

Origin of the anomalous electroclinic susceptibility exponent in a ferroelectric liquid crystal

Zili Li and Charles Rosenblatt

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106

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Crossed magnetic and electric fields were applied to the chiral liquid crystal *p*-decyloxybenzylidene-*p*'-amino-2-methylbutylcinnamate (DOBAMBC) in the smectic-*A* phase in such a way as to maintain the director orientation normal to the smectic layers. Near the smectic-*C** transition it was found that $E \propto H^2$ and that dE/dH^2 versus temperature exhibits behavior consistent with a temperature-dependent polarization-tilt coupling coefficient. This result offers an explanation for the anomalous electroclinic susceptibility exponent $\gamma=1.11$ observed by Garoff and Meyer [Phys. Rev. Lett. **38**, 848 (1977)].

In 1977 Garoff and Meyer demonstrated the existence of an electroclinic effect above the smectic-*A*-smectic-*C** transition in liquid crystals composed of chiral molecules.^{1,2} In this effect an electric field E is applied parallel to the plane of the smectic layers, coupling to the molecular dipole moment. If the molecules lack inversion symmetry, a nonzero molecular tilt angle θ obtains, such that $\theta \propto E$. Using the material *p*-decyloxybenzylidene-*p*'-amino-2-methylbutylcinnamate (DOBAMBC), they measured the electroclinic coefficient $d\theta/dE$ as a function of temperature above the Sm-*A*-Sm-*C** transition temperature T_{A-C^*} ; their results indicate that $d\theta/dE$ diverges as $(T - T_{A-C^*})^{-\gamma}$, where $\gamma = 1.11 \pm 0.06$. This exponent is inconsistent with both the mean-field value $\gamma=1$ and the three-dimensional *XY* value $\gamma=1.32$. During the intervening years no experiment has satisfactorily explained this anomalous behavior, although interest has remained high. Pozhidayev *et al.* used an indirect pyroelectric technique on DOBAMBC to show that the susceptibility exponent γ is consistent with the mean-field value.³ Beresnev *et al.* suggested that the anomalous electroclinic result is due to a temperature-dependent coupling between the molecular dipole and the optically polarizable molecular core,⁴ although they offered no evidence for this assertion. By contrast, Bahr and Heppke found that the induced tilt:polarization ratio in a different material is independent of temperature within the Sm-*A* phase.⁵ More recently, Qiu, Ho, and Hark used a three-component mixture to obtain a value $\gamma = 1.04 \pm 0.05$ in a direct electroclinic measurement.⁶ Although this value is again consistent with the mean-field-like exponents generally observed at the Sm-*A*-Sm-*C* phase transition⁷⁻⁹ it still leaves open the question of the anomalous Garoff-Meyer result in DOBAMBC.

In this paper we report on results from a "magneto-electroclinic" measurement in the smectic-*A* phase of DOBAMBC, whereby crossed magnetic and electric fields were applied so as to maintain the director orientation normal to the smectic layers. It was found that this perpendicular condition is always satisfied for $E \propto H^2$, although a weak temperature dependence to the quantity dE/dH^2 was observed. We feel that this temperature dependence provides an explanation for the anomalous

DOBAMBC result for γ .

