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Mechanical Shear of Layers in Smectic-A and Smectic-B Liquid Crystal

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The force transmitted through the layers of smectic-A and smectic-B phases of butyloxy-benzylidene-octylanine (4O.8) have been measured at frequencies between 1 and 10 000 Hz, in the presence of an ac shear parallel to the layers. It is found that the smectic-A behaves as a viscous fluid. The smectic-B shows an elastic response, with a shear modulus $C_{44} \sim 10^6$ cgs units. The low-frequency plastic behavior and the high-frequency dispersion which is related to internal friction are discussed.

Smectic liquid crystals are layered systems. Lower symmetry smectic phases, like the S_B, show a regular molecular ordering inside the layers, although higher symmetry ones, like the S_A, are considered as liquidlike inside the layers. Contrary to three-dimensional (3D) crystals, the smectic phases are defined through the ability of their layers to glide easily on top of each other. An important question is: Should smectic-B liquid crystals be considered true liquid crystals or 3D solids? Different models[1] have been proposed for the B phase, considered for instance[2] as a piling of two-dimensional crystals, with possible hexatic[3] order. Recent x-ray experiments on thin films[4] or in bulk[5] smectic-B samples demonstrate that on a 1 μm (or more) scale, the smectic-B appears as a 3D solid. Closer to the above accepted definition, mechanical experiments with use of ultrasonic techniques have been designed to observe the shear of the smectic layers on top of each other. The results indicated the existence of an elastic response to the shear, with an elastic modulus in the range of 10^8 cgs[6,7] or lower than 10^7 cgs.[8] However, all these results were obtained in the megahertz frequency range, too high to give definite conclusions in the presence of relaxation processes. We present here the first mechanical experiment in the very low-frequency range (down to 1 Hz), to test if the response of a smectic-B liquid crystal to a shear

parallel to the layers is elastic or viscous.

Our experimental setup is very similar to the one already described[9] with the only difference being that we use shear strains and stresses, instead of compression. The sample is butyloxy-benzylidene-octylanine (4O.8) which undergoes the following transitions:

$$C \xrightarrow{33\,°C} S_B \xrightarrow{49.5\,°C} S_A \xrightarrow{63.7\,°C} N \xrightarrow{79\,°C} I.$$

The sample is oriented homeotropically with use of a silane surface treatment of the two boundary glass plates (see inset of Fig. 1). The glass plates are cemented to a piezoelectric ceramic which is in turn cemented on a rigid holder, placed inside an oven and regulated to $\pm 0.05\,°C$. The ceramic is so polarized as to create a displacement δ parallel to the layers, when applying an electric field as shown in Fig. 1. Optical inspection is possible for the central region. The parallelism of the two glass plates can be trimmed with three adjustable spacers and screws, to within $\pm 10^{-4}$ rad. The thickness can be adjusted from 30 to 200 μm. The sample available surface is a 5×12 mm² rectangle. The upper ceramic is driven by an ac voltage $V_i \times \exp(i\omega t)$ (in the range of 10–100 V, from 0.1 to 10 kHz) to induce an ac shear strain parallel to the layers. The lower ceramic, submitted to the transmitted shear stress, gives an output voltage $V_0 \exp i(\omega t + \varphi)$ (in the range of 100–1000 μV). The
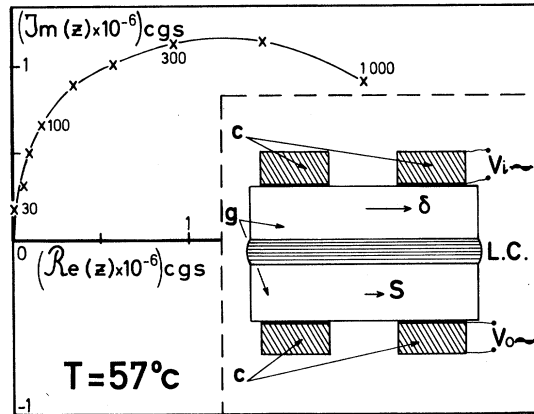
FIG. 1. Complex shear modulus Z in polar coordinates, for the S_A phase of 4O.8; the parameter on the curve is the frequency (Hz). The solid line is only a guide for the eye. Inset, schematic drawing of the sample geometry: c, piezoelectric ceramics; g, glass plates; L.C., liquid crystal; v_i, input voltage inducing the shear displacements δ; v_0, output voltage due to the transmitted force S.

FIG. 2. Complex shear modulus Z of the S_B phase of 4O.8. Details as in Fig. 1.

principle of the experiment is to measure (V_0/V_i) $\times \exp(i\varphi)$, proportional to the complex shear modulus Z of the liquid crystal. V_0 is amplified with a dc low-noise, high–input-impedance amplifier; with the 700 pF ceramic capacity, the resulting input time constant is ~80 sec, large enough not to introduce any dephasing in the lower-frequency range. V_0 is measured by a digital voltmeter and the phase φ is deduced from a recording of V_0 on a storage oscilloscope, with an accuracy of $\pm 2°$. To calculate Z, we use the ceramics calibration, given by the maker; the induced shear displacement δ is 4.0 Å/V and the detector sensitivity is 3.5 μV/dyn of the total stress force S. We have verified, using a thin steel spring squeezed between the plates, instead of the sample, that the response of our setup is purely elastic in the chosen frequency range. At higher frequencies, one starts observing mechanical resonances.

