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Tilt susceptibility at an antiferroelectric smectic-C_A^*–smectic-A phase transition

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Electroclinic measurements are reported for a liquid crystal around the antiferroelectric smectic-C_A^*–"disordered" smectic-A phase transition. It was found that the spatially averaged tilt susceptibility exhibits a slope discontinuity at the transition, and that the extrapolated divergence temperature of the susceptibility is only 1.1±0.1 °C below the Néel temperature. The relaxation times were found to be of the order of 1 μs. A simple mean-field model is presented.

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In the chiral smectic-C (Sm-C^*) phase the spontaneous polarization derives from a combination of the tilted smectic-C structure and absence of inversion symmetry [1]; the same holds true for the antiferroelectric liquid crystalline Sm-C_A^* phase. The Sm-C_A^* phase, however, is a tilted smectic phase in which the **c** direction (the projection of the molecular director $\hat{\mathbf{n}}$ into the smectic layer plane) rotates by approximately 180° in successive layers [2,3] (Fig. 1). The polarization, which within a given layer is oriented parallel to the layer plane and perpendicular to $\hat{\mathbf{n}}$, is, therefore, nearly antiparallel in successive layers; it thus vanishes on average. (It is the chiral nature of the molecule, and the resulting macroscopic helix, that prevents the polarizations in successive layers from being absolutely antiparallel.) Owing to their complex physical interactions and possible commercial uses, antiferrielectric liquid crystals—and related ferrielectric phases—have garnered considerable attention [4–15].

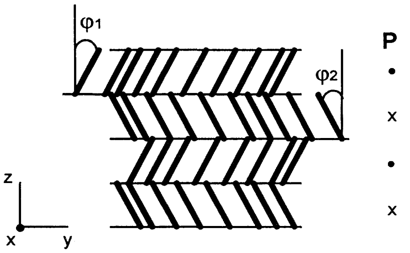

FIG. 1. Schematic representation of antiferroelectric liquid crystal for which the helix is unwound. Molecules in successive rows tilt by polar angles φ_1 and φ_2, both defined as positive for directions shown. The polarizations **P** in successive layers point in the $+x$ and $-x$ directions. The electric field **E** is applied along the x axis.

The molecule TFMHPOBC [4-(1-trifluoromethylhexyloxycarbonyl) phenyl 4′-octyloxybiphenyl-4-carboxylate; Fig. 2] has a particularly interesting phase diagram [16]. The enantiomer, for example, exhibits a smectic-A (Sm-A)–Sm-C_A^* phase transition, with no intermediate ferrielectric phases between the ordered antiferrolectric Sm-C_A^* phase and the higher temperature "disordered" Sm-A phase—disordered in the sense that the antiferroelectric order parameter vanishes. Additionally, over a large range of (left + right handed) enantiomeric mixtures, a ferroelectric Sm-C^* may occur between the Sm-A and Sm-C_A^* phases. The purpose of this paper is to report on tilt susceptibility measurements [9] of the optically pure enantiomer above and below the Sm-A–Sm-C_A^* phase transition. In a ferroelectric liquid crystal both the electroclinic coefficient $d\varphi/dE$ and the relaxation time τ diverge on approaching the Sm-A–Sm-C^* phase transition [17]. Here **E** is an electric field applied parallel to the layers and φ is the average tilt angle of the molecules with respect to the layer normal, where $\hat{\mathbf{n}}$ lies in a plane perpendicular to **E**. At the Sm-A–antiferroelectric-Sm-C_A^* transition, however, we find that the electrically induced structural tilt vs temperature exhibits a discontinuity in slope, and that the relaxation time is in the μs region. This behavior is consistent with a simple mean-field model which couples the tilt angles of successive layers.

A pair of indium-tin-oxide coated glass slides was dipped in a mixture of nylon 6/6 and formic acid, al-

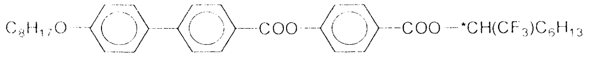

FIG. 2. Chemical structure of TFMHPOBC.

