PHYSICAL REVIEW A VOLUME 38, NUMBER 3 AUGUST 1, 1988

Electroclinic effect above the smectic-A –smectic-C^* transition

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(Received 4 April 1988)

The critical behavior of the electroclinic effect above the transition from the smectic-A to the chiral smectic-C^* phase has been studied using the experimental geometry of a surface-stabilized ferroelectric liquid-crystal cell. The value of the tilt susceptibility exponent γ is found to be 1.04 ± 0.05, consistent with the mean-field description of this transition.

A phenomenon related to the occurrence of ferroelectricity in chiral smectic-C^* (Sm-C^*) liquid crystals[1] is the existence of an electroclinic effect[2] in the smectic-A phase of these materials, that is, a direct coupling between the molecular tilt θ relative to the smectic-layer normal $\hat{\mathbf{n}}$ and an applied electric field $\mathbf{E}$. The electroclinic effect can be understood on the basis of a molecular symmetry argument.[3] In the smectic-A (Sm-A) phase, there is a uniaxial axis along $\hat{\mathbf{n}}$. This symmetry operation does not allow any average transverse component of a vectorial quantity in the plane perpendicular to $\hat{\mathbf{n}}$. If an electric field $\mathbf{E}$ is applied normal to $\hat{\mathbf{n}}$, the transverse component of the molecular dipole $\mathbf{P}$ would tend to align parallel to $\mathbf{E}$ by biasing the free rotation about the molecular long axis. Thus $\hat{\mathbf{n}}$ is no longer a symmetry axis, and a macroscopic polarization along the electric field direction appears. If the material is composed of chiral molecules, the plane containing $\hat{\mathbf{n}}$ and $\mathbf{P}$ is no longer a mirror plane as it is in a nonchiral Sm-A. So the free energy is not a symmetric function with respect to the tilt angle θ, and the molecular direction would deviate from the $\hat{\mathbf{n}}$-$\mathbf{P}$ plane until it reaches its equilibrium position.

The pretransitional increase of the electroclinic effect in a Sm-A liquid crystal in the vicinity of the Sm-C^* phase offers the opportunity to study the critical behavior of the tilt susceptibility. The Sm-A to smectic-C (Sm-C) or Sm-C^* transition was originally suggested to belong to the XY universality class.[4] Earlier light scattering experiments to determine the tilt susceptibility exponent γ at the Sm-A–Sm-C transition produced inconclusive results.[5] In the case of the electroclinic effect, the only experiment to date on p-(n-decyloxy-benzylidene)-p'-amino-(2-methylbutyl)cinnamate (DOBAMBC) yielded a result of $\gamma=1.11\pm0.06$,[3] which is between the values expected in the mean-field and XY models. More recent heat-capacity and other studies, however, strongly support the picture of a simple mean-field Sm-A–Sm-C transition with a sixth-order term in the Landau expansion.[6] It seems worthwhile to reexamine the pretransitional behavior of the electroclinic effect in light of these developments. In this Brief Report, we present the results of a new measurement of the critical behavior of the electroclinic effect above the Sm-A–Sm-C^* transition using a material that is chemically more stable than DOBAMBC and a sample geometry that is simpler and more convenient than that used previously.[2,3]

In the original study of Garoff and Meyer,[2] the electroclinic effect was induced by applying a transverse electric field to a homeotropic sample. As a result, the effect was best observed with a laser beam at an oblique angle to the sample. Our experiment was conducted with the sample in a geometry typical of a surface-stabilized ferroelectric liquid-crystal cell.[7] A planar sample with the smectic layers perpendicular to the surface was sandwiched between glass plates coated with transparent indium tin oxide electrodes and separated with a spacer of 1 μm nominal thickness, as shown in Fig. 1(a). The advantage of this geometry for using the electroclinic effect for device applications has been recently recognized.[8,9] Figure 1(b) shows the relation between the electric field and the molecular orientation. An electric field $\mathbf{E}$ parallel to the smectic planes will induce a molecular tilt in a direction perpendicular to $\mathbf{E}$. If the sample cell is placed between crossed polarizers with the first polarizer at an angle α to the director and light of intensity I_0 is incident perpendicularly to the sample, the transmitted intensity I is given by