We introduce the sample in the nematic phase to fill all the available volume. The thickness of the cell, d, is equal to 95 μm. We cool it down to the S_A phase at 57 °C. The optical observation through a polarizing microscope confirms that the sample is a S_A single crystal. Our shear modulus results are plotted in Fig. 1 with polar coordinates. The parameter characterizing each point is the frequency $\nu = \omega/2\pi$ Hz. When ν decreases, down to zero, one observes that Z becomes purely imaginary and proportional to ν.
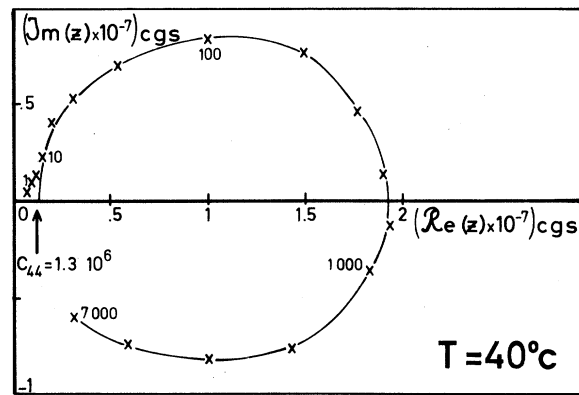
This indicates that the transmitted stresses are purely viscous, as expected for the A phase. From the data, we can deduce an apparent viscosity $\eta \sim 1.1 \times 10^3$ cgs units. For a normal viscous fluid, Z becomes real at a frequency ν_0 comparable to the damping frequency of vortices of wave vector π/d, i.e. $(1/2\pi)\eta(\pi/d)^2/\rho$, where ρ is the specific mass. In our experiment, ν_0 is of the order of 5 kHz, resulting in a viscosity of the order of 0.3 cgs unit comparable to the one expected from the simple layer friction. Clearly our smectic A does not behave as a simple viscous fluid, although transmitting only friction forces.

We now cool the sample down to the smectic-B phase at 40 °C. We can observe small defects in the form of small intercrossed dashed lines. We leave the sample undisturbed for two days for annealing. We do not see any more defects. We then measure the complex shear modulus (Fig. 2) as a function of ν. Here we also find a large frequency dispersion. Between 10 Hz and 7 kHz, the graph of Z is almost a circle. Extrapolating this curve down to zero frequency, we find within our experimental accuracy a real value corresponding to $\mathfrak{R}_e(Z) \equiv C_{44} = 1.2 \times 10^6$ cgs units. The uncertainty of the extrapolation procedure allows an error bar of $\pm 0.3 \times 10^6$ cgs units. However, our data for frequencies lower than 10 Hz show a clear departure from this extrapolation. For frequencies on the order of 0.1 Hz, Z goes to zero in an apparent viscous manner. Our present accuracy is not sufficient to analyze this behavior in great detail. It is interesting to compare the dispersion of Z in the A,B phases. Except for the real value C_{44} when $\nu \to 0$ in the B phase, the two graphs of

Z are similar, with scaling factors of 0.1 for the amplitudes and 10 for frequencies to go from the B to the A graphs. We discuss further a possible model for this viscoelastic relaxation.

The reproducibility of the experiment is good if we always take care to anneal the sample. The smallest value obtained for C_{44}, for the same sample thickness d, is $C_{44} = 0.5 \times 10^6$ cgs units. C_{44} depends thus more on the sample quality than on the questionable extrapolation procedure. A measurement before annealing gives in the B phases a similar diagram for Z, with a scaling factor of about an order of magnitude larger. Annealing decreases then the mechanical stresses transmitted through the sample. In the A phase, no significant difference appears before or after annealing. To test the physical origin of the observed increase of Z which is apparently correlated to optically visible defects, we have reproduced the experiment on a sample in which the plates were tilted at an angle of 5×10^{-3} rad. We believe them to have introduced mobile edge dislocations as previously observed.[10] After the same annealing procedure, we have found with the tilted-plates sample the same Z diagram as on a parallel-plate sample before annealing, i.e., an upscaling factor of about 10 for the amplitudes.

We have studied the thickness dependence of the mechanical response on thinner samples of 35 and 40 μm. We observe that the large quasi-circular dispersion of Z in thick samples flattens down. It is now difficult to extrapolate a zero-frequency–limit C_{44}, since the high-frequency dispersion is not as well separated from the low-frequency one ($\nu <$ a few hertz).

