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Temperature behavior of ferroelectric liquid-crystal thin films: A classical XY system

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Freely suspended films of the material DOBAMBC (*p*-decyloxybenzylidene-*p'*-amino 2-methyl butyl cinnamate), which has a layered ferroelectric liquid-crystalline phase (the chiral smectic C phase), are created across a rectangular hole in a glass microscope cover slide. The films are quantized in thickness, being one, two, three, or more monomolecular (smectic) layers thick. In the tilted smectic C phase, the films exhibit a net spontaneous electric polarization parallel to the smectic layers and in the plane of the film. A unique determination of the polarization, the Frank elastic constants, and the associated viscosities is made by comparing intensities of quasielastic Rayleigh-scattered light from orientational fluctuations of the molecular director in the presence and absence of an applied electric field. Measurements are performed on films three smectic layers thick as a function of temperature near the C-A transition. The relevence of our results to the theories of the classical two-dimensional XY transition will be discussed.

INTRODUCTION

During the past decade there has been considerable interest in two-dimensional phase transitions, most notably in superfluid and magnetic systems.[1-5] Seeing the eventual possibility of studying such two-dimensional phase transitions in a freely suspended liquid-crystal film, Young *et al.*[6] performed a light-scattering study of freely suspended ferroelectric smectic-C films. The films were formed over a small hole in a microscope cover slide and were quantized in thickness, being an integral number of monomolecular (smectic) layers. A weak electric field, which couples to the molecular dipoles, was then applied and resulted in a uniform average director orientation $\hat{n}_0$. Taking advantage of the large optical birefringence of the material, Young *et al.* performed time correlation measurements of thermal fluctuations of the director orientation. Thus they were able to determine K_b/P_0^2, K_s/η_s, and K_b/η_b, in the material 80.5*, where K_s (K_b) is the splay (bend) elastic constant, η_s (η_b) the corresponding viscous coefficient, and P_0 the electric dipole moment per unit area of the film.

In the Young experiment the projection into the film's plane of the molecular director $\hat{n}$ serves as the analog to magnetic spin in the XY model proposed by Kosterlitz and Thouless.[1,2] For sufficiently thin films, the energy of a director vortex increases logarithmically with the area of the film. Thus, one would expect director vortices to be bound in pairs at low temperatures. As the temperature is raised through T_c, entropy dominates and the vortex pairs can decouple. Kosterlitz and Nelson[7] have predicted that this transition occurs at a temperature $T_c = \pi K^*/2k_B$, where K^* is an appropriate elastic constant and k_B is Boltzmann's constant. At T_c, where unpaired vortices can exist, K^* is expected to fall discontinuously to zero and the film would appear to be in the uniaxial smectic-A phase. Thus, *absolute* measurements of the two-dimensional elastic constants K_s and K_b as a function of temperature would be of extreme interest in light of the Nelson-Kosterlitz prediction.

In an earlier paper[8] we reported on a refinement of the Young experiment, allowing us to make absolute measurements of the five parameters η_s, η_b, K_s, K_b, and P_0. Noting that a *strong* applied electric field couples to the molecular polarization and quenches the director fluctuations, we compared intensities of quasielastic Rayleigh-scattered light from director fluctuations in the presence and absence of a strong field. Ratios of these intensities are independent of geometric and cross sectional effects. By measuring these ratios as a function of scattering wave vector, we were able to determine absolutely the five parameters.

The first measurements[8] were made as a function of film thickness h at a fixed temperature, and several interesting features were noted. The effective dipole moment was measured. After dividing this result by film thickness and molecular tilt angle θ_T, the bulk polarization per radian of tilt was found to be 37 ± 4 esu/cm^2, comparing quite nicely with previously reported bulk mea-

surements of 33 (Ref. 9) and 36 (Ref. 10) esu/cm^2 performed on the same material DOBAMBC (*p*-decyloxybenzylidene-*p'*-amino-2-methylbutyl-cinnamate). Furthermore, we measured the two-dimensional elastic constants $K_{s,b}$. When scaled by the molecular tilt angle ($K_{s,b}/\sin^2\theta_T$), one expects the elasticity to be a linear function of h. It was noted, however, that the elasticity versus h is not linear, but rather exhibits a behavior which can be accounted for by a nonlocal elastic theory. Since the film thicknesses are of the same order as the correlation length, molecular interactions are abruptly cut off at the surfaces of the film. Thus $K_{s,b}/\sin^2\theta_T$ is reduced, especially in thinner films, from values predicted by linear behavior in h. The range of interactions was found to be about two smectic layers for T well into the smectic-C phase. Analogous results were found for viscosities.