$$I=I_0\sin^2(2\alpha)\sin^2(\phi/2)\ , \tag{1}$$

where ϕ is the phase shift through the sample, which depends on the birefringence $\Delta n=n_e-n_0$, the wavelength λ of the light in vacuum and the thickness d of the sample,

$$\phi=2\pi\Delta n d/\lambda\ . \tag{2}$$

When $\mathbf{E}$ is applied, the transmitted intensity will vary with the induced tilt angle θ. If θ is sufficiently small, differentiating Eq. (1) with respect to α and equating $\theta=\delta\alpha$ yields

$$\delta I=2I_0\sin(4\alpha)\sin^2(\phi/2)\theta\ . \tag{3}$$

Thus for a given $\mathbf{E}$ the condition $\alpha=22.5°$ gives the maximum intensity change δI. With this choice of α, the tilt angle can be determined by

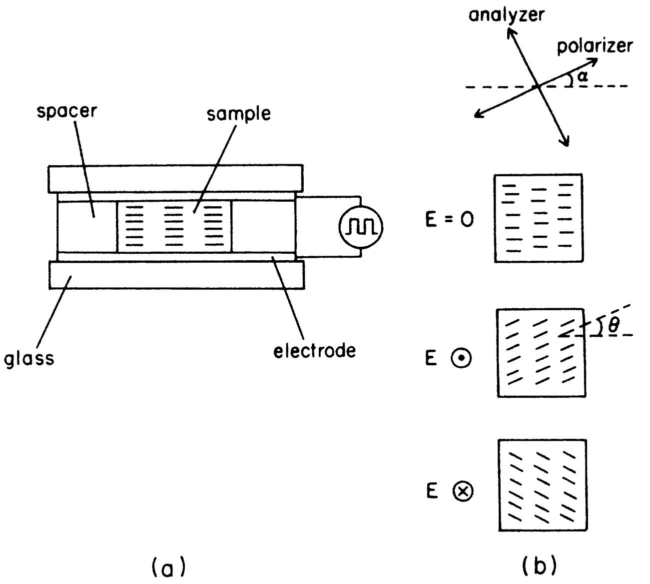

FIG. 1. Schematic representation of sample cell in (a) side and (b) top views.

$$\theta = \delta I / 4I \ . \tag{4}$$

In our experiment, the axis of the first polarizer was adjusted to make an angle of 22.5° with the layer normal in zero field. An ac field was applied and the modulation in the transmitted intensity was measured with a lock-in amplifier. A relatively low frequency of 2 kHz was chosen to minimize the effect associated with the dynamic response of the system. Our sensitivity in tilt angle measurement was estimated to be 0.002°. The material used in our study was a 1:1:1 mixture by weight of three Displaytech ferroelectric liquid crystals possessing a phenyl benzoate core designated as *W*7, *W*37, and *W*82.[10] The sample temperature was controlled with a stability of 2 mK.

To test the linearity of the electroclinic effect with field, Fig. 2 shows as an example the dependence of the induced tilt angle θ on **E** at 62 °C near the upper limit of the Sm-*A* phase. This excellent linearity throughout the range of parameters used in our study allowed us to vary the field to maximize the signal in the temperature sweep. Figure 3 shows the temperature dependence of θ at an equivalent field of 10^5 V/cm. It can be seen that θ shows a strong pretransitional increase near the Sm-*A*–Sc-C^* transition temperature T_c of 57.4 °C. The behavior below the transition is complicated by the occurrence of domains with different directions of the spontaneous tilt.

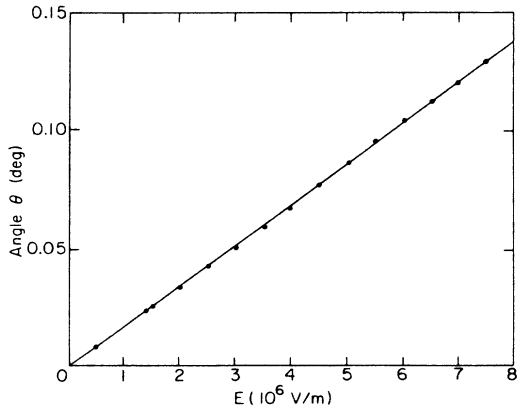

FIG. 2. Dependence of induced tilt angle θ on electric field at 62 °C. The line is a straight line.

