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Electroclinic Effect at the A–C Phase Change in a Chiral Smectic Liquid Crystal*

Stephen Garoff and Robert B. Meyer
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts 02138
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When a smetic-A phase is composed of chiral molecules, it exhibits an electroclinic effect, i.e., a direct coupling of molecular tilt to applied field. The pretransitional behavior of the electroclinic effect in the A phase is used to study the critical behavior near the second order, smectic-A–smectic-C phase transition. This behavior is measured by monitoring the change in birefringence of a sample as the electroclinic effect causes a tilt of the molecules. A large pretransitional effect is measured, and constants describing the critical behavior are determined.

Meyer *et al.*[1] established the existence and behavior of ferroelectric liquid crystals. Since then many of the properties of these liquid crystals have been investigated: synthesis and properties of several compounds which have enhanced ferroelectric properties[2-4]; optics and bulk properties[1]; polarization and helical pitch[5]; shear induced polarization[6]; pyroelectricity[7]; and fluctuations and domain walls in free smectic films.[8] Our experiment is a measurement of a new phenomenon—the electroclinic effect (ECE)—and the critical behavior on the smectic-A side of the smectic-A–smectic-C phase transition. Although this effect is very closely related to piezoelectricity in crystalline phases, we use a distinctive name because the fluid nature of the liquid crystalline phase does not allow the static shear strains associated with piezoelectricity. This work is one of the first detailed studies of the critical properties of this phase transition. Our results raise some question about the exact nature of the phase change.

A symmetry argument, similar to that predicting ferroelectricity in a chiral smectic-C,[1] describes the origin of the ECE in a smectic-A phase composed of chiral molecules. The application of an electric field parallel to the smectic layers of such a smectic-A biases the free rotation of the molecules and therefore produces a nonzero average of the transverse component of the molecular polarization. When such a dipole moment is present, a tilt of the long molecular axis (the director) is induced in a plane perpendicular to the dipole moment.

In an aligned smectic-A sample, a tilt of the director is directly related to a tilt of the optic axis; therefore, the ECE results in a linear electro-optic response. The electro-optic effect manifests itself as a modulation of the birefringence.

The ferroelectric smectic-A–smectic-C phase transition is second order and exhibits a divergence of the electric polarization susceptibility characteristic of a Curie point.[9] On the smectic-A side of the transition, a soft mode is observed for which the susceptibility A controlling tilt of the director goes to zero at the critical temperature T_c according to a power law:

$$A = a[(T - T_c)/T_c]^{\gamma}. \quad (1)$$

Despite the striking resemblances to the crystalline ferroelectric Curie point, the phase change is driven by the intermolecular forces inducing the smectic-C phase and not by the spontaneous polarization which is a minor perturbation on these forces. In this sense, we consider the pretransitional behavior of the ECE to be a probe of the critical behavior near the smectic-A–smectic-C phase transition rather than a measure of the effects of dipole-dipole interactions.

Because of the overall symmetry properties of the nonchiral smectic-A–smectic-C phase change, de Gennes has drawn an analogy between this transition and the normal-to-superfluid transition in ^{4}He where γ cannot be directly measured.[10] In the high-temperature-series expansion analysis, the asymptotic values for γ are 1.0 in the mean-field limit and 1.315 near the transition.[11]

The spatially homogeneous, static free-energy density of a chiral smectic-A in the presence of an electric field E parallel to the smectic layers

is

$$g = g_A + \tfrac{1}{2}A'(T)\theta^2 + \ldots + \tfrac{1}{2}\chi_p^{-1}P^2 - PE - 8\pi^{-1}\epsilon^0 E^2 - t\theta P, \quad (2)$$

in which θ is the molecular tilt normal to E, P is the component of the average molecular polarization parallel to E, ϵ^0 is the dielectric constant without contributions from the permanent dipole, χ_p is a generalized suspectibility, and t is the piezoelectric coupling constant. P and θ are treated as independent variables; therefore, the equilibrium values of these variables are found by setting the partial derivatives of the free-energy density with respect to P and θ separately equal to zero. This gives the following results:

$$A = A' - \tfrac{1}{2}\chi_p t^2,$$
$$\epsilon = \epsilon^0 + 4\pi\chi_p + 4\pi(\chi_p t)^2/A, \quad (3)$$
$$\theta = \chi_p tE/A.$$

In these equations, (1) the modification of A indicates that the coupling between P and θ slightly shifts T_c; (2) ϵ contains a divergent contribution from the susceptibility A; (3) θ is linear in E.

