PHYSICAL REVIEW A VOLUME 41, NUMBER 4 15 FEBRUARY 1990

Nematic electroclinic effect

Zili Li, Gregory A. Di Lisi, Rolfe G. Petschek, and Charles Rosenblatt
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106
(Received 2 August 1989)

A tilt θ of the principal axis of the optical dielectric tensor linear in a transverse electric field was observed for a surface-stabilized nematic liquid crystal. The electroclinic coefficient $d\theta/dE$ was observed to increase rapidly on approaching the nematic–smectic-*A* phase transition from above. This was not expected, and indicates that the incipient translational order is important to the electroclinic effect. The data are consistent with a critical exponent only over a narrow range of temperature, and in this range the apparent exponent is not that expected from theory. In addition, dielectric data are presented for this transition, and birefringence results are discussed. A simple theoretical discussion involving coupled order parameters is presented, and the experimental results are discussed in light of this model.

The traditional electroclinic effect was demonstrated by Garoff and Meyer in the late 1970s.[1,2] An electric field **E** is applied parallel to the smectic-*A* plane just above the smectic-*A*–chiral-smectic-C^* transition temperature $T_{\text{Sm-}A\text{-Sm-}C^*}$. Since the molecules lack inversion symmetry, a nonzero molecular tilt θ is obtained, such that $\theta \propto E$ and the tilt lies in the plane normal to **E**. Moreover, because the tilt restoring force vanishes at $T_{\text{Sm-}A\text{-Sm-}C^*}$, the electroclinic coefficient C_E ($\equiv d\theta/dE$) diverges at the transition. Early work by Garoff and Meyer[1,2] on the material (*p*-decyloxybenzylidene)-*p*′-amino-(2-methylbutyl)cinnamate (DOBAMBC) indicated an anomalous exponent $\gamma = 1.11 \pm 0.06$ for the tilt susceptibility (i.e., C_E), although it was suggested by Beresnev *et al.*[3] that this result may in fact be due to a temperature-dependent coupling between the dipole and optical core of the molecule. Recently this hypothesis was given added plausibility when Li and Rosenblatt measured[4] a magnetoelectroclinic response consistent with the results of Garoff and Meyer. In light of a mean-field exponent obtained by Qiu, Ho, and Hark on another material,[5] Li and Rosenblatt concluded that the susceptibility is, in fact, mean field, but is masked by molecular flexibility.

Owing to the rapid optical response of the electroclinic effect, as well as its fundamental scientific interest, efforts have also been made to study this effect in phases other than the Sm-*A* phase. For example, Bahr and Heppke observed a molecular tilt linear in electric field in both the Sm-*B* and Sm-*E* phases.[6,7] As is the case with the Sm-*A* phase, these electroclinic effects rely on the existence of smectic symmetry. Recently, however, we showed that smectic ordering is *not* essential for the existence of a tilt linear in *E*.[8] Using a long-pitch chiral nematic phase in a thin sample, unwound by means of surface stabilization, we observed a tilt θ of the principal eigenvector of the optical dielectric tensor proportional to an applied electric field. In addition, we observed a rapid increase in the magnitude of this effect just above the nematic–smectic-*A* (*N*–Sm-*A*) phase transition temperature $T_{N\text{-Sm-}A}$. In this paper we report on detailed measurements of the electroclinic coefficient $C_E = d\theta/dE$ in the nematic phase just above $T_{N\text{-Sm-}A}$. Our central result is that because the magnitude of the electroclinic effect increases rapidly as the critical temperature is approached from above, the data can be fitted to a power law over only a narrow temperature region (less than one decade of reduced temperature, or of order 150 mK). Moreover, range shrinking indicates a nonconvergent exponent. In this region general theoretical considerations suggest that the microscopic environment of any molecule should *not* change rapidly. Thus this result suggests that the coupling of the electroclinic effect to smectic fluctuations and the resultant critical behavior near $T_{N\text{-Sm-A}}$ is considerably more complicated than we had originally proposed.[8]

We studied the material SCE12, which was kindly supplied to us by BDH Ltd. through EM Industries. The material was used as is. SCE12 is a compensated mixture with a pitch of many tens of microns over a temperature range several degrees above $T_{N\text{-Sm-}A}$. The material was inserted between two indium tin oxide–coated glass microscope slides, which had been treated with the polymer nylon 6/6 and rubbed to give homogeneous orientation. The sample spacing was nominally 25 μm, as determined by the thickness of a pair of Mylar spacers. Prior to the experiment the sample was checked by means of optical polarizing microscopy for the quality of alignment; excellent defect-free extinction was obtained when the director was oriented parallel or perpendicular to the polarizer. The sample was then housed in a well-insulated brass oven, where the temperature was controlled by a YSI model 72 controller to ±0.0015 °C; this stability is an order of magnitude better than in our original experiment reported in Ref. 8. The temperature differential across the sample was kept well under 0.001 °C by means of a focused laser spot. At the temperatures under investigation (within 3 °C of the *N*–Sm-*A* transition), the pitch is sufficiently large that the sample unwinds and is completely oriented by the action of the polymer treated surface.

The beam from a He-Ne laser, attenuated to approximately 0.1 mW, was incident along the x axis (Fig. 1) and polarized by a Glan-Thompson polarizer at an angle $\phi=\pi/8$ from the z axis in the y-z plane. The beam then passed through a 1.5-mm-diam pinhole and a lens of focal length 98 mm, such that it was focused to a spot with a diameter of approximately 65 μm at the sample. After being recollimated by a second lens, the beam passed through an analyzer and into a photodiode detector.