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lowed to dry, and then rubbed unidirectionally along the z axis. The liquid-crystal cell was constructed by cementing together the two slides, which were separated by Mylar spacers of nominal thickness 2 μm. The cell was heated and filled with the right-handed enantiomer of TFMHPOBC in the isotropic phase, and cooled slowly into the Sm-A phase to avoid the appearance of focal conic texture [18]; a clean bookshelf geometry was obtained (Fig. 1). The cell was then transferred to an oven that was temperature controlled to better than 20 mK. In the electroclinic geometry [19], the beam from a He-Ne laser, focused to a diameter < 100 μm, was incident perpendicular to the cell along the x axis and polarized at an angle $\pi/8$ from the z axis in the yz plane. After passing through a crossed polarizer, the beam intensity was measured with a photodiode. Applying an ac field $\mathbf{E}$ across the sample along the x axis changes the average director tilt $\varphi[\propto E]$ in the yz plane. When such a tilt change occurs, there is a concomitant change in the intensity δI at the detector, such that $\varphi = \delta I / 4 I_o$, where I_o is the (much larger) dc intensity. To measure the electroclinic coefficient $d\varphi/dE$, an ac voltage at frequency $\nu = 317$ Hz (much smaller than $1/\tau$) was ramped from 0 to 4.5 V rms over 120 s and δI [$\propto$ applied voltage] was measured with a lock-in amplifier. The dc detector output I_o was measured simultaneously with a dc voltmeter. To obtain the relaxation time τ [20], the in-phase and 90° out-of-phase (quadrature) components of δI were measured at $V = 4.5$ V rms and at frequency $\nu = 35.3$ kHz, and τ was obtained from the relationship $\tau = (2\pi\nu R)^{-1}$, where $R \equiv \delta I^{\text{in-phase}} / \delta I^{\text{quad}}$.

The electroclinic coefficient $d\varphi/dE$ vs temperature is shown in Fig. 3 and the relaxation time τ is shown in Fig. 4. As the direction of the tilt angle in the Sm-C_A^* phase alternates from layer to layer (see Fig. 2), light at optical wavelengths can sample only the *average* tilt angle $\varphi = \frac{1}{2}(\varphi_1 - \varphi_2)$, where φ_1 and φ_2 correspond to the tilt angles of the odd and even layers. Note that we have defined both φ_1 and φ_2 as positive quantities even though the corresponding $\mathbf{c}$ directors are antiparallel. In the disordered Sm-A phase the electroclinic coefficient increases on decreasing temperature. However, unlike the case of a ferroelectric liquid crystal in which $d\varphi/dE$ diverges on approaching the transition [17], we find that the electroclinic coefficient remains finite—but with a slope discontinuity—at the transition to the antiferroelectric phase. A finite response was also observed by Orihara *et al.* [21] and Hiraoka *et al.* [22] in dielectric experiments at the same transition. Moreover, this sort of susceptibility behavior is reminiscent of ordinary antiferroelectric crystals or antiferromagnets, although the liquid crystal has much more highly anisotropic structural interactions. Note that some question still exists about the order of the phase transition in TFMHPOBC, as our electroclinic data and Hiraoka's dielectric and dielectric anisotropy data [22] appear to be continuous at the transition, with the only hint of first-order behavior being a phase boundary observed under the microscope [22]. Thus, *if* the transition in TFMHPOBC is first order, it is *extremely* weakly so. Additionally, notice that the magnitude of $d\varphi/dE$ is comparable to that near the ferroelectric liquid crystalline phase of SCE12 (Merck) [23]. This is expected if the propensity of the molecules in successive layers to tilt in opposite directions in the Sm-C_A^* phase is small, and if the transverse molecular dipole is large; this is apparently the case for TFMHPOBC (see below). Below the transition temperature $T_N = 113.16 \pm 0.04$ °C we find a rapid decrease of $d\varphi/dE$ with decreasing temperature. Since the reported pitch over the measured temperature range varies between 0.5 and 1 μm [24], the helix *may* be only partially unwound in the 2 μm thick cell. In Fig. 4, however, we see that the relaxation time is much faster than $1/\nu$, and is comparable to relaxation times found several degrees above the Sm-A–Sm-C^* phase transition in ferroelectric liquid crystals [23]. Thus the rapid response time in the antiferroelectric phase may actually indicate that the helix is *completely* unwound and surface stabilized, as the response time associated with the changes in the helical structure would be expected to be much slower than those observed.