Finally, we noted that for all film thicknesses, $K_s \gg K_b$. In bulk the chiral smectic-C phase exhibits C_2 symmetry. Thus, if the molecules were to contain a longitudinal dipole moment $\vec{P}_m$, symmetry requires that $\langle \vec{P}_m \rangle = 0$ in the bulk. However, at the surfaces of a film, the molecules may preferentially orient such that the longitudinal molecular dipoles point either inward or outward, resulting in a nonzero value of $\langle \vec{P}_m \rangle$ at one surface and a value $-\langle \vec{P}_m \rangle$ at the other surface. It was shown that splay-type fluctuations can thus create a periodic electric field inside the film. The energy associated with the field is proportional to $q_1^2 h \langle \vec{P}_m \rangle^2 \sin^2\theta_T$, which is of the same form as the Frank elastic energy of a splay wave. Thus, the effective splay elastic constant is renormalized upward to account for the additional dipolar energy. It was also shown that K_b is unaffected by this preferential ordering. As further evidence, we note that generally $K_s \simeq 7K_b$ for films two smectic layers or thicker. For a one layer film, in which the above preferential ordering is meaningless (there is no "inward" or "outward" direction), $K_s = 4.3K_b$. In this last case there can be no contribution from the longitudinal dipoles.

Motivated by the Nelson-Kosterlitz predictions and our earlier experiments, we now report on measurements performed on a three-layer film as a function of temperature. We observe anomalous behavior in the polarization at high temperatures. Finally, we measure the elastic constants both far below and near the phase transition, noting evidence for XY-like behavior.

THEORY

Freely suspended smectic films are created by drawing the material DOBAMBC over a hole in a glass microscope cover slide. The high energy associated with the edge of a smectic layer constrains the quantized layers of the film to be parallel to the hole, i.e., in the plane of the film. In the higher-temperature A phase the director $\hat{n}$ lies locally perpendicular to the film; however, in the lower temperature C phase the director tilts by some angle θ_T from the normal, where θ_T is a function of both the number of smectic layers N and temperature T. [Pindak *et al.* have determined $\theta_T(N,T)$ for DOBAMBC using ellipsometry techniques.[11]] As a result, for a given θ_T, one can define the system by specifying $\vec{n}_p$, which is the projection of the vector $\hat{n}$ lying in the plane of the film. For fixed θ_T, $\vec{n}_p$ has only one degree of freedom, an azimuthal rotation by an angle ϕ about the normal to the film.

It has been shown by Meyer *et al.*,[12] that a smectic-C system composed of a chiral molecules exhibits a spontaneous electric dipole moment, to lowest order proportional to θ_T,[13] which lies perpendicular to the long molecular axis ($\hat{n}$) and parallel to the smectic layers. A small dc electric field ($E_a \sim 4$ V/cm) applied parallel to and in the plane of the film locally couples to the electric dipoles and thereby orients them such that $\vec{P}_0 \| \vec{E}_a$, minimizing $-\vec{P}_0 \cdot \vec{E}_a$. As a result an average director orientation $\hat{n}_0$, and hence $\langle \vec{n}_p \rangle$, is established, such that $\langle \vec{n}_p \rangle \perp \vec{E}_a$. P_0 is the net dipole moment per unit area of the aligned film.

Thermal fluctuations of the tilt angle θ_T decrease rapidly below T_{CA},[14] and are disregarded. On the other hand, azimuthal fluctuations of $\vec{n}_p$ by an angle ϕ about the normal to the layers are significant and result in scattering of light.[6] The free energy due to azimuthal orientational fluctuations is given by[6]

$$F = \tfrac{1}{2}\int d^2r \left[K_b\left(\frac{\partial\phi}{\partial r_\parallel}\right)^2 + K_s\left(\frac{\partial\phi}{\partial r_\perp}\right)^2 + P_0 E \phi^2\right] + \tfrac{1}{2}\int\int d^3r\, d^3r' \frac{(\nabla\cdot\vec{P}_0)(\nabla'\cdot\vec{P}_0)}{|\vec{r}-\vec{r}'|}. \quad (1)$$