In the absence of an electric field the molecular director (and principal optical eigenvector) is oriented along the z axis. The eigenvectors of the optical dielectric tensor then correspond to the x, y, and z axes in the laboratory frame, and $\epsilon_z > \epsilon_x = \epsilon_y$. In the presence of an electric field E_x, however, the optical dielectric tensor undergoes a tilt θ in the y-z plane; this corresponds to the nematic electroclinic effect. It should be emphasized that this effect need *not* involve a net physical tilt of the molecule. Rather, for a molecule possessing an optical dielectric tensor which is not codiagonal with, for example, its inertial tensor, a rotational biasing of the molecule will result in an apparent tilt with respect to the z axis of the *rotationally averaged* optical tensor. This will be discussed in more detail below. Upon tilting, then, the eigenvectors of the dielectric tensor now correspond to

$$e_1 = y\sin\theta + z\cos\theta \ ,$$

$$e_2 = y\cos\theta - z\sin\theta \ ,$$

$$e_3 = x \ .$$

In the molecular frame ϵ_1 remains the largest eigenvalue. In principle ϵ_2 may remain equal to ϵ_3 if the tensor undergoes a simple tilt; in the nematic electroclinic effect reported herein, however, the system is expected to become slightly biaxial ($\propto E^2$). We note that in the laboratory frame the tilt θ corresponds to $\epsilon_{yz}/(\epsilon_{zz}-\epsilon_{yy})$. One can then show that to order θ the intensity at the detector is given by[5,6,9]

$$I \propto (\sin^2 2\phi - 2\theta\sin 4\phi) f(\Delta n) \ , \tag{1}$$

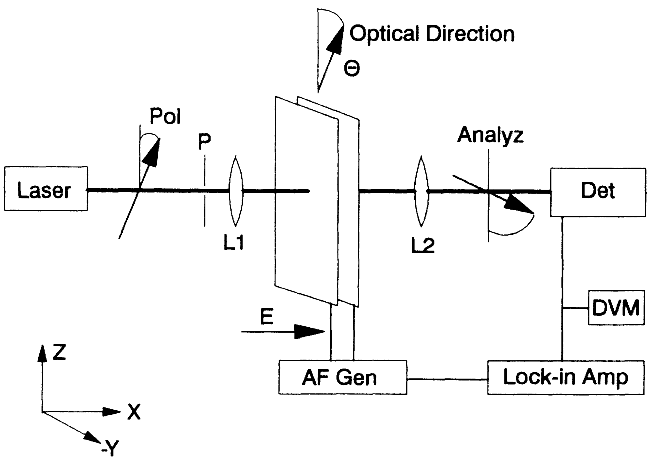

FIG. 1. Schematic model of experimental apparatus. $L1$ and $L2$ are lenses, and DVM is a digital voltmeter (see text).

where the function $f(\Delta n)$ accounts for not only the optical phase shift though the sample, but for reflectivities at the various surfaces as well. For $\phi=\pi/8$, we find $I \propto (1-4\theta) f(\Delta n)$.

An af generator at frequency $\nu = 2$ kHz was swept linearly in amplitude over approximately 85 s, resulting in a corresponding ramp in E_x. (In our earlier experiment it was found that the response was insensitive to frequency from 250 Hz to at least 10 kHz.) The tilt angle θ was therefore a sinusoid at frequency ν with amplitude increasing linearly in time. At the detector the intensity contained two components, given by Eq. (1). The dc term I_0 was measured using a digital voltmeter with a 22-s time constant filter. The ac term δI at frequency ν was measured with a lock-in amplifier referenced to the applied field and computer recorded every 0.3 s during the sweep. Taking the ratio of the ac to the dc terms, we find that

$$\theta = \delta I / 4 I_0 \ , \tag{2}$$

where $f(\Delta n)$ has dropped out. Figure 2 shows a typical plot of the deduced tilt angle θ versus the applied field from the computer recorded data. The electroclinic coefficient C_E is defined by the slope $d\theta/dE$. A typical experimental run is shown in Fig. 3, where the nematic–smectic-A transition temperature was determined to be 82.202±0.001 °C.

In measuring the nematic electroclinic effect, it was important to account for several potential artifacts. First, we have chosen a material with a negative low-frequency dielectric anisotropy. This avoids the possibility of a Fréedericksz transition, although the experiment must be performed at a sufficiently high frequency to avoid a Carr-Helfrich instability.[10] We also considered the effects of a tilt in the x-z plane. In that case it can easily be shown that δI to lowest order would scale as θ^2, and no signal would be observed at the modulation frequency. Finally, in order to verify that the effect requires chiral symmetry, we measured the electroclinic coefficient in the nonchiral material methoxybenzylidene butylanaline (MBBA) in the nematic phase near room temperature. As is the case with SCE12, the low-frequency dielectric anisotropy is negative. Within the resolution of our apparatus ($d\theta/dE \sim 1.5\times10^{-13}$ m/V), no electronic effect was observed.