Samples of DOBAMBC were obtained from two sources. One lot was synthesized by Dr. Patrick Keller in 1977; T_{A-C^*} was approximately 95.3°C. A second lot was obtained from Aldrich Chemicals; despite attempts at recrystallization, the second material exhibited an Sm-*A*-Sm-*C** transition temperature approximately 10 K lower, with a purity estimated at about 97%. Nevertheless, both materials gave quantitatively very similar results in the experiment, and we feel that it is unlikely that the effect reported herein is strongly purity dependent. This conclusion is also consistent with the observations of Ref. 1. The sample was housed between two glass microscope slides separated by a pair of 125- μ m-diam gold-plated molybdenum wires. The parallel wires, separated by 0.55 cm, also served as electrodes, permitting the application of an electric field E in the plane of the slides. The slides were treated with the surfactant hexadecyltrimethyl ammonium bromide, resulting in homeotropic orientation of the director on cooling from the isotropic into the smectic-*A* phase [see Fig. 1(a)]. The sample was then placed in a brass oven, temperature controlled to 5 mK, which in turn was housed in the bore of a superconducting magnet with optical access. In terms of the coordinate convention at the bottom of Fig. 1, the director was oriented at an angle $\pi/4$ relative to the z axis in the xz plane, the magnetic field was oriented parallel to the z axis, the electric field parallel to the y axis, and the incident laser light along the x axis. For $H \neq 0$ the director underwent a finite tilt $\theta \propto H^2$ [Fig. 1(b)], resulting in a linear change in the optical birefringence Δn .⁷ (The birefringence apparatus, which is based upon a modulated Pockels cell and sensitive to phase shifts $\Delta\phi \sim 10^{-4}$, is described in detail elsewhere.¹⁰) Application of an electric field along the y axis then induced a reverse tilt $-\theta \propto E$, returning the orientation and birefringence to their original values [Fig. 1(c)]. The tilt θ with electric field is just the usual electroclinic effect. At each temperature T in the smectic-*A* phase several values of H were applied up to approximately 25 kG. For each magnetic field, we measured the value of the applied electric field E which was necessary to return the orientation to $\theta=0$. Despite the diverging response of Δn as the Sm-*A*-Sm-*C** transi-

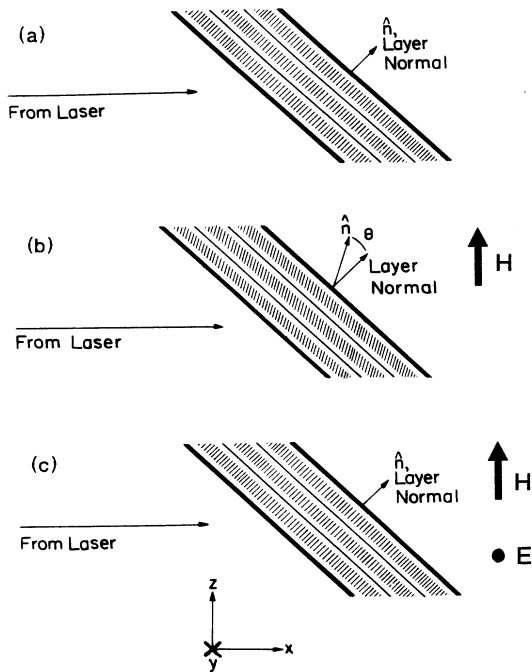


FIG. 1. Schematic view of experimental arrangement. (a) Undisturbed smectic- A sample. (b) Tilt of director in the presence of a magnetic field. (c) Crossed E and H fields, causing the director to tilt by equal and opposite amounts, resulting in zero net tilt. The coordinate system is at the bottom of figure.

tion was approached, it was found that E was linear in H^2 for all temperatures. The slope dE/dH^2 was then obtained by a linear least-squares fit for each temperature, and the results are shown in Fig. 2.

In order to understand the results one needs to investigate the free energy g for the smectic- A -smectic- C^* transition. Adopting the notation of Ref. 1, we find

$$g = g_A + \frac{1}{2} A'(T) \theta^2 + O(\theta^4) + \frac{1}{2} \chi_P^{-1} P^2 - PE - 8\pi^{-1} \epsilon^0 E^2 - t\theta P - \frac{1}{4} \chi_M H^2 \theta. \quad (1)$$