The first two terms are the two-dimensional analogs to the Frank elastic terms[15]; $r_\parallel$ and $r_\perp$ are coordinates which run, respectively, parallel and perpendicular to $\langle n_p \rangle$ (see Fig. 1); and K_b and K_s are their respective elastic constants (in units of energy). In terms of the usual bulk elastic constants, K_b and K_s can be written

$$K_s = h\kappa_{11}\sin^2\theta_T, \qquad K_b = h\sin^2\theta_T[\kappa_{22}\cos^2\theta_T + \kappa_{33}\sin^2\theta_T], \quad (2)$$

where h is the film thickness. (It should be pointed out that $K_{s,b}$ are no more nor less fundamental than the three-dimensional Frank constants once a given tilt angle θ_T is selected. For a given θ_T

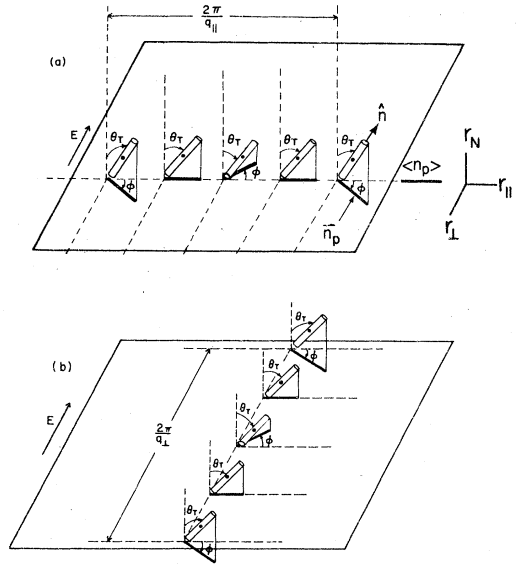

FIG. 1. Schematic representation of molecules for one layer of the tilted chiral C phase. $\vec{n}_p$ is the projection of the molecule into the layer, and ϕ is the azimuthal fluctuation of $\vec{n}_p$ about $\langle n_p \rangle$. For the bend mode (a), the wave vector $q_{\parallel}$ is parallel to $\langle n_p \rangle$; for the splay mode (b), the wave vector is perpendicular to $\langle n_p \rangle$.

and N, $K_{s,b}$ are constants of the system.) The third term, arising from an external electric field E coupling to the dipole moments, is just the first nonstatic term in the Fourier expansion of $-P_0 E\cos\phi$. Finally, the fourth term is the energy associated with an electric field arising from a spontaneous space charge when the director, and therefore $\vec{P}_0$, undergoes local orientational fluctuations.

Equation (1) is Fourier transformed and the equipartition theorem is applied. The result is

$$\langle \phi_q^2 \rangle \propto \frac{k_B T}{K_b q_{\parallel}^2 + K_s q_{\perp}^2 + 2\pi P_0^2 |q_{\parallel}| + P_0 E}. \tag{3}$$

To lowest order in ϕ_q the space-charge effect is seen only in the parallel ("bend") mode.

In performing a light-scattering experiment, the scattered intensity $I_s \propto |\vec{f} \cdot \delta\vec{\epsilon}(\vec{q}) \cdot \vec{i}|^2$, where $\vec{f}$ and $\vec{i}$ are the scattered and incident electric field vectors, and $\delta\vec{\epsilon}(\vec{q})$ is the $\vec{q}$th Fourier component of the dielectric tensor resulting from fluctuations in $\vec{n}_p$. Making the approximation that the smectic C is a tilted uniaxial system[16,17] (rather than biaxial), it can be shown that the off-diagonal elements of $\delta\vec{\epsilon}(\vec{q})$ are proportional to ϕ_q and modulated by a factor accounting for the finite thickness of the film. Thus, to lowest order in ϕ_q, the scattered intensity is depolarized and

$$I_s \propto |\phi_q|^2 \sin^2 \tfrac{1}{2} q_N h, \tag{4}$$

where q_N is the component of $\vec{q}$ normal to the film and h is the film thickness. Thus, $\langle I_s \rangle$ is proportional to $\langle \phi_q^2 \rangle$ in Eq. (3). The scattering geometry can be arranged such that only one mode is probed at a time. Setting $q_{\perp} = 0$, the average scattered intensity $I_{off}^{\parallel}(q_{\parallel})$ is measured in the presence of a small aligning field $E = E_a$. A large field E_0 is then added to E_a, quenching fluctuations (since P_0 couples strongly to $E_a + E_0$). Defining $I_{on}^{\parallel}(q_{\parallel})$ as the average intensity in the presence of the strong field, the quantity $L_{\parallel}(q_{\parallel})$ is defined such that