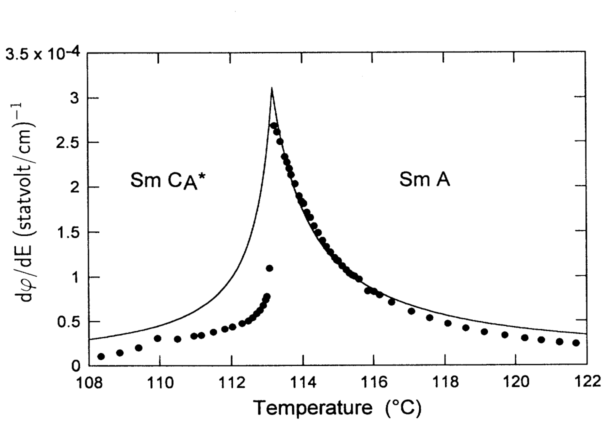

FIG. 3. Electroclinic coefficient vs temperature. The solid line in the high temperature Sm-A phase represents a fit to the model, and the solid line in the Sm-C_A^* phase corresponds to the model calculation using the two fitting parameters obtained in the Sm-A phase.

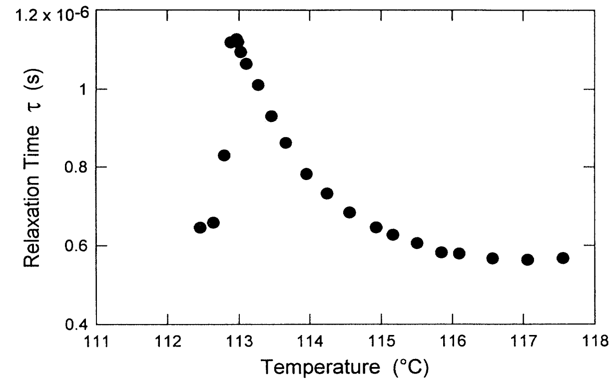

FIG. 4. Relaxation time vs temperature.

To understand the behavior shown in Figs. 3 and 4, we adopt a Landau mean-field model with sufficient parameters to afford a qualitative understanding of the data. The model below is a simplification of the disordered-ferroelectric-ferrielectric-antiferroelectric model proposed by Orihara and Ishibashi [7], and is similar to the ferroelectric free energy first written down by Garoff and Meyer [17]. Defining E, φ_1, and φ_2 as above, we express the free energy density in the disordered high temperature phase

$$F=\tfrac{1}{2}a'\varphi_1^2+\tfrac{1}{2}a'\varphi_2^2+\tfrac{1}{2}\chi^{-1}P_1^2+\tfrac{1}{2}\chi^{-1}P_2^2+P_1E$$
$$-P_2E-t\varphi_1P_1-t\varphi_2P_2-c\varphi_1\varphi_2 \ , \tag{1}$$

where χ is a generalized polarization susceptibility, t is a coefficient that couples the tilt and polarization within a layer, $a'=a_0(T-T_c')$, $a_0>0$, and T_c' is the tilt transition temperature for a layer of nonchiral material in the absence of interlayer coupling. The last term is the only interlayer coupling term we include, and has the effect of promoting equal and opposite tilts in successive layers. (Recall that φ_1 and φ_2 are both defined as positive quantities.) Finally, note that quartic terms are unnecessary in the Sm-A phase. In order to keep the model uncomplicated, an important assumption was made in Eq. (1): we have simplified the free energy by omitting interlayer couplings involving terms like φ_iP_j and P_iP_j, where $i,j=1,2$ and $i\neq j$ (see below). This is physically equivalent to assuming that interactions involving the spontaneous polarizations are localized within a layer. The free energy is thus a function of four variables: φ_1, φ_2, P_1, and P_2. Minimizing F with respect to P_1 and P_2, we can rewrite the free energy as

$$F=\tfrac{1}{2}a\varphi_1^2+\tfrac{1}{2}a\varphi_2^2+t\chi\varphi_1E-t\chi\varphi_2E-c\varphi_1\varphi_2 \ , \tag{2}$$

