

## Surface Electroclinic Effect in Chiral Smectic-*A* Liquid Crystals

Jiuzhi Xue and Noel A. Clark

*Department of Physics and Center for Optical Computing Systems, University of Colorado,  
Boulder, Colorado 80309*

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The polar interaction between a chiral smectic-*A* liquid crystal and a solid substrate results in an induced ferroelectric polarization and chiral reorientation of the director in the liquid crystal near the surface.

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Based on an argument similar to that for ferroelectricity in the tilted phases of chiral smectic liquid crystals (LC's), Garoff and Meyer<sup>1</sup> predicted the existence of the electroclinic effect, a chirally symmetric molecular rotation proportional to the applied electric field in the smectic-*A* ( $S_A$ ) phase of a liquid crystal composed of chiral molecules. They first experimentally demonstrated the electroclinic effect in *p*-(*n*-decyloxy-benzylidene)-*p'*-amino-(2-methylbutyl)cinnamate (DOBAMBC),<sup>1</sup> and it has since been studied as a probe of critical behavior near the smectic-*A* to smectic- $C^*$  ( $S_{C^*}$ ) transition,<sup>2-4</sup> and to develop useful electro-optic devices.<sup>5,6</sup>

In this Letter, we report the surface electroclinic effect in the  $S_A$  phase, a chiral rotation of the  $S_A$  director away from the layer normal in the vicinity of the LC-solid interface.

In recent experimental work, we have shown that in the  $S_{C^*}$  phase, the interface interaction between the liquid crystal and solid bounding surfaces is polar, the surface preferring to have a particular sign of  $\mathbf{P} \cdot \mathbf{s}$ , where  $\mathbf{P}$  is the ferroelectric polarization and  $\mathbf{s}$  is the surface

normal directed into the LC.<sup>7</sup>

Here we probe the  $S_A$  phase, in which this polar interface interaction acts like an externally applied field, causing the molecules near the surface to tilt in a chirally symmetric way, as shown schematically in Fig. 1(a), with respect to the smectic-layer normal. This molecular tilt can be measured by detecting the depolarization ratio  $R$  of light totally reflected from the solid isotropic glass-uniformly aligned  $S_A$  interface, under conditions of evanescent propagation in the LC.

The sample geometry is the surface-stabilized ferroelectric-LC (SSFLC) geometry<sup>8</sup> with the LC between a clean indium-tin-oxide (ITO) coated glass plate and the flat part of a high-index glass hemisphere ( $n_g = 1.9082$ ) coated with a thin layer ( $\sim 120$  Å) of ITO. The cell is filled by capillary suction by heating the liquid crystal to the isotropic phase. A uniformly arranged smectic-*A* phase is obtained by shearing the sample cell near the  $N^*$  to  $S_A$  transition in both the  $N^*$  and  $S_A$  phases.<sup>8</sup> The hemisphere-sample assembly is shown in Fig. 1(b).

To theoretically describe the surface electroclinic effect, we use a Landau description, writing the bulk elastic free energy per unit area of a chiral  $S_A$  phase as<sup>1</sup>

$$G = G_A + \int \left[ \frac{1}{2} A'(T) \theta^2 + \cdots + \frac{1}{2} \gamma k_B T P^2 - t \theta P + \frac{1}{2} K_2 \left( \frac{d\theta}{dx} \right)^2 + \int dx' \frac{(dP/dx')(dP/dx)}{|\mathbf{r} - \mathbf{r}'|} \right] dx, \quad (1)$$

where  $\theta(x)$  is the angle between the layer normal  $z$  and the director  $\mathbf{n}$  [cf. Fig. 1(a)],  $P(x)$  is the component of the average molecular polarization perpendicular to the bounding surfaces,  $\frac{1}{2} \gamma k_B T P^2$  is the entropy cost of dipolar reorientation,  $t$  is the piezoelectric coupling constant,  $K_2$  is the twist elastic constant, and  $\theta(x)$  and  $P(x)$  are assumed to depend only on  $x$ , the coordinate normal to the interface. The last term in Eq. (1) comes from the electrostatic self-interaction of the polarization charge  $\rho = -\nabla \cdot \mathbf{P}$ . Because of the one-dimensional spatial variation of  $P$ , this term reduces to  $2\pi P(x)^2/\epsilon$ , where  $\epsilon$  is the dielectric constant.