$$L_{\parallel}(q_{\parallel}) = \frac{E_0}{q_{\parallel}} \left(\frac{I_{on}^{\parallel}(q_{\parallel})}{I_{off}^{\parallel}(q_{\parallel}) - I_{on}^{\parallel}(q_{\parallel})} - \frac{E_a}{E_0} \right) = \frac{K_b}{P_0} q_{\parallel} + 2\pi P_0, \tag{5}$$

where $\langle \phi_q^2 \rangle$ from Eq. (3) has been substituted into Eq. (4). [Note that by taking the ratio of intensities at fixed $\vec{q}$, $L_{\parallel}(q_{\parallel})$ is independent of q_N.] Thus, by measuring $L_{\parallel}(q_{\parallel})$ at a given film thickness h and tilt angle θ_T, one can retrieve the absolute polarization P_0 and elastic constant K_b.

Rearranging the light-scattering geometry such that $q_{\parallel} = 0$ and probing $q_{\perp}$, one can write

$$L_{\perp}(q_{\perp}) = \frac{E_0}{q_{\perp}} \left(\frac{I_{on}^{\perp}(q_{\perp})}{I_{off}^{\perp}(q_{\perp}) - I_{on}^{\perp}(q_{\perp})} - \frac{E_a}{E_0} \right) = \frac{K_s}{P_0} q_{\perp}. \tag{6}$$

Having already obtained P_0, one now retrieves K_s.

The dynamic behavior of the fluctuations can also be studied. The modes for this system are diffusive; one can therefore write

$$\langle \phi_{q_{\parallel}}(0) \phi_{q_{\parallel}}(t) \rangle = \langle \phi_{q_{\parallel}}^2 \rangle \exp[-\Gamma_{\parallel}(q_{\parallel}) t],$$

where $\Gamma_{\parallel}(q_{\parallel})$, a measurable quantity, can be expressed in terms of an orientational viscosity η_b and the constants K_b and P_0:

$$\Gamma_{\parallel} = (K_b q_{\parallel}^2 + 2\pi P_0^2 |q_{\parallel}| + P_0 E)/\eta_b. \tag{7}$$

A similar expression for the perpendicular mode can also be written, where

$$\Gamma_{\perp} = (K_s q_{\perp}^2 + P_0 E)/\eta_s. \tag{8}$$

If coupling to other modes (particularly the diffusive shear modes) is weak, η_s and η_b are nearly identical and can be taken as η, a constant.

Instead of performing an autocorrelation to determine η, it can be shown that the intensity of scattered light, upon application of the electric field $E_0 (E_0 \gg E_a)$, decays from I_{off} to I_{on} in time $\tau = [2\Gamma]^{-1}$. By measuring τ as a function of $\vec{q}$ (for each of the two modes), one can write

$$\eta_b = 2\tau(q_{\parallel})(K_b q_{\parallel}^2 + 2\pi P_0^2 |q_{\parallel}| + P_0 E), \qquad \eta_s = 2\tau(q_{\perp})(K_s q_{\perp}^2 + P_0 E). \tag{9}$$

Thus, by measuring I_{off}, I_{on}, and the associated decay time, one can determine all the phenomenological parameters necessary to characterize the space-time behavior of the films.

EXPERIMENT

The film is drawn over a 3 mm × 9 mm hole in a glass microscope cover slide called the holder (Fig. 2). A second microscope cover slide tilted about 20° with respect to the holder and with one edge against it, is first drawn over the DOBAMBC, then over the open hole; a film of N smectic layers is thus created. It can be shown that the intensity of laser light specularly reflected from the film is approximately proportional to N^2.[18] Thus the specular reflection permits a fast and accurate measurement of film thicknesses up to approximately $N=12$.

Electric fields are applied by means of silver electrodes which are vapor deposited along the two long edges of the rectangular hole. The deposition is performed on the surface of the glass opposite the spreader. Since the thickness of the glass holder (~150 μm) is much less than the width of the hole (~3 mm) (and hence the separation of the electrodes), the electrode-film configuration is, for calculational purposes, taken to be a single plane. The electric field E as a function of applied voltage V has been calculated at all points in the plane of the film by conformal mapping techniques. Although the field is spatially inhomogeneous, it is nevertheless uniform to better than 1.5% over the central 400 μm of the film (the diameter of the laser beam used as the probe).