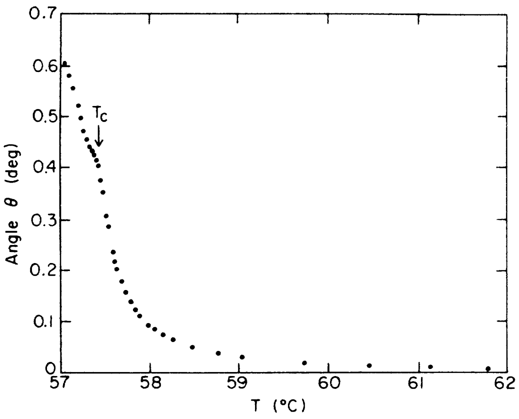

FIG. 3. Temperature dependence of induced tilt angle θ in the presence of an electric field of 10^5 V/m.

To analyze the data above T_c, we note that for a dc field θ is expected to have the dependence

$$\theta = cE/A \ , \tag{5}$$

where $A = a[(T-T_c)/T_c]^{\gamma}$ and c is the electroclinic coupling constant between θ and E. In the presence of an ac field at an angular frequency ω, however, the amplitude of the alternating tilt angle will depend on an effective viscosity Γ governing the response time in the form[2]

$$\theta = cE(A^2 + \omega^2\Gamma^2)^{-1/2} \ . \tag{6}$$

Equation (6) can be rewritten as

$$(\theta^{-2} - \theta_0^{-2})^{1/2} = a[(T-T_c)/T_c]^{\gamma} \ , \tag{7}$$

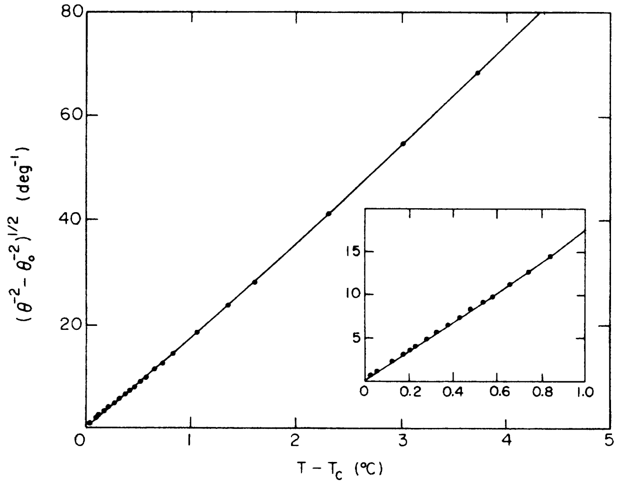

FIG. 4. Temperature dependence of $(\theta^{-2} - \theta_0^{-2})^{1/2}$. The insert contains data within 1 °C of the transition. The line is Eq. (7) with $\gamma = 1.04$.

where

$$\theta_0 = cE/\omega\Gamma \ . \qquad (8)$$

We have fitted our data to Eqs. (7) and (8) with Γ either held constant or allowed to have a typical Arrhenius-form temperature dependence $\Gamma = \Gamma_0 \exp(B/k_B T)$. We find that both approaches gives essentially the same value of $\gamma = 1.04 \pm 0.05$. This result is illustrated by the almost linear temperature dependence of $(\theta^{-2} - \theta_0^{-2})^{1/2}$ in Fig. 4. The fit is quite satisfactory with the exception of small systematic deviations near T_c, where the response-time corrections are presumably most important. The value for γ provides additional supporting evidence for the validity of the mean-field description of the Sm-A–Sm-C transition.

In summary, we have reexamined the critical behavior of the electroclinic effect above the Sm-A–Sm-C^* transition using a surface-stabilized ferroelectric liquid-crystal cell. The value of the tilt susceptibility exponent γ obtained is consistent with the mean-field expectation for this transition.

The work was supported by grants from the National Science Foundation and the U.S. Office of Naval Research.

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