In Eq. (1),  $P$  and  $\theta$  are treated as independent variables. Minimizing the free energy with respect to  $P$

gives

$$P = \chi_p t \theta, \quad (2)$$

$$g = \frac{1}{2} A \theta^2 + \frac{1}{2} K_2 (d\theta/dx)^2, \quad (3)$$

where  $\chi_p = \gamma k_B T + 4\pi/\epsilon$  is a generalized susceptibility, and  $A = a(T - T_c)/T_c$  is the effective susceptibility controlling the tilt of the director near the smectic-*A* to smectic- $C^*$  phase transition.<sup>1</sup> The solution to the Euler equation resulting from Eq. (3), when the correlation length  $\xi = (K_2/A)^{1/2}$  is much less than the sample thickness, is

$$\theta = \theta_0 e^{-x/\xi}, \quad (4)$$

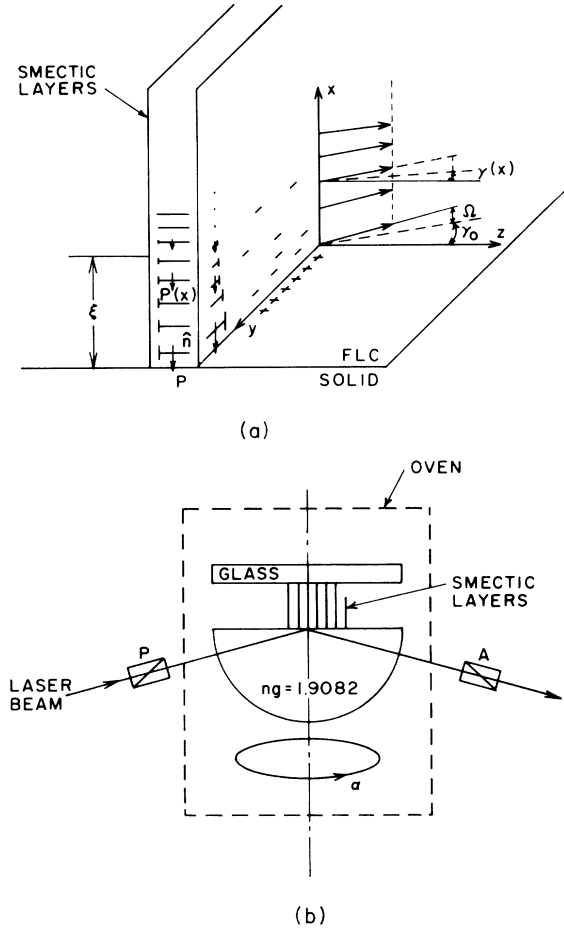


FIG. 1. (a) Schematic of the surface electroclinic effect in the chiral  $S_A$  phase and the coordinate system of the sample geometry. The  $z$  axis is along the layer normal, and the  $x$  axis is perpendicular to the glass plates. The polar surface interaction intrinsic to the solid-LC induces a spontaneous polarization and the director orientation near the surface. (b) The hemisphere-sample assembly. A hemisphere is used in order to obtain the cylindrical symmetry needed for the experiment.

which gives a net bulk elastic free energy per unit area as  $G_b = \int_0^\infty g(x) dx = \frac{1}{2} \theta_0^2 A \xi$ .

Assuming the surface energy per unit area due to the surface interaction between the FLC's and the solid surface is polar, and is proportional to the spontaneous polarization  $\mathbf{P}$ ,  $G_s = -\lambda_2 P \equiv -\lambda_2 \chi_p t \theta_0$ , then the total free energy per unit area of the system is obtained by adding up the bulk and the surface energy:

$$G_t = G_b + G_s = -\lambda_2 \chi_p t \theta_0 + \frac{1}{2} \theta_0^2 A \xi, \quad (5)$$

where  $\lambda_2$  measures the strength of the polar interaction. Note that there is an implicit sign dependence in the polar interaction  $\lambda_2$ . If  $\lambda_2 > 0$ , then the  $P > 0$  state is favored, corresponding to the surface favoring the  $\mathbf{n} - \mathbf{P}$  structure with the spontaneous polarization pointing into the FLC, and vice versa.