A small electric field E_a (~4 V/cm) is applied along the $r_\perp$ axis to align the molecular dipole moments (Fig. 1) and thereby creates a monodomain sample such that $\langle \vec{n}_p \rangle \perp \vec{E}_a$. To observe the film a small microscope equipped with a polarizer is inserted into the side of the oven and pointed normal to the film. Immediately after creating the film, numerous domain walls, some being closed loops and others ending in disclinations, are detected. Over time (several minutes) the walls heal away (either by the loops collapsing or by the movement of the disclinations), resulting in a homogeneous sample. The quality of alignment is determined by means of the polarizer mounted inside the microscope, such that the scattered light is nearly extinguished when the polarizer is crossed with respect to the polarization of the incident laser light. In the aligned film $\langle \vec{n}_p \rangle \| \hat{r}_{\|}$; azimuthal fluctuations by angle ϕ result in $\delta \vec{n}_p = \hat{r}_\perp \phi \sin\theta_T$.

A Spectra-Physics Model 165 argon-ion laser, operating at 5145 Å, is used as the incident light source. The polarization of the incident beam is along the $\hat{r}_\perp$ axis and typical powers are about 200 mW, although higher powers are occasionally used to increase the scattered signal. A lens of focal length 600 mm is placed approximately a focal length in front of the film to focus the beam to a spot of 400 μm in diameter. Although this lens thus introduces a spread in the incident wave vector, the resulting spread is not significant.

The film is rotated 45° with respect to the incident beam (see Fig. 3). Since $\hat{n}_0$, and therefore $\langle \hat{n}_p \rangle$, lie in the $\hat{r}_N$-$\hat{r}_{\|}$ plane, the incident beam has ordinary polarization. Azimuthal fluctuations of the molecules out of the $\hat{r}_N$-$\hat{r}_{\|}$ plane thus result in a depolarized scattering intensity proportional to Eq. (4).

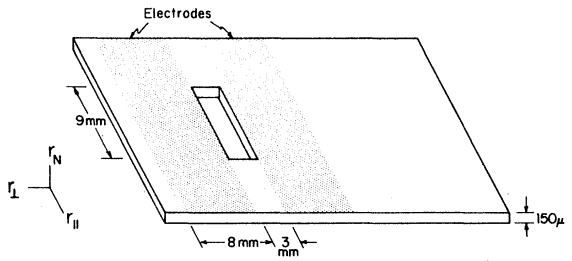

FIG. 2. Sample holder. A hole is cut into a glass microscope cover slide and silver electrodes are deposited on one surface of the glass.

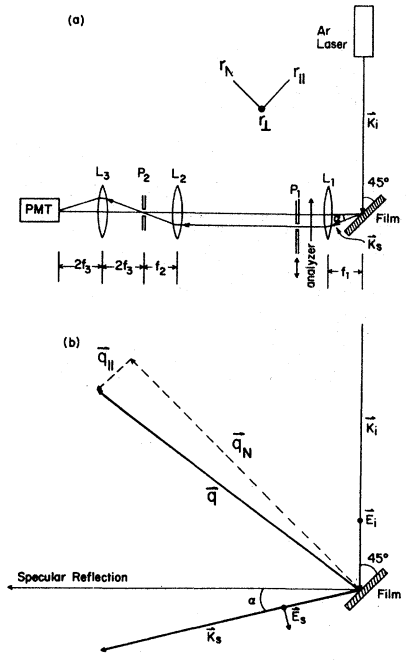

FIG. 3. Optical arrangement. (a) Physical setup, and (b) determination of the scattering vector. Angle α, which is set by positioning pinhole P_1 (a), fixes $\vec{q}$. Note that q_N does not appear in Eqs. (5) and (6).

The collection axis is fixed at an angle of 90° with respect to the incident beam. A three-element lens, L_1, of effective focal length $f_1 = 216$ mm is placed a distance f_1 from the film. Scattered light from the film at some angle α with respect to the collection axis (specular reflection) is thereby focused to infinity by f_1. A 400-μm pinhole P_1 is placed on a micrometer translator behind L_1, and is thus used to select the scattered wave vector. Lens L_2 ($f_2 = 200$ mm) is placed behind P_1 and focuses the scattered light through a spatial filtering pinhole P_2 of diameter 400 μm. Finally a third lens, L_3 ($f_3 = 75$ mm), focuses the light into an FW130 photomultiplier tube biased at 2200 V. The PM signal is amplified and shaped, and the resulting pulses are fed into a Hewlett-Packard multichannel analyzer (MCA).