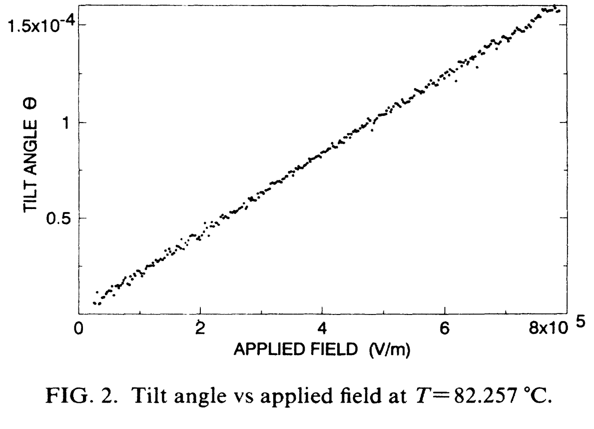

FIG. 2. Tilt angle vs applied field at $T=82.257$ °C.

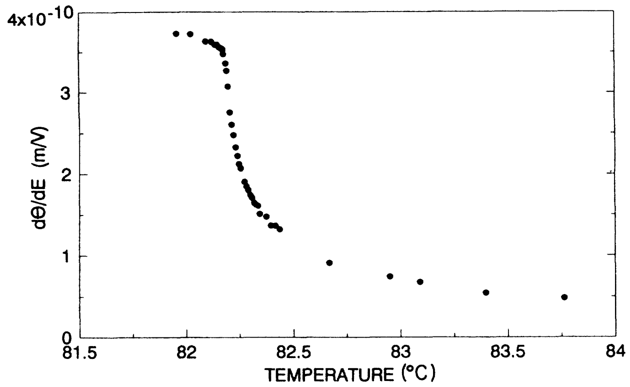

FIG. 3. Electroclinic coefficient vs temperature. Note rapid change in $d\theta/dE$ just above $T_{N\text{-Sm-}A}=82.202$ °C.

In order to ascertain the effects of a magnetic field, the sample was installed in the bore of an 8.2-T superconducting magnet with field **H** oriented along the z axis and possessing transverse-optical ports. At a fixed temperature $T=83.42$ °C, $d\theta/dE$ was measured as a function of field, and the results are shown in Fig. 4. Although a very slight increase in C_E was observed at higher fields, we feel that this effect is due to the magnetic field slightly improving the surface-induced alignment, rather than to any underlying physics. This conclusion is confirmed by the fact that $d\theta/dE$ approaches a constant value at high fields, whereas the most rapid change in $d\theta/dE$ occurs at fields below 1 T. In this range of fields the magnetic penetration depth ξ, the distance over which any surface misalignment is rotated parallel to **H**, crosses over from being larger than to being smaller than the sample spacing. Here $\xi=(K_{22}/\Delta_\chi H^2)^{1/2}$, where K_{22} is the twist elastic constant and Δ_χ is the magnetic susceptibility anisotropy. Thus magnetic fields of these magnitudes seem to play no role in the nematic electroclinic effect.

If the order parameter were spatially varying there would be a linear coupling between the director and the electric field—the so-called flexoelectric effect.[11] We have checked the possible flexoelectric terms, however, and find that they are small in our geometry. Moreover, as discussed above, our large magnetic field would be expected to significantly alter the director if it were indeed spatially varying. Because the total optical phase shift of the sample is of the order 60π, a flexoelectric effect would imply a rapidly varying optical signal as the applied magnetic fields were altered. This was not observed. Similarly, if the effect were actually a surface phenomenon rather than a bulk electroclinic effect, the optical signal would be expected to vary rapidly with sample thickness, which was not observed either.

Consider now a simple symmetry-based model of the electroclinic effect in a uniaxial phase.[8] If only one traceless, symmetric, second-rank tensor order parameter is considered, then it is easy to see that there are no symmetry-allowed terms linear in the electric field, i.e., no terms which can be responsible for the electroclinic effect. In order to describe the electroclinic effect, in consequence, we consider two distinct order parameters Q and T (Fig. 5). We will assume, although this is not necessary, that Q describes the orientation of the long axes of the molecules which are aligned by strong microscopic interactions, and that T describes the order of some less anisotropic axis of the molecules. This axis is aligned because it is in an anisotropic environment; thus T is small compared to Q. For a one-component system a microscopic model for $Q=\langle q\rangle$ and $T=\langle t\rangle$ could be

$$q_{ij}=n_{1i}n_{1j}-\tfrac{1}{3}\delta_{ij}\ ,$$

$$t_{ij}=n_{1i}n_{2j}+n_{2i}n_{1j}-\tfrac{2}{3}\delta_{ij}\mathbf{n}_1\cdot\mathbf{n}_2\ ,$$

where $\mathbf{n}_1$ is a unit vector along the main axis of the molecule and $\mathbf{n}_2$ is a unit vector along some other axis of the molecule. For a multicomponent system like SCE12 the tensor q, at least, should be appropriately averaged over

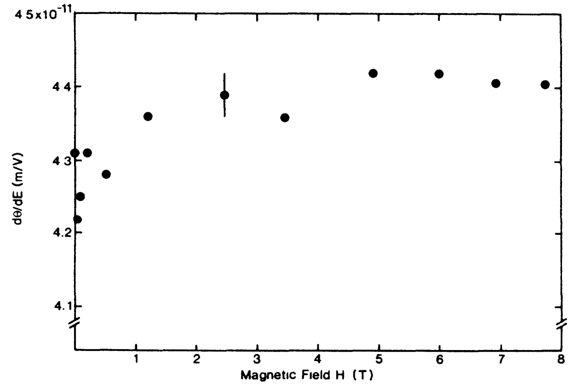

FIG. 4. Electroclinic coefficients vs magnetic field at $T=83.42$ °C.

