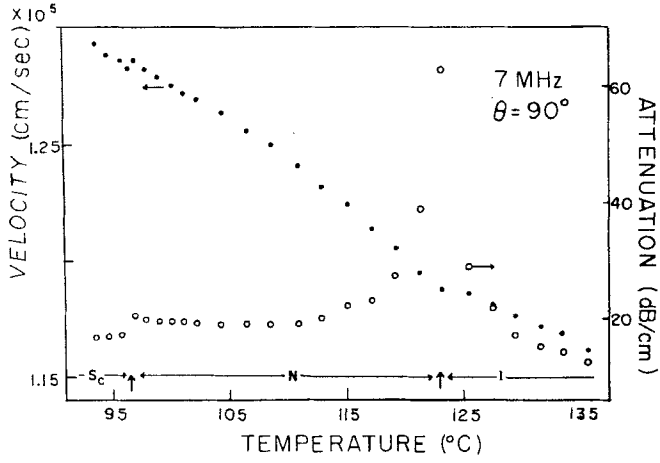

FIGURE 3 Temperature-dependence of the velocity and attenuation of sound with $\mathbf{q}_{sound}$ perpendicular to **H**.

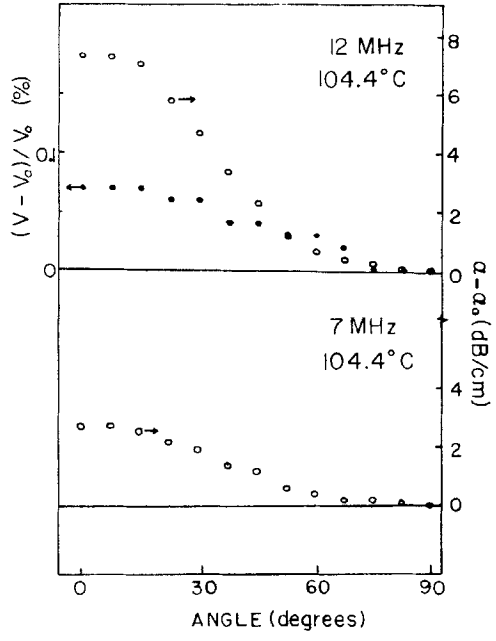

FIGURE 4 The anisotropy of the velocity and the attenuation in the nematic phase.

frequency of 12 MHz, however, the velocity anisotropy was larger, as expected. No velocity anisotropy was seen within our experimental accuracy when the magnet was rotated in the smectic-C phase. An anisotropy in the attenuation, however, was seen by rotating the field which is shown in Figure 5(b). The attentuation ansiotropy showed a finite hysteresis and its magnitude was approximately one-half of that obtained in the nematic phase.

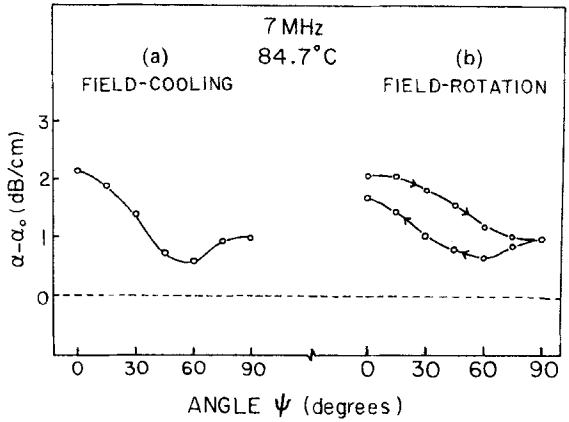

FIGURE 5 The anisotropy in the attenuation in the smectic-C phase produced by (a) field-cooling and (b) field-rotation.

The presence of an attenuation-anisotropy and the absence of a velocity anisotropy suggested that once the smectic layers had set in, the applied magnetic field was not sufficient to rotate them. In the hydrodynamic limit, the velocity is dependent only on the angle between the layer normal and the sound wave vector and thus no velocity anisotropy is expected. The molecules themselves, on the other hand, are free to follow the field-direction subject to the condition that they stay at 45° with respect to the plane-normal (see Figure 1). Part of the attenuation anisotropy is therefore due to the rearrangement of the molecules within the planes as the field is rotated. When the sample is cooled from the nematic phase at a particular orientation of the field, the individual molecules lie parallel to the direction of the field in which it is cooled. When the field is rotated subsequently, the director in each domain reorients so as to minimize the free energy. For a complex multidomain structure in a finite sample with specific boundary conditions the process of rearrangement can presumably be a slow one.

As was discussed in Section I, the smectic-C phase has the broken translation symmetry of the smectic-A phase in a direction parallel to the plane-normal. In addition, it has broken azimuthal rotational symmetry within the planes. One can separate the effects of planar structure from those of the

molecular orientation within the planes by subsequently rotating the field in the smectic-C phase.

Figure 5(a) shows the anisotropy in attenuation obtained by field cooling for a frequency of 7 MHz. Comparing this with Figure 5(b) one can see the effects of field-cooling as opposed to those of field-rotation. It was, however, pointed out by Martin *et al.* that a smectic-C liquid crystal contains 13 independent viscosity coefficients and 21 dissipative coefficients in all. Measurements of the anisotropic attenuation of longitudinal ultrasound are not sufficient to reveal the dissipative processes completely.