P_1 is first translated a small distance l (shown by the arrow) to choose a scattering angle α. As long as P_1 remains in the $\hat{r}_N$-$\hat{r}_{\parallel}$ plane, only $q_{\parallel}$ will be sampled ($q_{\perp} = 0$). When the MCA is triggered, pulses are counted (proportional to intensity I_{off}) for 3 ms, using 300 channels at 10 μs/channel (Fig. 4) Typical count rates run upward from 40 000 counts/s at $q_{\parallel} = 6000$ cm^{-1} to 200 000 counts/s at $q_{\parallel} = 2000$ cm^{-1}, with a dark-current of 30 counts/s. At the end of the 3-ms period, the high field ($E_0 \sim 300$ V/cm) is turned on for 1.8 ms, quenching fluctuations. Channels 301 through 480 of the MCA record a decaying exponential, where the decay time is typically 100–300 μs (10–30 channels) and the base line is proportional to I_{on} (Fig. 4). At the end of the 4.8-ms sequence, the high field switches off and the scattered signal exponentially increases back to I_{off}. The process is repeated every 110 ms, and in this way a signal profile is generated over the course of some 10^4 trigger pulses. After obtaining an adequate profile, P_1 is translated back toward $\alpha = 0$ (always in one direction to minimize hysteresis) to sample another $q_{\parallel}$. Data are typically collected at seven values of $q_{\parallel}$ for $\alpha > 0$ and seven at $\alpha < 0$. A similar procedure is used to sample $q_{\perp}$, except P_1 is translated vertically.

It should be noted that by significantly increasing the trigger repetition rate, we run the risk of creating instabilities in the film. Since the high voltage pulse is always positive, a long duty cycle creates a significant dc component of E_0 (much greater than E_a), which can couple to the molecular dipoles as well as to the ionic impurities. The result is a flow of the molecules, as well as an orientational instability in the film's alignment. Consequently we are restricted to a short duty cycle.

Values for I_{on}, I_{off}, and decay time τ at a given $\vec{q}_{\parallel}$ are obtained by means of a least-squares fit. [It should be noted that for fixed q, Eq. (5) is linear in E_0 up to $E_0 = 600$ V/cm to better than 2%.] The most significant source of error is statistical noise due to the relatively small number of counts (typically 10^3–10^4) per channel. Since the errors in I_{on} and I_{off} can be as much as 0.5%, the net error in $L(\vec{q})$ [Eq. (5)] can be quite large, often as much as several percent. Furthermore, since $2\pi P_0$ [Eq. (5)] can be small (particularly near T_{CA}) when compared to $(K_b/P_0)q_{\parallel}$ ($2000 < q_{\parallel} < 6000$ cm^{-1}), the net effect is to introduce errors as much as 10% for P_0. This figure may be even higher when P_0 is small. Other errors due to dark noise, hysteresis in the translation stage, and spread in $\vec{q}$ are generally small and can be compensated for. Anomalous scattering from dust and from objects in the oven is generally polarized, although a small amount of depolarized scattering contributes to the overall signal.

RESULTS

The results for $K_{s,b}$, $\eta_{s,b}$, and P_0 as a function of film thickness at a fixed temperature were discussed earlier.[8] The second set of data was taken using a fixed layer thickness ($N = 3$), and at temperatures varying between T_C and $T_C - 20$, where T_C is approximately 388.2 K for a three-layer

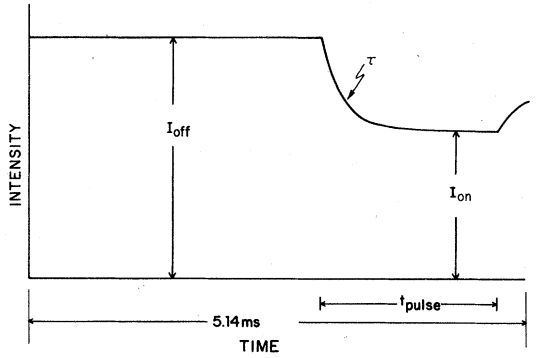

FIG. 4. Idealized representation of MCA profile.

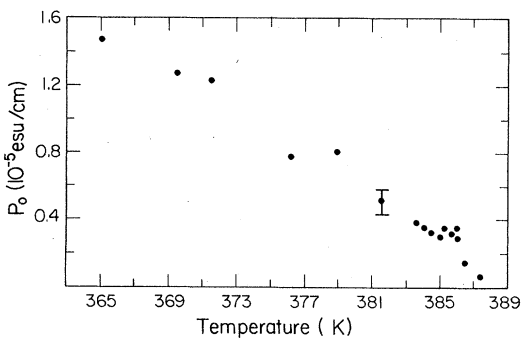

FIG. 5. P_0 vs T for three-layer film.