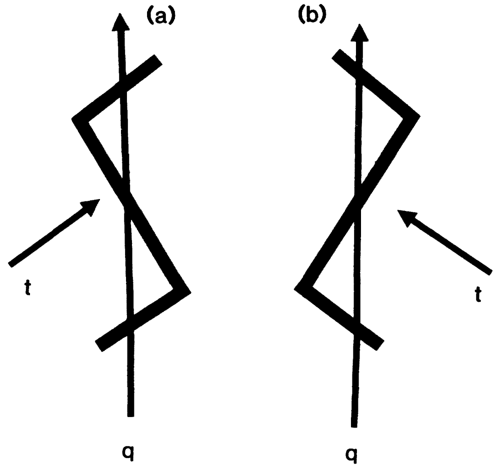

FIG. 5. Schematic representation of molecules. Arrows indicate the principle directions of tensor q and t. For $E=0$, both configurations are equally likely and Q and T are codiagonal. For $E\neq 0$ either (a) or (b) is preferred, such that Q remains unchanged but T is no longer codiagonal with Q.

the various molecular species. In terms of these order parameters and in the absence of a magnetic field the allowed terms in the free energy, in addition to the usual terms in the order parameter Q, are

$$\Delta F = a\epsilon_{ljk}E_l Q_{ik}T_{ij} - bQ_{ij}T_{ij} + \tfrac{1}{2}cT_{ij}T_{ij} \ . \tag{3}$$

Here and below we use the convention that repeated indices are summed over. Minimizing Eq. (3) with respect to T results in an electroclinic effect proportional to a/c.

The electroclinic term, that is, the term proportional to a, can on a microscopic basis be understood heuristically as follows. Suppose that the chiral group is attached directly to the rigid part of the molecule so that its orientation can be described by $\mathbf{n}_1$ and $\mathbf{n}_2$, and that $\mathbf{n}_2$ is chosen to be a unit vector both perpendicular to the dipole of the chiral group and not parallel to $\mathbf{n}_1$. The chiral electric dipole is then

$$\mathbf{d} = \mu\mathbf{n}_1 \times \mathbf{n}_2 = \mu\mathbf{x}_l \epsilon_{ljk} q_{ik} t_{ij} \ , \tag{4}$$

where $\mathbf{x}_l$ is the unit vector in the l direction and μ is related to the magnitude of the chiral electric dipole. Then the average of the energy of this dipole in the electric field, $-\mathbf{E}\cdot\mathbf{d}$, has exactly the form of the electroclinic term in the free energy.

There is no essential change in this analysis at the nematic–smectic-A transition. Only the rotational symmetry, which does not change at the nematic–smectic-A transition, is important to the argument. Thus it is expected that the electroclinic coefficient should have the same critical behavior as the energy. More explicitly it is expected that the only effect of this transition on the electroclinic effect is that the coefficients a and c become functions of the square of the smectic order parameter ψ and that they and the electroclinic coefficient $d\theta/dE$ can be expanded in the form $A + B\langle|\psi|^2\rangle$ near the transition. This expansion is expected to be valid unless the parameter c is close to zero near the transition. When c is zero, however, there is a transition to a tilted, e.g., smectic-C, phase. As it is known that there is a wide smectic-A range, it is not expected that c is close to zero at the N–Sm-A transition, as it would be if this point were close to an N–Sm-A–Sm-C point.

The proposed model suggests that owing to smectic fluctuations, a cusp would be expected near the N–Sm-A transition. The associated critical exponent would be $\Omega = 1 - \alpha$, commensurate with the exponent for the short-distance correlation function $|\langle\psi^2\rangle|$. To date, however, the critical exponents associated with the N–Sm-A transition have been somewhat equivocal.[12–17] Values reported for the exponent α, for example, have ranged from near tricritical ($\alpha = 0.5$) for some materials to slightly less than zero for others. It has been suggested[12,14] that this variation is due to the presence of a nearby tricritical point, such that a large crossover regime exists. That being the case, we would ideally like to use a material with well-defined critical behavior. In principle, a material with a very large nematic range is unlikely to be close to a nematic–smectic-A tricritical transition; we expect this to be the case for SCE12, the material discussed herein, whose nematic range is nearly 40 °C. The exponent α is thus expected to be near zero for this material, although an attempt by Huang and Johnson to measure the specific-heat exponent was thwarted by the otherwise useful large nematic range and concomitant small experimental signal.[18]

Given the expected behavior of α, we have attempted to fit the electroclinic data in the nematic phase in order to determine whether the effect is consistent with an exponent $\Omega = 1$. Three separate experimental runs were analyzed, all with similar results. The data were first numerically differentiated with respect to temperature, and the transition temperature $T_{N\text{-Sm-}A}$ was chosen at the point where $|dC_E/dT|$ is maximum. Owing to the steep rise in $\delta\theta/dE$ near the transition, it was possible to easily locate $T_{N\text{-SM-}A}$ to within 1 mK. (A more accurate determination of $T_{N\text{-Sm-}A}$ is physically insignificant owing to the inherent temperature stability of the apparatus.) A least-squares fit was then performed to extract the three remaining parameters in the function