Minimizing the total free energy with respect to  $\theta_0$ , we get

$$\theta_0 = \frac{t \chi_p \lambda_2 \xi}{K_2} = \frac{t \chi_p \lambda_2}{(a K_2)^{1/2}} \left( \frac{T - T_c}{T_c} \right)^{-0.5}, \quad (6)$$

showing that a polar interaction between the LC and the bounding plate induces a director tilt in the  $S_A$  phase dependent on temperature, and that an electroclinic effect should be observable. Using values typical to FLC's,<sup>9</sup> the correlation length  $\xi = (1000 \text{ \AA}) / (\Delta T)^{1/2}$ , where  $\Delta T \equiv T - T_c$  ( $^\circ\text{C}$ ).

As in Ref. 7, we have used total-internal-reflection (TIR) technique to probe  $\mathbf{n}$  near the LC-glass interface. The experimental setup is identical to the one used in Ref. 7 except the hemisphere assembly is now temperature controlled and the detection system employs a lock-in amplifier. A thermistor is placed on top of the flat surface of the hemisphere to give an accurate reading of the sample temperature. The depolarization ratio of the reflected beam,  $R(\alpha)$ , is measured as a function of  $\alpha$ , the angle between the layer normal and the plane of incidence, versus temperature in the  $S_A$  and  $S_{C^*}$  phases.

The liquid crystal used in the experiment is the BDH electroclinic mixture 764E, with phases

$$I \leftrightarrow N^* \xleftrightarrow{89^\circ-92^\circ} S_A \xleftrightarrow{73^\circ} S_{C^*} \xleftrightarrow{26^\circ} S_{C^*},$$

which was kindly provided to us by EM Industries. The material was chosen because it has a large electroclinic tilt per unit of applied electric field. In our experiment, the angle of incidence  $\Theta$  is set to be  $81.3^\circ$ , giving optical penetration depths of  $l = 880 \text{ \AA}$  for the ordinary wave and a maximum of  $l = 1174 \text{ \AA}$  for the extraordinary wave in a LC material with refractive indices of  $n_o = 1.50$  and  $n_e = 1.68$  for an incident wavelength of  $\lambda = 6328 \text{ \AA}$ .

Figure 2 shows measurements of  $R(\alpha)$  at three different temperatures, two in the  $S_A$  phase, close to the  $S_A$ -to- $S_{C^*}$  transition, and one in the  $S_{C^*}$  phase. As can be readily seen in Fig. 2, as the sample temperature decreases, the amplitude of the depolarization ratio increases slightly, which most likely indicates that the birefringence of the liquid-crystal slab is increasing. It can also be observed that the depolarization-ratio curve shifts slightly to larger  $\alpha$  with decreasing  $T$ , which means that with decreasing  $T$  the director  $\mathbf{n}$  near the surface is rotating about  $\hat{\mathbf{x}}$ , the surface normal, relative to  $\hat{\mathbf{z}}$ , the smectic-layer normal.

The experimental data are fitted with the theoretical  $R(\alpha)$  obtained assuming the LC to be a uniaxial slab of birefringence  $n_e - n_o = \Delta n$  and optic-axis (director) orientation  $n(\theta_{op}, \Omega)$ ; cf. Fig. 1. This is justified as follows: As  $\Delta T$  increases, both  $\theta_0$  and  $\xi$  decrease. Clearly we have  $\theta_0 \ll 1$  rad, and for most of the temperature range studied  $\xi < l$ . Under these circumstances, the twisted director structure should behave approximately