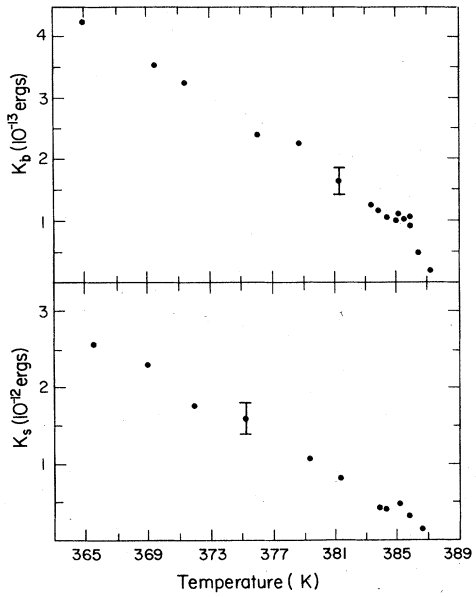

FIG. 6. (a) K_b vs T for three-layer film. (b) K_s vs T for three-layer film.

film. $N=3$ was chosen because it is the thinnest film that remains stable against rupture as T is elevated through T_C.[19] The data for P_0, K_b, and K_s are shown in Figs. 5, 6(a), and 6(b), respectively, where the data have been corrected for a 7 mK/h drift of T_C.

Noting that $|P_0|$ scales as $\sin\theta_T$,[12,13] it is instructive to look at the ratio

$$K_s/P_0^2 \propto 1/h = 1/(3a_0\cos\theta_T),$$

where $a_0 = 33$ Å, the thickness of a smectic-A layer. Since θ_T is generally less than 25°, the $\cos\theta_T$ correction is at most 10%, and hence we expect K_s/P_0^2 to be nearly constant [see Eq. (2)]. In Table I we list K_s, P_0, K_s/P_0^2, $\sin\theta_T$, $K_s/\sin^2\theta_T$, and $P_0/\sin\theta_T$ at various values of $T_C - T$. Values of $\sin\theta_T$ as a function of T are taken from Ref. 11. It is easily seen that K_s/P_0^2 near T_C is much greater (by a factor of 3) than the value of K_s/P_0^2 far below T_C. Obviously, one or both of P_0 and K_s are not scaling as expected with tilt angle. However, we also note that $h\kappa_{11} = K_s/\sin^2\theta_T$ is relatively insensitive to temperature (in this range), whereas $P_0/\sin\theta_T$ is much smaller at higher temperatures than at lower temperatures. These results suggest that at higher temperatures ($T > 370$ K) the molecules can become both less rigid and couple less strongly to the local C_2 environment. These two effects are manifest in a reduced polarization.[12]

The viscosity results are shown in Fig. 7. As expected, the viscosities scale in the same manner as the elastic constants; $\eta_{s,b}/\sin^2\theta_T$ show only a weak temperature dependence. It is interesting to note that values of $\eta_{s,b}/\sin^2\theta_T$ are higher at lower temperature; that is, the system is more viscous at lower temperatures, as is typical for liquids.

In a Landau-Ginzburg mean-field theory of the A-C phase transition, in which θ_T serves as the order parameter, θ_T should scale[15] as $(T_{CA} - T)^{1/2}$. Since $K_{s,b}$ scales as θ_T^2 for small θ_T, we would expect $K_{s,b}$ to scale as $(T_{CA} - T)$. In Fig. 6 it is seen that for temperatures below 385 K, $K_{s,b} \propto (T_{CA} - T)$. Around 388 K, however, this $(T_{CA} - T)$ behavior is cut off, and $K_{s,b}$ goes to zero rather sharply.

In recent years Kosterlitz and Thouless, as well as others, have addressed the question of a two-dimensional XY phase transition.[1,2,7] In the liquid-crystal system being studied, the projection of the director $\vec{n}_b$ into the film's plane serves as the analog to the two-dimensional magnetic spin. Consequently, Nelson and Kosterlitz[7] have predicted a transition at

$$T_C = \pi K_C^*/2k_B, \tag{10}$$

at which point one expects a spontaneous breaking of vortex pairs, as well as a continous drop to zero of the effective two-dimensional elastic constant $K^* = \frac{1}{2}(K_s + K_b)$.[20] Corrections to this model from ferroelectric dipolar forces are small due to their limited range.[20] From the data in Table I, and noting that $K_s \approx 6.5K_b$ over all T from Fig. 6, we expect $K_s \simeq 10^{-11}\sin^2\theta_T$ and $K_b \simeq 1.5\times10^{-12}\sin^2\theta_T$ (in ergs). Hence, $K^* \simeq 5.7\times10^{-12}\sin^2\theta_T$. Taking T_C to be equal to T_{CA} (≈388 °K), one expects [Eq. (10)] K_C^* to be approximately 3.4×10^{-14} erg at a temperature just below T_C. If we can extrapolate the

TABLE I. Various measured parameters as a function of temperature for a three-layer film. Note that $K_s/\sin^2\theta_T$ is relatively insensitive to temperature.