$$\frac{d\theta}{dE} = C_E^0 - k(T - T_{N\text{-Sm-}A})^{\Omega} \ , \tag{5}$$

where C_E^0 is the electroclinic coefficient at the N–Sm-A transition and k is a constant. Because of the extremely rapid decrease of $d\theta/dE$ with temperature just above the N–Sm-A transition it was not possible to fit Eq. (5) over a large temperature range. (Note that there is no reason why $d\theta/dE$ cannot change sign above some temperature, although experimentally it appears that $|d\theta/dE|$ decreases monotonically with increasing temperature.) Moreover, because of the rapid change in C_E, we have omitted from Eq. (5) the term linear in temperature, which would not only be difficult to fit, but would also be unlikely to play a significant role. Thus, with the somewhat severe limitation of using only those data which fall within approximately 150 mK of $T_{N\text{-Sm-}A}$, we utilized a range-shrinking procedure to determine a converging limit for the exponent Ω. We chose the first 13 points above $T_{N\text{-Sm-}A}$, then the first 12, then the first 11, and so on, successively fitting each set of points to Eq. (5). Figure 6 represents a log-log plot of one such fit, where the

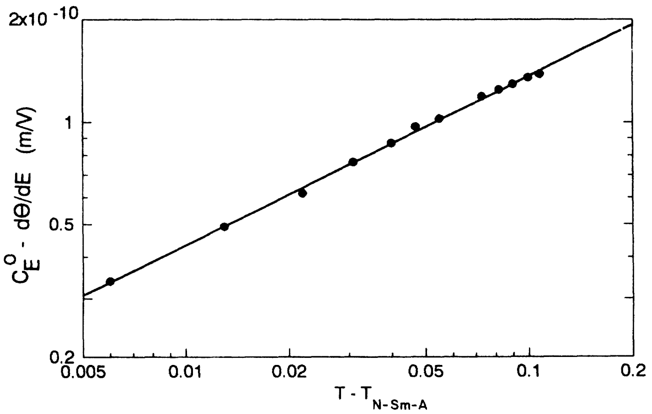

FIG. 6. Log-log plot of $dh/dE\text{-}C_E^0$ vs reduced temperature using 12 points in the fit.

slope corresponds to a value $\Omega=0.503$. (Notice that at higher temperatures the data points, had they been shown, would curve over, with a slope decreasing to a limiting value of zero.) In this manner we obtained the best-fit exponent Ω as a function of the number of points chosen for the fit. This result is shown in Fig. 7, where the temperature corresponds to the temperature of the nth point in a set of n data points. From Fig. 7 it is clear that, even over this small temperature range very close to $T_{N\text{-Sm-}A}$, there appears to be no convergence of Ω, which suggests that the electroclinic coefficient is not well described by Eq. (5).

In order to better understand these apparently anomalous results, we have measured the birefringence and low-frequency dielectric constants of SCE12. The birefringence apparatus, which is based upon a modulated Pockels cell, is described in detail elsewhere.[19] Near the N–Sm-A transition a small increase in the slope $d\Delta n/dT$ was observed, although owing to experimental noise it was difficult to reproduce the shape of the curve, and impossible to extract information about the critical behavior. Without a doubt our difficulties arise from the fact that the nematic temperature range is so large that the nematic order parameter is already close to 1. The coupling to smectic order would thus be quite small.

The dielectric results, on the other hand, were considerably cleaner. Two indium tin oxide–coated slides were etched to leave small conducting squares of area 5.5×10^6 μm^2 which served as the capacitor plates. Homogeneous orientation was obtained by unidirectional rubbing and homeotropic orientation by the deposition of the surfactant hexadecyltrimethylammonium bromide; alignment quality was checked with a polarizing microscope. Sample spacing was controlled by Mylar spacers, such that the spacing was approximately 10 μm for the homogeneous orientation and 25 μm for the homeotropic orientation. Capacitance measurements were performed using a dedicated oven and an Andeen and Associates model CGA-83 capacitance bridge operating at 1 V and 1000 Hz. The parallel dielectric constant (homeotropic orientation) was obtained assuming a nominal sample thickness of 25 μm. The perpendicular dielectric constant (homogeneous orientation) was obtained by using a thickness 10.23 μm, a value obtained from the ratio of capacitances from the two samples at a temperature $T=132.46$ °C in the isotropic phase. The results are shown in Fig. 8. Although the relative results are highly precise, the absolute accuracy may be in error by as much as ±15% owing to the uncertainty in the original (25 μm) sample thickness and temperature gradients across the active area of the plates.

We now turn to a discussion of these results. The fact that the electroclinic effect grows rapidly on approaching the smectic-A phase is of considerable interest. By changing the temperature it is possible to change in a straightforward and easily controllable way the microscopic environment in a manner which is shown experimentally to strongly affect the electroclinic behavior. As the electroclinic coefficient in an untilted phase is proportional to the polarization in the corresponding tilted phase, this suggests that translational order is of considerable importance (at least in SCE12) to the polarization of the tilted (smectic-C) phase. The hypothesis that translational order is important to the polarization of the chiral smectic-C phase is supported by magnetoelectroclinic measurements[4] near the Sm-A–Sm-C transition in DOBAMBC, which show that the coupling between the tilt of the optical dielectric tensor and the polarization varies more rapidly with temperature than does the coupling between this tilt and the magnetic susceptibility anisotropy. Since the translational order varies much more rapidly with temperature than most common microscopic properties (for example, the free-space probabiilty for a carbon-carbon bond to be *trans* or *gauche*), this result would be expected if translational ordering were very important to the electroclinic effect and polarization of liquid crystalline phases. Thus it is of basic and applied interest to understand the relationship between translational ordering and electrical properties.