If inertial terms are neglected, the dynamics of the ECE are described by

$$\Gamma\dot{\theta} + A\theta = cE, \quad (4)$$

in which Γ is a viscosity and is assumed to follow a simple Arrhenius form $\Gamma = \Gamma_0 e^{B/T}$ and $c = \chi_p t$ is the coupling constant between θ and E. If E is sinusoidal with angular frequency ω, then the induced tilt is described by an amplitude θ_0 and a phase δ relative to the applied field:

$$\theta_0 = cE/(A^2 + \omega^2\Gamma^2)^{1/2},$$
$$\delta = \tan^{-1}(-\omega\Gamma/A). \quad (5)$$

Because of the critical behavior of A, the ECE should show the following features: (1) As T approaches T_c, the amplitude rises and the phase shifts through $-90°$. (2) Near T_c, the viscosity term in the amplitude dominates and the response is strongly frequency dependent. (3) Far from T_c, the elastic term is dominant and the response shows dispersion only at high frequencies. Although the divergence of A is most clearly seen for a dc applied field, frequencies above 5 kHz are used in this experiment to avoid electrohydrodynamic phenomena.

As mentioned above, the ECE causes a tilt of the optic axis of an aligned smectic-A sample, thereby inducing a linear modulation of the birefringence of the sample. This modulation is best measured by placing the sample between crossed polarizers and measuring the transmission of the system with the input laser beam at an oblique angle to the sample. The sensitivity of this method is maximized by choosing the largest practical angle of incidence such that the output beam from the sample is circularly polarized (i.e., at the half-intensity point of a ring on the uniaxial conoscopic image), and by selecting the input polarization to produce equal amplitudes in the ordinary and extraordinary rays in the sample (i.e., at 45° to the arms of the uniaxial cross of the conoscopic image). Using this operating point and phase-sensitive detection of the modulation of the transmitted light intensity, molecular tilts as small as 5 μrad are easily measurable.

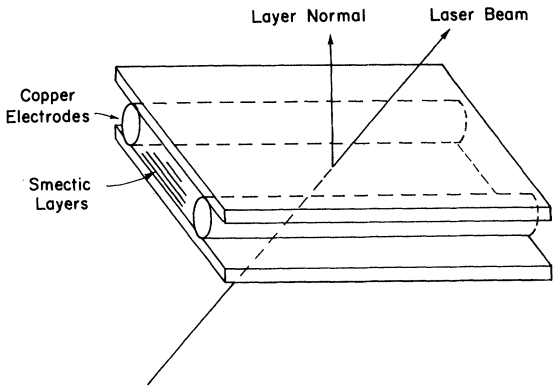

FIG. 1. Sample geometry.

The chiral compound used is p-decyloxybenzylidene-p'-amino-2-methylbutylcinnamate.[2] In the sample geometry shown in Fig. 1, the copper wires, which are 120 μm in diameter and 1.5 mm apart, act both as electrodes and spacers. The homeotropic alignment is produced by use of hexadecyl-trimethyl ammonium bromide surfactant. For this geometry, the ECE causes a molecular tilt in the plane in incidence of the light.

The amplitude and phase of the electro-optic signal is recorded from 0.5 K below T_c to 15 K above T_c. Periodically, during each temperature scan, the drift of the transition temperature is measured. Assumption of a linear drift of T_c with time gives excellent reproducibility of the data near the transition. Temperature scans are made for several frequencies of the applied field. Typical data are shown in Figs. 2 and 3.

The electro-optic response itself provides a measure of T_c. At the transition, both the phase and amplitude of the electro-optic response show

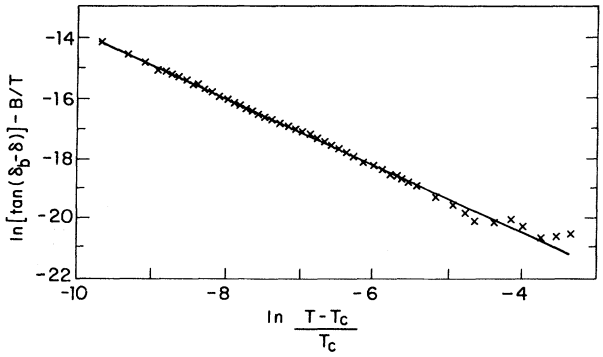

FIG. 2. Typical data and fitted curve for Eq. (6). $B = 6000°K$ and $\omega = 12.6 \times 10^4$ sec^{-1}.