P is the component of polarization parallel to E , ϵ^0 the dielectric constant in the absence of a permanent dipole, χ_P the generalized susceptibility, t the coefficient coupling θ and P , and χ_M the magnetic susceptibility anisotropy. Note that the last term in Eq. (1) is linear in θ because H is oriented at an angle $\pi/4$ relative to the layer normal. Since P and θ are treated as independent variables, g must be minimized with respect to both. We thus find that

$$\theta = \frac{tE\chi_P + \frac{1}{2} \chi_M H^2}{A(T)}, \quad (2)$$

where $A(T) = A'(T) - \chi_P t^2$. $A(T)$, of course, corresponds to the strength of the smectic- A restoring force and vanishes at the smectic- A -smectic- C^* transition; the presence of the term $\chi_P t^2$ just introduces a slight shift in T_{A-C^*} . From Eq. (2) we immediately find the magneto-clinic coefficient $d\theta/dH^2 = \frac{1}{2} \chi_M/A(T)$ and the electro-clinic coefficient $d\theta/dE = t\chi_P/A(T)$. In principle, both quantities should exhibit identical critical behavior deter-

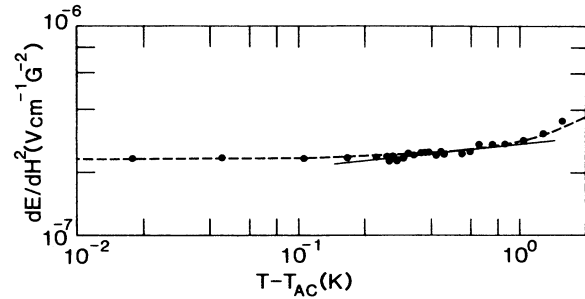


FIG. 2. dE/dH^2 vs $T - T_{A-C^*}$. The solid line segment represents an algebraic fit to the data over a finite-temperature region (see text). The dashed line represents a fit using Eq. (3) and assuming that $t = t_0 + t_1 T$. Error bars in dE/dH^2 are approximately $\pm 3\%$.

mined by $A(T)$, assuming t is constant. (Although χ_P and χ_M are functions of temperature, they are only weakly so, and have little effect on dE/dH^2 .) Thus, taking the ratio of the magneto- and electroclinic coefficients, we obtain

$$\frac{dE}{dH^2} = \frac{\chi_M}{2t\chi_P}, \quad (3)$$

a quantity which should be nearly constant if t were indeed independent of temperature. From Fig. 2, however, we see that dE/dH^2 exhibits a clear, albeit weak, T dependence. In fact, since the region $0.15 \leq T - T_{A-C^*} \leq 1.5$ K appears to emulate an algebraic temperature dependence, we can fit this region to the form $dE/dH^2 = a(T - T_{A-C^*})^b$. We obtain an exponent $b = 0.12 \pm 0.06$ (shown by the solid line), where the error in b is due to the scatter in the data which, although small, becomes significant when the slope is nearly flat. Closer to the transition the experimental values of dE/dH^2 approach a constant, a reasonable result since there is no physical justification for expecting that dE/dH^2 vanish as $T \rightarrow T_{A-C^*}$.

We now compare our experimental results to the electroclinic data in Ref. 1. There it was found that $d\theta/dE \sim (T - T_{A-C^*})^{-\gamma}$, where $\gamma = 1.11 \pm 0.06$. It has also been established in a variety of systems that the smectic- A -smectic- C phase transition is mean-field-like, with a susceptibility exponent $\gamma = 1$.⁷⁻⁹ This mean-field value, in fact, was also obtained in DOBAMBC using the pyroelectric technique,³ and was found for the magneto-clinic coefficient in butyloxybenzylidene heptylaniline (4O.7).⁷ Thus, if we reasonably assume that the magneto-clinic coefficient $d\theta/dH^2 \sim (T - T_{A-C^*})^{-1}$, and take the ratio of this coefficient to the electroclinic coefficient $d\theta/dE \sim (T - T_{A-C^*})^{-1.11}$ reported in Ref. 1, we find from the literature that $dE/dH^2 \sim (T - T_{A-C^*})^{0.11}$. This exponent, obtained over a two-decade region of reduced temperature¹ which brackets our own fitting range, corresponds quite nicely to our fitted value $b = 0.12$. Thus, at least in this region, our "magneto-electroclinic" results are completely consistent with the anomalous electroclinic exponent obtained by Garoff and Meyer.^{1,2}