Our problem is to understand the large and similar dispersions of Z in the B and A phases. We must explain this kind of resonance by the motion of defects which exist in the two phases. The simplest idea is to admit that pairs of edge dislocations of smectic layers, when submitted to a shear, induce an ensemble rotation of the layers, i.e., couple the shear to the layer compression. The resulting normal forces cannot be observed on our experimental setup. We can, however, estimate the resonance frequency of this internal friction mechanism by the following simple argument. Let us call $b = N\lambda$ the Burgers vector of the edge dislocation, λ the layer thickness, a the distance across the layers separating the two dislocations, x_0 the equilibrium distance between dislocations along the layers, and B and $K = B\lambda^2$ the compression and curvature elastic modulus. Balancing the compression free energy $B(b/a)^2 x_0 d$

(per unit length of dislocation), with the curvature energy associated with the layer bend $(K/x_0^2)(b/x_0)^2 x_0 a$, one finds an equilibrium distance $x_0^2 \sim \lambda(ad)^{1/2}$. The resonance frequency ω is defined by the balance between inertia and elastic torques on the volume distorted around the dislocation pair. This results in $\omega \sim (B/\rho)^{1/2} N\lambda^{1/2}/(ad)^{3/4}$, where $N = b/\lambda$ is the number of layers associated with b. Assuming $a \sim d$, a second sound velocity $(B/\rho)^{1/2} \sim 10^4$, $N \sim 1$, we find ω in the kilohertz range, as observed.

In conclusion, we have measured the stress-strain relationship for shear parallel to the layers in the smectic-A and -B phases of 4O.8. The smectic A behaves as a viscous fluid, but with a very large friction and frequency dispersion. The B phase shows, for $\nu \sim$ a few hertz, an elastic response with a shear modulus in the range of 10^6 cgs units or lower. This value is two orders of amplitude lower than the one observed by ultrasonic techniques[6,7] and by neutron measurements[11]; it compares with the value estimated in Ref. 8 also with use of an ultrasonic technique. At lower frequencies, we observe a plastic relaxation, probably due to individual mobile edge dislocations. The similar relaxation at high frequencies observed in the A and B phases could be attributed to internal resonances of other defects, for instance pairs of edge dislocations, which would couple the shear to layer compression. This later mechanism could, for high shears, generate layer kinks and explain the observed occurring of focal conics.[12] From this mechanical experiment, we draw the conclusion that the smectic-B phase of 4O.8 is a 3D crystal exhibiting a low-frequency, plastic mechanical response.

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Inelastic Electron Scattering by a Collective Vibrational Mode of Adsorbed CO

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The C–O stretching vibrational mode of the Cu(100) + $c(2 \times 2)$CO system has been examined by angle-dependent inelastic electron scattering. The mode is collective and its dispersion is found to be dominated by dipole-dipole interactions among the adsorbed molecules. The vibrational excitation cross section is satisfactorily described by dipole scattering theory.

One important feature of high-resolution electron-energy-loss spectroscopy (EELS) as a tool to study surface vibrations is the potential ability to measure normal-mode dispersion relations for ordered structures of atomic and molecular adsorbates. In this Letter we will explore this ability in order to investigate the collective behavior of vibrationally excited CO molecules in the $c(2 \times 2)$CO structure on Cu(100). Infrared spectroscopy studies of isotopic mixtures of adsorbed CO have revealed a composition-induced "coupling shift"[1-4] of about 40 cm^{-1} (~5 meV) for the C–O stretching vibrational mode. Dipole-dipole interaction between the vibrating molecules has been considered as a possible cause of this frequency shift.[1,2,4-6] In principle the strength as well as the nature of the interaction should be revealed in a straight-forward manner by measuring the phonon dispersion relation in an inelastic-electron-scattering experiment. In practice this is still a quite difficult experiment since the frequency shifts are small and the experiments have to be performed at optimum resolution of present instruments (~4 meV).

The spectroscopic measurements reported here were carried out with use of a new high-resolution electron spectrometer consisting of a monochromator and an analyzer, both of cylindrical-mirror design. The analyzer and the specimen can be rotated such that the polar angles of collection θ (measured with respect to the specularly scattered electron beam, positive towards the surface normal) and incidence α (measured with respect to the surface normal) can be varied independently. The experimental data (shown in Figs. 1–3) were obtained for an energy $E_0 = 3$ eV (relative to the vacuum level) and angle $\alpha = 65°$ of the incident electron beam. The spectrometer was operated at an energy resolution of 4.5 meV which is only slightly poorer than the designed resolution 4 meV at the employed pass energy 0.4 eV. The angular acceptance of the analyzer was a cone of half angle 1.0°. The scattering plane containing the incident and the scattered beams was defined by the surface normal and the [100] crystal direction in the surface plane.

Figure 1 shows an EEL spectrum for the Cu(100) + $c(2 \times 2)$CO system measured in the specular direction, i.e., $\theta = 0°$, at 80 K specimen temperature. The experimental procedure concerning the specimen cleaning and the CO adsorption has been described previously.[7] The two loss peaks at 42.5 and 259 meV correspond to the excitation of the fundamental Cu-CO and C-O