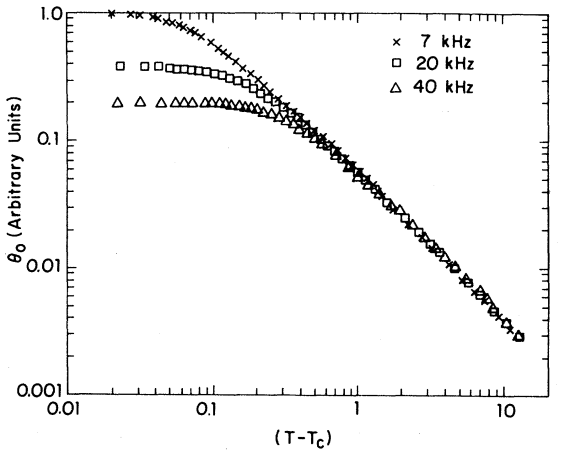

FIG. 3. Log amplitude of the electro-optic response vs $\log(T - T_c)$ for three frequencies of the applied field.

a marked discontinuity with a width of about 20 mK. T_c can be assumed to lie within this discontinuous region. Thus far, the reasons for the finite width of this region are not clear. The width may arise from a smearing of the transition due to impurities in the sample, or it may be an indication of fluctuations containing motion of the phase angle of the director and small effects of the helical structure of the smectic-C phase.[12]

The parameters in Eqs. (5) are determined from the data by a least-squares analysis. The expression for the phase of the ECE is rewritten as

$$\ln[\tan(\delta_b - \delta)] = (B/T) - \ln(\omega\Gamma_0/a) - \gamma \ln[(T - T_c)/T_c] \quad (6)$$

in which δ_b is the constant background phase shift of the electronics. For each set of values of T_c, δ_b, and the activation energy B, the amplitude and phase data are fitted by nonlinear and linear techniques, respectively.[13] The data analysis is performed both for a temperature-independent critical exponent as well as for an exponent which exhibits the temperature dependence characteristic of the crossover between the asymptotic behaviors predicted by the high-temperature-series expansion.[14] The data did not fit Eqs. (5) with the temperature-dependent exponent as well as it did those with a temperature-independent exponent.[15] For some data sets, the actual minimum of the mean square deviation χ^2 occurs outside the allowed ranges of T_c and B[16]; however, by allowing χ^2 to increase, physical values of T_c and B are reached. Further, these deviations from the absolute minimum in χ^2 cause only very small changes in the critical exponent and relaxation time ($=\Gamma/A$) obtained from the least-squares fits.

All theoretical curves and error bars have not been shown in Figs. 2 and 3 since they cannot be discriminated from the data in the figures. The error bars needed to account for the random scatter seen in the data indicate small experimental error: 1.5% in the amplitude measurement and 0.3° error in the phase measurement.

The critical exponent determined from the data analysis is $\gamma = 1.11 + 0.06$. The uncertainty for each set of data is slightly smaller than 0.06; however, some small discrepancies do occur for the values obtained from different runs. The error bar of ± 0.06 represents the full range of uncertainty based on all runs. As yet, no dependence of γ on the minor impurity levels in the sample or on the frequency of the applied field has been found. The disagreement between this value of γ and the theoretical predictions for the nonchiral smectic-A–smectic-C transition may be due to the fact that the helical structure of the smectic-C phase causes the symmetry of the transition in chiral phases to be different from that of the nonchiral phase transition. A mean-field-like exponent has been measured by light scattering at the nonchiral transition.[17] The relaxation time at 0.1 K above T_c is 15 ± 2 μsec. If the viscosity at 100°C is assumed to be on the order of 10 cP and the elastic constant K to be on the order of 10^{-6} cgs units, then the susceptibility A is about 10^4 cgs units at 0.1 K above T_c and the coherence length at absolute zero is about 10 Å or roughly a molecular dimension.

Several possibilities exist for additional temperature and frequency dependencies of the critical dynamics of the ECE. The viscosity Γ may

show some very weak critical behavior. Because of the manner in which Γ appears in the phase and amplitude equations (5), such a temperature dependence would be seen as a systematic difference between the γ obtained from the phase and amplitude data for a given run. This discrepancy has not been observed. Stabilization of T_c would enable further investigation of the region $T - T_c < 20$ mK and would allow exploration of possible helical fluctuations. However, unless independent, accurate measurements of the parameters of the dynamical equation are available, adding unknown parameters to the least-squares fitting process is of questionable value. Despite these reservations, the quality and self-consistency of our data lends credence to the value of γ determined.

Beyond the exploration of critical phenomena near the smectic-*A*–smectic-*C* transition, this experiment has measured a new electro-optic phenomenon in liquid crystals. The picture of the electroclinic effect derived from this work adds consistently to the phenomenology of ferroelectric liquid crystals.

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