We have argued that the parameter c does not vary

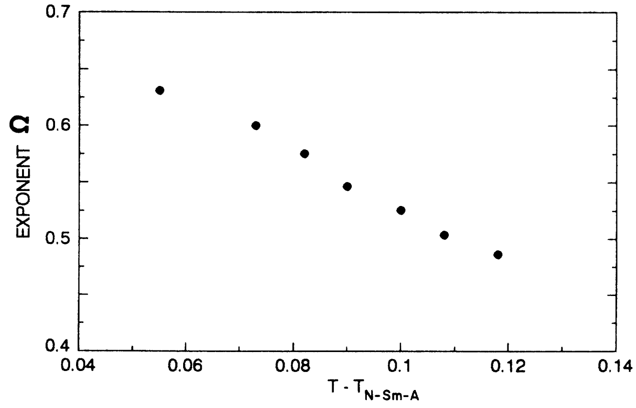

FIG. 7. Exponent Ω [cf. Eq. (5)] vs reduced temperature. To obtain Ω, all points lying between $T_{N\text{-Sm-}A}$ and the temperature shown were used in the fit. Note that Fig. 6 represents one of these points.

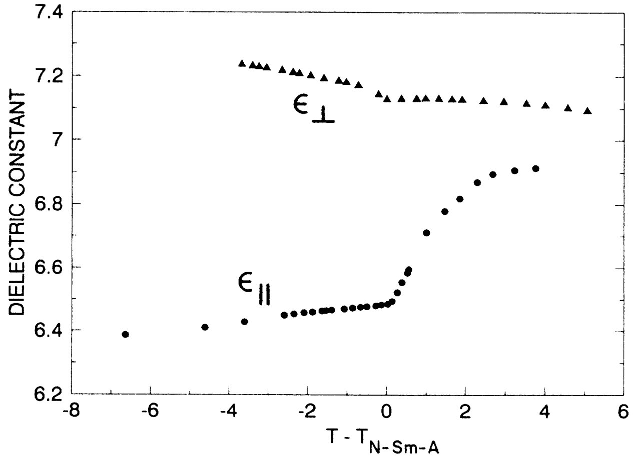

FIG. 8. Parallel and perpendicular dielectric constants of SCE 12 vs temperature.

rapidly.[8] It follows that a, which depends on the magnitude of Q, the low-frequency dielectric constant, and the smectic order parameter, must grow rapidly with the local smectic order. From the point of view of a symmetry based Landau theory all these effects are identical, since at the transition each of these effects is expected to vary as a function of the square of the smectic order parameter $|\psi|^2$. Different microscopic mechanisms, however, will distinguish between these different effects, as will various quantities other than the electroclinic effect.

One such quantity is the birefringence of light in the region of the transition. As discussed above, this shows a smooth increase with decreasing temperature and only a small, virtually undetectable cusp at the transition temperature. This demonstrates that the degree of nematic order, and by inference the magnitude of the order parameters Q and T, do not change rapidly near the transition. Thus variation in these parameters does not seem to be the reason for the rapid variation in the electroclinic effect.

The dielectric data also give important qualitative information. Data for the dielectric constant parallel and perpendicular to the director show slow variation (at least compared to $d\theta/dE$) in the region of the transition. This shows that there is no rapid change either in dipole correlations or in the coupling of the average dipole to the electric field at the transition.[20] In consequence, a rapid increase in the coupling between the average dipole and the electric field, that is, an increase in the effective field on the molecular dipoles, does not seem to be the reason for the increase in the electroclinic effect.

Finally we stress that all these measured quantities are expected, *a priori,* to have the same dependence on temperature as the electroclinic effect. However, none of these quantities has in common with the nematic electroclinic effect the fact that it (i) changes greatly in magnitude on approaching the N-Sm-A transition and (ii) seems to have a strong cusp at the transition. Thus it is difficult to explain the behavior of the electroclinic effect on the grounds that $|\psi|^2$ has an anomalous behavior near the N–Sm-A transition in SCE12.

It would therefore appear that the increase in the electroclinic effect, in a microscopic sense, is due directly to the increase in smectic order. However, examination of Landau-like models, e.g., those for the N–Sm-A–Sm-C point,[21,22] which involve both tilted molecules and translational ordering, does not seem to give any insight into this issue. A symmetric tensor which plays an important role in the Chen-Lubensky theory can be formed from derivatives of the smectic order parameter ψ,

$$t'_{ij}=(\partial_i\psi)(\partial_j\psi^*)-\tfrac{1}{3}\delta_{ij}|\nabla\psi|^2\ . \tag{6}$$

This tensor and, in fact, the (pseudovector) tilt of the layer spacing relative to the director $p_l=\epsilon_{ljk}Q_{ij}t'_{ik}$ is essentially taken to be the order parameter for the smectic-C phase. In a chiral material there is the possibility of a term of the form $\mathbf{E}\cdot\mathbf{p}$ in the free energy. Such a term has exactly the same form as the electroclinic term in Eq. (3) with t' replacing t; it is therefore expected to result in an electroclinic effect. A difference, however, is that the susceptibility for the tensor t' is not a parameter of the theory but must be deduced from the fluctuations in ψ. The integral giving this susceptibility, assuming Gaussian fluctuations around the mean-field solutions, is infrared convergent but ultraviolet divergent (the integrand goes as $k^{d-1}dk$ for large k, the spatial dimensionality being $d=3$), that is, it depends largely on short-range fluctuations which are expected to change only slowly at the transition. It is therefore expected to behave like the energy, exactly as suggested for the susceptibility c above.