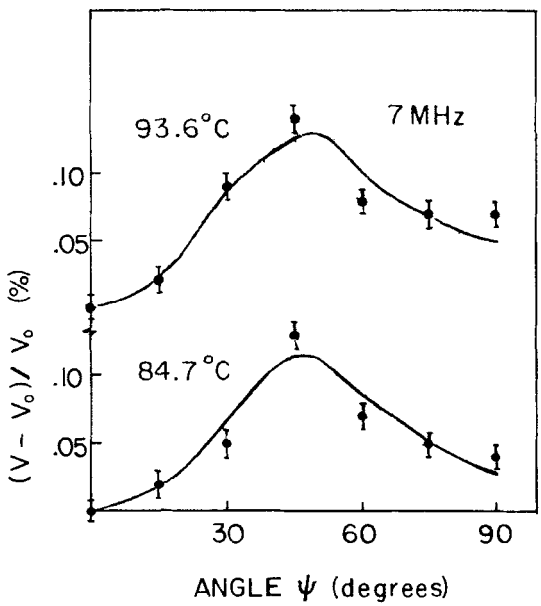

FIGURE 6 The anisotropy in the velocity in the smectic-C phase at two different temperatures produced by field-cooling. The solid lines are the least-square fit using Eq. (5).

Figure 6 shows the field-cooled velocity anisotropy in the smectic-C phase at 93.6°C and 84.7°C for a frequency of 7 MHz. The shape of the velocity anisotropy curve differs from that usually observed in smectic-C materials; however, it is not surprising in the light of the complex averaging involved in Eq. (5). Note that the magnitude of the velocity anisotropy is extremely small. Part of the smallness is due to the fact that the averaging process used to arrive at Eq. (5) has the effect of reducing the anisotropy with respect to the fully aligned monodomain sample; part may also be due to a breakdown of our assumption that the director remains parallel to the field on cooling through the N–C transition.

By least square fitting the data using Eq. (5) one gets the following numbers: At 93.6°C, $C_{11} = 1.6755 \times 10^{10}$ cm^2/sec^2; $C_{33} = 1.6799 \times 10^{10}$ cm^2/sec^2; $C_{13} = 1.6640 \times 10^{10}$ cm^2/sec^2 and at 84.7°C, $C_{11} = 1.7369 \times 10^{10}$ cm^2/sec^2; $C_{33} = 1.7426 \times 10^{10}$ cm^2/sec^2; $C_{13} = 1.7250 \times 10^{10}$ cm^2/sec^2.
Note that these values satisfy the stability conditions mentioned in section I. Two combinations of these elastic constants, namely,

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

and

$$(C_{11} + C_{33} - 2C_{13}) = \frac{1}{\rho}\left(\frac{\partial \Phi_3}{\partial \nabla_3 x}\right)_{s\rho}$$

refer to derivatives of quantities with respect to the gradient of the deformation of the smectic layers. The weak temperature dependence of these two combinations compared to $C_{11} = (\partial p/\partial \rho)_{sx}$ indicates that once the smectic layers set in, the tilt angle does not change significantly with temperature. This agrees with the observations in NMR experiments.[13,14] The magnitude of the velocity anisotropy in the fully-aligned monodomain smectic-C, as calculated from the values of the elastic constants, is comparable with that of CBOOA which is small compared with other smectics.[11]

Figure 7 shows the anisotropy in the velocity and the attenuation at 84.7°C produced by field-cooling for a frequency of 12 MHz. The magnitude

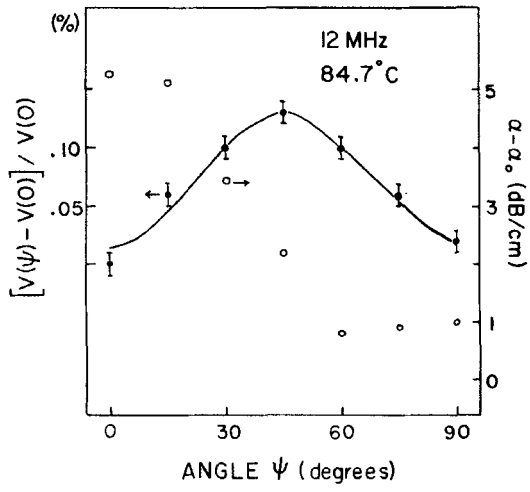

FIGURE 7 The anisotropy in the velocity and attenuation in the smectic-C phase at a frequency of 12 MHz. The solid line is the least-squares fit using Eq. (5).

and the shape of the velocity anisotropy curve do not differ significantly from those for 7 MHz. Comparing this velocity-anisotropy with the one observed in the nematic phase we identify the two sources of velocity anisotropy in liquid crystals. One is the dispersion, as seen in nematics, arising from the presence of one or more slow internal relaxation process connected to the average molecular orientation, i.e., the director. This anisotropy, as seen in our data, decreases with frequency and vanishes in the hydrodynamic limit. The other one is truly hydrodynamic in character, connected to the appearance of smectic planes. From our data in the smectic-C phase, this anisotropy seems to be frequency independent within the range used and appears to be finite in the hydrodynamic limit.

The nematic–smectic-C phase-transition showed very striking features. A distinct velocity minimum was seen at the transition, but no maximum in attenuation was observed. The sharp decrease in attenuation at the transition could be due to a sudden decrease in diffusivity on the appearance of smectic layers. A detailed study of this phase transition would be desirable.

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