As pointed out earlier, however, there is no physical basis for expecting true critical behavior in dE/dH^2 . In

fact, close to T_{A-C^*} , our data indicates that dE/dH^2 approaches a constant and, for $T - T_{A-C^*} > 1$ K, there appears to be some upward curvature (cf. Fig. 2). In light of this behavior, we therefore believe that our experimental exponent $b = 0.12 \pm 0.06$ is only an artifact, resulting from a purely algebraic fit over a *finite*-temperature region. We suspect that dE/dH^2 actually varies smoothly with temperature and arises from a noncritical and relatively uninteresting temperature dependence of the θP coupling "constant" t , which will be discussed below. Consequently, it seems probable that the anomalous electroclinic exponents in Ref. 1 comes about from this same temperature dependence in t . In other words, by fitting the electroclinic data over a finite-temperature range, the

slowly varying coupling coefficient t would cause an otherwise mean-field susceptibility exponent γ to mimic some other value. It is unlikely, therefore, that the electroclinic data reflect a true critical exponent, and, thus, a small amount of curvature should, in principle, be present in a log-log plot. Given experimental noise in the data,¹ however, as well as the steep slope of $d\theta/dE$ vs $T - T_{A-C^*}$, the electroclinic data in Ref. 1 could easily emulate an algebraic form with a single exponent over a very wide temperature range.

We now turn to the temperature dependence of t . If we assume that t varies linearly in temperature and that χ_M and χ_P are nearly constant in T , we find from Eq. (3) that the data can be fitted to the form

$$\frac{dE}{dH^2} = [4.36 \times 10^6 - 8.01 \times 10^5 (T - T_{A-C^*})]^{-1} \text{ V cm}^{-1} \text{ G}^{-2} \propto t^{-1}. \quad (4)$$

Equation (4), which is shown by the dashed line in Fig. 2, not only fits the data quite well over the entire temperature range, but emulates the apparent critical behavior in the intermediate-temperature region as well. Although Beresnev *et al.* never quantitatively explained the electroclinic anomaly, our data is clearly consistent with their suggestion of a temperature-dependent coupling of the central molecular core to the moiety possessing the transverse dipole moment.⁴ In fact, Eq. (4) also indicates that t becomes smaller at elevated temperatures in the smectic- A phase; this result is consistent with an apparent electroclinic exponent $\gamma > 1$. It should be pointed out that Qiu *et al.* obtained an electroclinic exponent $\gamma = 1.04 \pm 0.05$.⁶ Inasmuch as the temperature dependence of t is *not* universal but rather related to molecular structure, the effective exponent depends not only on the temperature range of the experiment but on the material under investigation as well. At this time, unfortunately, we cannot determine the origin of the temperature dependence of the coupling coefficient. t could depend upon a number of macroscopic properties, such as the magnitude of the orientational order parameter $\langle P_2(\cos\theta) \rangle$, the smectic order parameter, or on some property of the incipient smectic- C^* phase. It is also possible that the usual temperature behavior of the molecular conformation drives t ,

although one would probably not expect such large (relatively speaking) changes in dE/dH^2 over such a small temperature range. One must obviously use other complementary probes, such as NMR, to ascertain how and why t depends on temperature.

In summary, we have performed a "magneto-electroclinic" measurement in the smectic- A phase of DOBAMBC, finding that dE/dH^2 exhibits behavior consistent with the anomalous electroclinic result of Garoff and Meyer.^{1,2} Upon closer examination, however, we obtain a better fit over a wider temperature range if we assume that the coefficient t which couples tilt and polarization has a simple linear dependence on T . Such a dependence, moreover, coupled with a mean-field susceptibility exponent $\gamma = 1$, could also have been used to fit the electroclinic data in Ref. 1. Finally, this behavior is completely consistent with the argument of Beresnev *et al.*,⁴ who suggested that the central core of the molecule, which is responsible for the optical response¹¹ and couples strongly to a magnetic field, couples only weakly to the dipole moment along the flexible tail.

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