The more involved treatment of fluctuations given by Grinstein and Toner[22,23] results in the same conclusion. In the smectic phase, which is the basis of these treatments, this term results in a nonsingular modification of the layer fluctuations. However, it is the conclusion of Ref. 23 that the detailed nature of the layer fluctuation amplitude is irrelevant to the N–Sm-A transition. Thus we see that there is no reason to suppose that the increase in smectic order or the formation of cybotactic layers should have significant effects on the electroclinic effect. We also conclude that there is no way at the level of critical phenomena to distinguish between the effects of a coupling between the director q and t, a tensor internal to the molecules, or t', a tensor having to do with the relative positions of different molecules. In fact it is certainly the case that a complete micoscopic treatment would involve both these tensors. A possible microscopic origin of the coupling of the electric field to the two tensors (q,t) describing single molecules seems clear from the discussion above, whereas the effects of the relative positions of other molecules are not as immediately clear. However, even if the molecular interaction effects are the major cause of the electroclinic effect, they are not expected to result in the observed rapid variation in the electroclinic effect, provided they are short ranged.

We now consider the possibility that the anomalous behavior of the electroclinic effect arises from an interaction which is long ranged; for example, an electric field on one molecule inducting a tilt on distant molecules. We do not believe that this can be the case. There is no reason to suppose that the molecular interactions are long ranged. In this sense long ranged means decaying more slowly than the inverse cube of the distance on length scales larger than or comparable to the correlation length. It is expected on dimensional grounds that this correlation length should be of order $(10\ \text{Å})\times t^{-\nu}$, where ν is between 0.5 and 0.7. If correlation lengths were much shorter than this it would imply a larger singularity in the specific heat than has been observed by Huang and Johnson.

Long-range interactions might also arise from elastic distortions of the nematic director. However, it is clear from rotation invariance that an electric field perpendicular to the director will not produce any torque with a component parallel to this electric field. (The electroclinic effect does not result from such a torque, but rather from the biasing of the rotation around the director.) Indeed, no net torque linear in the electric field is possible in the nematic phase. It follows that the electroclinic tilt induced by an electric field in one region of space does not induce any elastic distortions in the surroundings. This is important as such a tilt would (i) be long range and (ii) depend on the elastic constants of the nematic, which are known to vary rapidly near the N–Sm-A transition and could well result in an anomalous behavior of the electroclinic effect. We have verified this lack of torque and elastic distortion by examining Landau free energies in which there are several tensor order parameters which can vary in space and including electroclinic interactions of the form of Eq. (3). It can readily be verified that the electric field does not couple to the elastic distortions. The essential point is that in a uniaxial nematic phase, on sufficiently long distance scales, elastic distortions can be described by a single traceless, symmetric, unimodular tensor $Q_{ij}(x)=\frac{1}{2}[3n_i'(x)n_j'(x)-\delta_{ij}]$ where n' is a unit vector field and the elastic free energy given by the usual Oseen-Frank free energy is a function of n'. No gradient-free term proportional to the electric field is allowed with this single tensor. In fact any such chiral term involves at least two gradients. As all elastic distortions can be described by this tensor, independent of the detailed Landau free-energy functional, it follows that there is no effective torque on long length scales where the elastic description is valid.

Thus the only explanation consistent with our observations appears to be that the microscopic source of the electroclinic effect is such that it depends unexpectedly strongly on the *local* smectic order and, for example, may not be well approximated by a term proportional to $|\psi|^2$. This is of interest because microscopic theories of the polarization depend on the pair interactions between molecules.[3,24] These interactions may vary quite rapidly with the relative displacement of the molecules along the director or layer normal, for displacements large compared to the typical atomic radius of a few angstroms. They are therefore expected to increase with increasing smectic order. However, the probability that molecules have relative displacements small compared to a typical atomic size is significant even in the nematic phase, and is not expected to vary rapidly near the nematic–smectic-A transition, as is confirmed by x-ray measurements on other materials. Thus, it is unclear how arguments based on the changing averages of pair potentials between a single species of rigid molecules can result in an electroclinic effect with the observed rapid variation.

Rapid variation of the electroclinic effect would be expected, however, if it arises from a state which is quite unlikely in the nematic phase but whose probability *increases rapidly* in the smectic state. In particular, suppose that the electroclinic effect arises from a state whose free energy, relative to the Gibbs potential of the mesogen, is given by $A\text{-}B|\psi|^2$, where the units of ψ are such that $|\psi|=1$ corresponds to a perfectly ordered smectic. Moreover, if B is positive and has a magnitude a few times the thermal energy, then the probability of this state and, by hypothesis the electroclinic coefficient, will increase rapidly with increasing smectic order. For this to be consistent with the known properties of phase transitions A must also be of order of B or larger, otherwise the change in the probability of this state will make too large a contribution to the entropy change, or equivalently to the specific heat. The above scenario is consistent with the small size of the electroclinic effect and with the fact that the polarization, even for the highly tilted molecules well into the Sm-C phase, is small [approximately 0.1 D/(rad molecule)] compared to the typical molecular dipole of 2–5 D per molecule.