where $a=a'-\chi t^2$. Thus, chirality has the effect of increasing the transition temperature of an uncoupled layer, such that $T_c=T_c'+\chi t^2/a_0$ where T_c is the transition temperature of the *chiral* material in the absence of interlayer coupling. Further minimizing F with respect to φ_1 and φ_2, we easily find that $\varphi_1=-t\chi E/(a+c)$, $\varphi_2=+t\chi E/(a+c)$, and $d\varphi/dE\equiv\frac{1}{2}d(\varphi_1-\varphi_2)/dE=-t\chi/(a+c)$. According to the sign convention adopted above, we find that $|\varphi_1|=|\varphi_2|$, that both odd and even layers tilt *in the same direction* in the Sm-A phase, and that the average tilt φ as measured in our optical experiment is simply the magnitude of the induced layer tilt. Additionally, we note that the presence of the coupling term reduces the effective divergence temperature $\theta[=T_c-c/a_0]$ of the susceptibility, essentially converting what would be an algebraic divergence into a slope discontinuity, even though the model transition is second order. Correspondingly, the Néel temperature $T_N=T_c+c/a_0=\theta+2c/a_0$. However, unlike an antiferromagnet where θ may become negative, θ for the liquid crystal is likely to remain positive and nearly equal to T_N, given that interlayer interactions tend to be weak [25]. Finally, we note that from a physical standpoint, terms like P_iP_j may actually be *more* important than $-c\varphi_1\varphi_2$ in Eq. (1) [10,12,14]. Had we included these terms, the form for Eq. (2) and the Curie-Weiss susceptibility would still have obtained—except that the coefficients in Eq. (2) would involved the coefficients of the additional polarization terms.

In Fig. 3, we show a two parameter least-squares fit of the electroclinic data to the form $d\varphi/dE=-t\chi/[a_0(T-T_N)+2c]$, where we have empirically fixed $T_N=113.16\pm0.04$ °C. We find that $-a_0/t\chi=(2980\pm100)$ statvolt/cm K and that $-c/t\chi=(1610\pm100)$ statvolt/cm. The resulting divergence temperature of the electroclinic coefficient $\theta\approx T_N-1.1\pm0.1$ °C, which is only a small shift from T_N. Note that the stated error bars in the fitting parameters arise principally from the mediocre quality of the fit, as the data clearly depart from classical Curie-Weiss behavior. The origin of this deviation is not yet known, although a temperature dependence of the coefficients c, t, and χ—in addition to that of the coefficient a—is a likely candidate. Nevertheless, two important points emerge: θ and T_N are in close proximity and the susceptibility can be approximately represented by a Curie-Weiss law.

Analysis of the data is much more difficult in the antiferroelectric phase, where $d\varphi/dE$ changes rapidly but apparently continuously. If we again neglect interlayer interactions and assume that the polarizations have a negligible effect on the equilibrium angles $\varphi_1(T)$ and $\varphi_2(T)$, the free energy would have two additional terms, viz. $\frac{1}{4}e\varphi_1^4$ and $\frac{1}{4}e\varphi_2^4$, where e is a constant. Proceeding as above, we find $d\varphi/dE=-t\chi/[-2a_0(T-T_N)+2c]$. Using the parameters obtained from the fit in the Sm-A phase, the calculated form of $d\varphi/dE$ vs temperature in the Sm-C_A^* phase is shown in Fig. 3. The model is clearly insufficient, and would likely require biquadratic coupling terms like $\varphi_i^2P_i^2$. Sufficiently far below T_N, moreover, the model is simply invalid: the tilt order parameter and resulting polarizations are large and partially saturated, the susceptibility is reduced, and the Landau expansion completely breaks down. Additionally, in the ordered phase the electric field also tends to induce azimuthal reorientations of the polarizations, necessitating an additional azimuthal term in the free energy.

Antiferroelectric liquid crystals, in which the polarization is inexorably coupled to the molecular tilt, in many ways mimic the behavior of ordinary antiferroelectrics and antiferromagnets. We find, however, that the far more anisotropic liquid crystal may be modeled for both chiral and racemic materials [4] as a transition from a Sm-A to a tilted phase. An additional term, due in part to molecular dipole interactions, promotes antiparallel **c** directors—which in turn couple to P_i—in alternating layers. The role of terms like P_iP_j in Eq. (1) is not yet clear [10,12,14], although they do not change the basic form of the Curie-Weiss-like susceptibility. Nevertheless, the presence of the $-c\varphi_1\varphi_2$ term causes the tilt susceptibility to remain finite at T_N, with a simple change in the slope of $d\theta/dE$ vs temperature. Moreover, since interlayer interactions in liquid crystals tend to be weaker than intralayer interactions, this term can be much smaller than the term that drives the structural Sm-A–Sm-C phase transition. In consequence, the divergence temperature θ of $d\varphi/dE$ is only slightly smaller than T_N.

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