$T_C - T$	K_s (10^{-12} erg)	P_0 (10^{-5} esu/cm)	K_s/P_0^2 (10^{-2} cm)	$\sin\theta_T$	$K_s/\sin^2\theta_T$ (10^{-11} erg)	$P_0/\sin\theta_T$ (10^{-5} esu/cm)
4	0.50	0.35	4.08	0.23	0.92	1.50
8	1.00	0.65	2.37	0.33	0.94	1.99
12	1.48	0.90	1.83	0.39	0.99	2.33
16	1.88	1.15	1.40	0.42	1.05	2.74
20	2.32	1.36	1.25	0.47	1.05	2.90

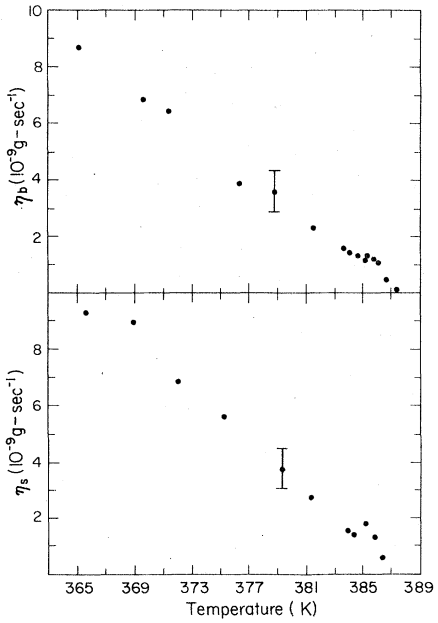

FIG. 7. (a) η_b vs T for three-layer film. (b) η_s vs T for three-layer film.

form for K^* (that is, $K^* \simeq 5.7 \times 10^{-12} \sin^2\theta_T$) down to K_C^*, we then expect $\sin\theta_T = (K_C^*/5.7 \times 10^{-12})^{1/2}$, or $\theta_T = 4.5°$ at the XY transition. (Actual measurements of $K_{s,b}$ near T_C are difficult due to the small values of $K_{s,b}$.) By means of ellipsometry techniques, Pindak *et al.*[11,21] have measured θ_T both as a function of N and T. Using electric fields varying between 6 and 330 V/cm, they have observed a sharp drop in θ_T of between 4° and 5° near T_c. These results compare remarkably well with our extrapolated value of $\theta_T = 4.5°$, indicating XY-like behavior.

We note in passing that for thicker films (but not so thick as to be considered three-dimensional), the coefficient C in $K^* = C \sin^2\theta_T$ is larger than in thinner films. Hence, it is known that T_C (and therefore K_C^*) is constant to within 7% for all N,[11] one would necessarily expect the tilt angle θ_T just below T_C to be a decreasing function of N. Again, this is reasonable in that at a fixed temperature, θ_T is smaller for thicker films [see Fig. 5(a)].

In addition to the quantitative measurements performed near the supposed XY transition, a very interesting visual observation was also made. If a weak temperature gradient is present, such that one section of the film appears "calm" and unresponsive to an applied electric field (A) and the other is "turbid" and responds readily to a field (C), the interface appears very sharp under the microscope (resolution to approximately 10 μm). This observation is both consistent with the Kosterlitz-Thouless model (which presents a rather sudden appearance of isolated vortices destroying any net polarization) and inconsistent with the usual second-order C–A phase transition, thus further supporting the conjecture that an XY-like transition is found in this system.

In this paper we have reported the temperature behavior of $K_{s,b}$, P_0 and $\eta_{s,b}$ in ferroelectric thin films. We have found that $K_{s,b}$ scales with both θ_T and $(T_{CA} - T)$ as expected, away from T_{CA}. At higher temperatures, $K_{s,b}$ falls off rapidly, where the observed behavior is very consistent with an XY-like phase transition. It was also noted that P_0 falls off more rapidly than expected at high temperatures, indicating intramolecular flexing and weaker coupling to the C_2 environment than at lower temperatures.

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