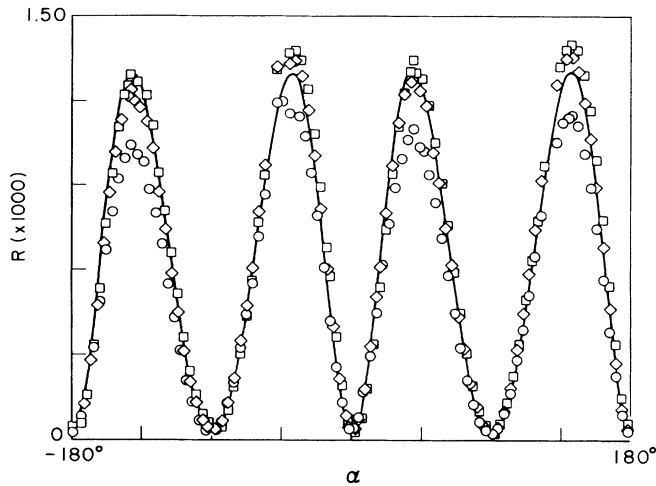


FIG. 2. Depolarization ratio  $R(\alpha)$  vs  $\alpha$ , the angle between the layer normal and the plane of incidence, at three different temperatures:  $\circ$ :  $T = 58.3^\circ\text{C}$  ( $S_A$ );  $\diamond$ :  $T = 27.6^\circ\text{C}$  ( $S_A$ );  $\square$ :  $T = 22.5^\circ\text{C}$  ( $S_{C^*}$ ). The solid curve is the best fit for the experimental results at  $27.6^\circ$ , which is representative of the fits assuming a homogeneous uniaxial medium. The difference in the width of the peaks of  $R(\alpha)$  can be qualitatively understood as due to the asymmetry of the effective refractive index about  $\alpha = 45^\circ$ , where the induced dipole moment producing the depolarized radiation maximizes.

as a uniform structure having an average rotation

$$\theta_{op} \approx l^{-1} \theta_0 \int_0^l e^{-x/\xi} dx \approx \theta_0 \xi / l \propto \xi^2. \quad (7)$$

A nonlinear least-squares fitting routine was used to determine the orientations ( $\theta_{op}$ ,  $\Omega$ ) and  $\Delta n$ .

The depolarization ratio  $R(\alpha)$  is not a sensitive function of  $\Omega$  when  $\Omega$  is small.<sup>7</sup> We find that all experimental data are fitted well with any  $\Omega < 3.5^\circ$ , with a slightly better fit for smaller  $\Omega$ 's, which indicates that the molecules stay parallel or almost parallel to the interface throughout the temperature range studied. In what follows, the initial fitting value for  $\Omega$  is chosen to be  $0.5^\circ$  for convenience.

Figure 3 shows the fitted  $\Delta n$  as a function of temperature. As can be readily seen, there is a small increase in  $\Delta n$  as the temperature of the cell is lowered. The nematic order parameter  $S$  describing the ordering of the director field should increase slightly as the temperature is decreased, and as a result,  $\Delta n$ , which is proportional to  $S$ , should also increase accordingly.<sup>10</sup>  $\Delta n$  was measured by transmission birefringence to be 0.18 at  $20^\circ\text{C}$ , in very good agreement with the fitted value 0.177 at  $22.5^\circ\text{C}$ .

The best-fitted values for  $\theta_{op}$  along with its standard deviation versus  $T$  are also shown in Fig. 3. The  $S_A$ - $S_{C^*}$  transition temperature  $T_{AC}$  was determined from a simultaneous optical-microscopy observation of the appearance of domain walls and hysteresis in the bulk optical response to applied field characteristic of the  $S_{C^*}$  phase. The transmission electro-optic effect was linear