One possible microscopic interpretation of such a variation is that in the nematic state the molecule is flexible between the chiral center and the optically responsive part of the molecule, so that the coupling between the dipole on the chiral center and the optically responsive part of the molecule averages out.[3,4] In the smectic state, moreover, this flexibility is decreased, for example, because the bent configurations which result in this flexibility have significantly higher energy because they result in conformations inconsistent with the increasing translational order. A rapid variation in $d\theta/dE$ would then be obtained near $T_{N\text{-Sm-}A}$. Along similar lines smectic ordering in mixtures may favor orientational ordering of molecules with strong optical anisotropy only when they are in close register with the chiral molecules. Still other explanations are possible and, given that the structure of SCE12 is not known to us, we will not speculate further.

Finally, we must consider the possibility that the nematic–smectic-A transition for SCE12 is not, in fact, well described by the classical XY picture. Rather, the transition may be closer to a tricritical point than we assumed above, despite the extremely large nematic temperature range. If this were the case the value of the heat capacity exponent α might actually be of order 0.1 or 0.2, values not inconsistent with our measurements of Ω. Nevertheless, both the dielectric and heat capacity results argue against such a scenario, as does the fact that the electroclinic effect is much smaller far above $T_{N\text{-Sm-}A}$. We intend to investigate this further.

In conclusion we have measured the electroclinic effect in a nematic liquid crystal. As this quantity is not closely related to the smectic-A order parameter, it is predicted to vary slowly close to [within O(1 K)] the transition. Experimentally, however, it increases rapidly in this region and, even within 100 mK of the transition, does not seem to have the critical behavior expected from symmetry-based theories within the range of our experiments. We conclude that translational order is quite important for the electroclinic effect and, in consequence, is likely to be important to the polarization in the smectic-C phase, at least in this material. We have speculated that the microscopic reason for this is that there is relatively little coupling between the chiral dipole and the optically responsive part of the material in the nematic phase, but that their coupling is appreciably increased by the smectic order.

We have benefited from conversations with Noel Clark, Carl Garland, Robert Akins, and Donald Scheule. In particular, we wish to thank Jing Huang and David Johnson for sharing their heat capacity results for SCE12 with us. This work was supported by the National Science Foundation, Division of Materials Research, under Grant Nos. DMR-8796354 and DMR-8614093, and by the Ohio Board of Regents.

---

[1] S. Garoff and R. B. Meyer, Phys. Rev. Lett. **38**, 848 (1977).

[2] S. Garoff and R. B. Meyer, Phys. Rev. A **19**, 338 (1979).

[3] L. A. Beresnev, L. M. Blinov, M. A. Osipov, and S. A. Pikin, Mol. Cryst. Liq. Cryst. **158A**, 3 (1988).

[4] Z. Li and C. Rosenblatt, Phys. Rev. A **39**, 1594 (1989).

[5] R. Qiu, J. T. Ho, and S. K. Hark, Phys. Rev. A **38**, 1653 (1988).

[6] Ch. Bahr and G. Heppke, Liq. Cryst. **2**, 825 (1987).

[7] Ch. Bahr and G. Heppke, Phys. Rev. A **37**, 3179 (1988).

[8] Z. Li, R. G. Petschek, and C. Rosenblatt, Phys. Rev. Lett. **62**, 796 (1989); **62**, 1577(E) (1989).

[9] G. Anderson, I. Dahl, P. Keller, W. Kuczynski, S. T. Lagerwall, K. Skarp, and B. Stebler, Appl. Phys. Lett. **51**, 640 (1987).

[10] See P. G. deGennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, England, 1975).

[11] R. B. Meyer, Phys. Rev. Lett. **22**, 918 (1969).

[12] C. W. Garland, M. Meichle, B. M. Ocko, A. R. Kortan, C. R. Safinya, L. J. Yu, J. D. Litster, and R. J. Birgeneau, Phys. Rev. A **27**, 3234 (1983).

[13] D. Davidov, C. R. Safinya, M. Kaplan, S. S. Dana, R. Schaetzing, R. J. Birgeneau, and J. D. Litster, Phys. Rev. B **19**, 1657 (1979), and references therein.

[14] J. Thoen, H. Marynissen, and W. Van Dael, Phys. Rev. Lett. **52**, 204 (1984).

[15] J. Thoen, H. Marynissen, and W. Van Dael, Phys. Rev. A **26**, 2886 (1982).

[16] C. A. Schantz and D. L. Johnson, Phys. Rev. A **17**, 1504 (1978).

[17] P. Brisbin, R. DeHoff, T. E. Lockkart, and D. L. Johnson, Phys. Rev. Lett. **43**, 1171 (1979).

[18] D. L. Johnson and J. Huang (private communication).

[19] C. Rosenblatt, J. Phys. (Paris) **45**, 1087 (1984).

[20] W. H. deJeu, W. J. A. Goossens, and P. Bordewijk, J. Chem. Phys. **61**, 1985 (1974).

[21] J.-H. Chen and T. C. Lubensky, Phys. Rev. A **14**, 1202 (1976).

[22] G. Grinstein and J. Toner, Phys. Rev. Lett. **51**, 2386 (1983).

[23] J. Toner, Phys. Rev. B **26**, 402 (1982).

[24] M. A. Osipov, Ferroelectrics **58**, 305 (19984).