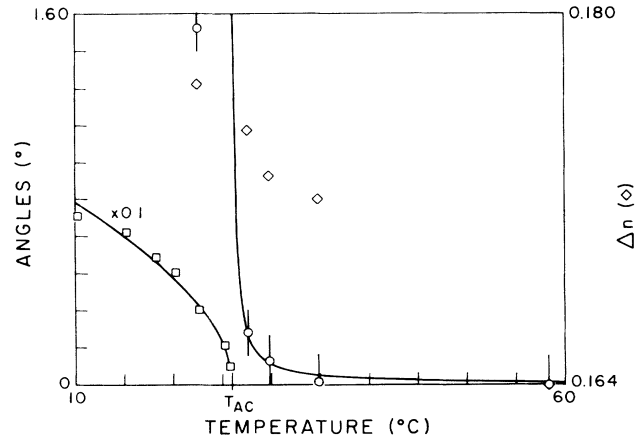


FIG. 3. Director rotation  $\theta_{op}$  ( $\circ$ ) along with a fit by the theory (solid curve) near the ITO surface vs temperature ( $T$ ) in the  $S_A$  phase of BDH 764E. The increasing  $\theta_{op}$  as  $T$  is decreased indicates the surface electroclinic effect. The error bars indicate the standard deviation calculated from the fit by  $R(\alpha)$ . Also indicated is the birefringence  $\Delta n$  ( $\diamond$ ) obtained from the fits. The  $S_{C^*}$  ( $\square$ ) tilt angle is obtained from transmission birefringence measurements, with the solid curve being the mean-field description of the transition behavior. The difference between the angles measured by the TIR technique and the optical measurement indicates that the molecules are tilted by a small angle near the interface (Ref. 7).

(electroclinic) at temperatures where  $S_A$  data were taken. There is an obvious increase in  $\theta_{op}$  in the  $S_A$  phase as the temperature is decreased, which can only be explained by the polar interaction between the LC and the ITO surface, as realized in Eq. (6). The observed surface electroclinic effect is small and at present the data, although demonstrating its existence, do not allow a quantitative test of Eqs. (6) and (7). From Eq. (7) we expect  $\theta_{op} \sim \xi^2 \sim 1/(T - T_{AC})$ , and Fig. 3 shows a fit by this function. With the quoted values of  $\xi$  and  $l$ , we find that  $\theta_0 = 0.248^\circ$  at  $T = T_{AC} + 1.6^\circ$ , the closest our current temperature control will enable us to come to  $T_{AC}$ .

The spontaneous polarization  $\mathbf{P}$  of the mixture 764E, when in the smectic- $C^*$  phase, is negative. From the geometry of the TIR experiment, we find that the surface favors the state with  $\mathbf{P}$  pointing into the glass and away from the FLC. This indicates that the polar interaction may be material dependent as we found  $\mathbf{P}$  pointing into the LC for the Displaytech mixtures employed in Ref. 7.

To conclude, we have demonstrated the surface electroclinic effect induced by the polar interaction between a chiral LC and its bounding plate. We find that the surface interaction in this case favors the spontaneous polarization of the LC pointing into the solid.

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<sup>1</sup>S. Garoff and R. B. Meyer, Phys. Rev. Lett. **38**, 848 (1977).

<sup>2</sup>R. Qiu, J. T. Ho, and S. K. Hark, Phys. Rev. A **38**, 1653 (1988).

<sup>3</sup>Z. Li, R. G. Petschek, and C. Rosenblatt, Phys. Rev. Lett. **62**, 796 (1989).

<sup>4</sup>C. Bahr and G. Heppke, Phys. Rev. A **37**, 3179 (1988).

<sup>5</sup>G. Andersson, I. Dahl, P. Keller, W. Kuczynski, S. T.

Lagerwall, K. Skarp, and B. Stebler, Appl. Phys. Lett. **51**, 640 (1987).

<sup>6</sup>K. Nakagawa, T. Shinomiya, M. Koden, K. Tsubota, T. Kuratate, Y. Ishii, F. Funada, M. Matsuura, and K. Awane, Ferroelectrics **85**, 39 (1988).

<sup>7</sup>J.-Z. Xue, N. A. Clark, and M. R. Meadows, Appl. Phys. Lett. **53**, 2397 (1988).

<sup>8</sup>N. A. Clark, M. A. Handschy, and S. T. Lagerwall, Mol. Cryst. Liq. Cryst. **94**, 213 (1983).

<sup>9</sup>S. Dumrongrattana and C. C. Huang, Phys. Rev. Lett. **26**, 464 (1986).

<sup>10</sup>P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).