

## Anticlinic coupling between layers of an antiferroelectric liquid crystal

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The anticlinic interlayer coupling coefficient  $U$  was evaluated as a function of temperature for a pitch-compensated liquid crystal by optical observation of the electric field-induced optic mode.  $U$  was found to exhibit an unusual “S-shaped” dependence on temperature, with values ranging between  $0.4 \times 10^4$  and  $2.2 \times 10^4$  erg cm<sup>-3</sup> over a 10 °C temperature range below the smectic- $A$ –smectic- $C_A^*$  phase-transition temperature. The results are in good agreement with estimates for  $U$  based upon the threshold field for the onset of solitary waves, and provide strong support in the low-field regime for the single Fourier component model proposed by Li *et al.* [Phys. Rev. B **52**, R13 075 (1995)]. [S1063-651X(99)08408-1]

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Antiferroelectric liquid crystals, which were first observed by Chandani *et al.* in 1989 [1], have been of great scientific and increasingly technological importance. Experimentally it is known that the layer structure of these materials in the smectic- $C_A^*$  phase has anticlinic director ordering, viz., the molecules in neighboring layers have the same polar tilt angle  $\theta_i$  with respect to the layer normal, but differ in azimuthal orientation  $|\varphi_i - \varphi_{i+1}|$  by approximately  $\pi$  [2]. Here  $i$  corresponds to the layer index. For a sufficiently large electric field  $\vec{E}$  perpendicular to the molecular tilt plane, a transition to synclinic ordering is observed, where the azimuthal angle becomes the same for all layers and there exists a nonzero polarization  $P_0$  perpendicular to the tilt plane. This switching from anticlinic to synclinic order has been observed to occur via solitary waves, where fingers of synclinic order invade the anticlinic region [3]. Understanding the origin of anticlinic ordering and the anticlinic-to-synclinic transition is a topic of considerable interest, and the mechanisms are still not clear. Early on, Nishiyama and Goodby [4] suggested that steric interactions may play an important role in anticlinic ordering. On the other hand, Takanishi *et al.* [5] have proposed a molecular pairing model wherein interacting dipoles orient perpendicularly to the tilt plane, giving rise to anticlinic order. Recently, Miyachi *et al.* [6] suggested the importance of a dipole component *parallel* to the tilt plane and residing at the smectic layer boundary. The common thread that runs through these ideas is a coupling between adjacent smectic layers. To date the coupling energy only has been inferred from measurements of the threshold field  $E_{th}$  at the anticlinic-synclinic transition. Such a determination has two shortcomings: It relies on a specific model for the transition and it reflects the behavior of the system at high field and where  $|\varphi_i - \varphi_{i+1}|$  may deviate significantly from  $\pi$ . Given that the very mechanism of the anticlinic interaction is still in question, the purpose of this paper is to report on a direct perturbative evaluation of the interlayer coupling coefficient as a function of temperature.

A schematic representations of the sample cell is shown in Fig. 1. Cells were constructed of two glass plates. In order to generate an in-plane electric field, one side of one of the plates was coated with electrically conducting indium-tin-oxide (ITO) and etched to form an 800- $\mu$ m gap. To achieve planar alignment of the liquid crystal, the plates were cleaned, spin-coated with the polyimide CU-2012 (Merck), and baked. The substrates were then rubbed unidirectionally with a cotton cloth using a dedicated rubbing machine. A pair of treated glass plates—one plate with ITO and one without—was separated by Mylar spacers of nominal thickness  $d = 3 \mu\text{m}$ , and cemented together with the rubbing directions parallel to each other. Because the cell thickness  $d \ll 800 \mu\text{m}$ , the resulting electric field was nearly parallel to the substrates, especially in the midregion between the electrodes.

Because of the tight helical pitch associated with most antiferroelectric liquid crystalline materials, it is often difficult to achieve a surface-stabilized, unwound anticlinic phase. To circumvent this problem, we used a binary mixture of (*R*)-TFMHPOBC [4-(1-trifluoromethylhexyloxycarbonyl)phenyl 4'-octyloxybiphenyl 4-carboxylate] [7] and (*R*)-MHPOBC [4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate] [8]. The polarizations of these materials add constructively, but their helices wind in opposite directions [9]. We found that for temperatures just below the smectic- $A$ –smectic- $C_A^*$  (anticlinic) phase-transition temperature  $T_{SmA-SmCA^*}$ , a 70:30 wt. % mixture of (*R*)-TFMHPOBC and (*R*)-MHPOBC provides a very long pitch ( $> 10 \mu\text{m}$ ) that easily could be surface-stabilized in the bookshelf geometry [10,11]. We also note, however, that the pitch is sensitive to temperature: At lower temperatures the pitch becomes tighter, thereby preventing surface-induced unwinding of the helix. This mixture undergoes an isotropic–smectic- $A$  phase transition at approximately 138 °C, and a transition from the smectic- $A$  to smectic- $C_A^*$  phase at slightly above 120 °C.

The cell was mounted in a temperature-controlled oven stable to 2 mK and filled with the mixture above the isotropic–smectic- $A$  phase-transition temperature. The sample was then gradually cooled into the smectic- $C_A^*$  phase. Because of the long chiral pitch in this temperature region, the anticlinic smectic- $C_A^*$  phase was aligned in the bookshelf geometry (cf. Fig. 1).

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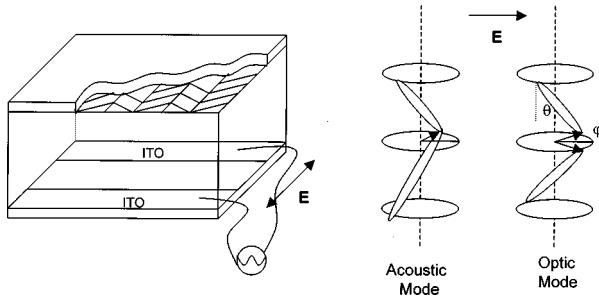


FIG. 1. Schematic representations of the sample cell and anti-clinic ordering.  $\theta$  and  $\varphi$  correspond to the polar and azimuthal molecular angles. Representations of the optic mode and acoustic mode are also shown. ITO corresponds to the indium-tin-oxide electrodes.

A schematic diagram of the electro-optic setup is shown in Fig. 2. The sample cell was placed between crossed polarizers, where the angle between the two polarizers and the  $z$  axis was  $45^\circ$ . Light from a 5 mW He-Ne laser was focused on an aperture of diameter  $\sim 50 \mu\text{m}$  in front of the sample. The laser beam passed through the sample at the midpoint between the two electrodes, was recollimated before passing through the analyzer, and then into a photodiode. A sinusoidal voltage at frequency  $\omega = 628 \text{ s}^{-1}$  (corresponding to 100 Hz) was applied to the sample, and the optical signal from the detector at frequency  $2\omega$  was measured with a lock-in amplifier. Note that  $\omega$  is well below the characteristic frequencies of the optic mode, which are typically  $\sim 10^4 \text{ Hz}$  [12,13]. The dc intensity  $I_{dc}$  at  $E=0$  was also measured. Measurements were made at several temperatures on cooling through the smectic- $C_A^*$  phase.

Figure 3 shows the electric field dependence of the quantity  $I_{2\omega}(E)/I_{dc}$  at  $T=113^\circ\text{C}$ , where  $I_{2\omega}$  is the component of intensity at frequency  $2\omega$ . Up to an electric field of about  $4 \text{ statvolt cm}^{-1}$ ,  $I_{2\omega}$  exhibits a quadratic dependence on  $E$  that corresponds to the optic mode in the anticlinic phase (Fig. 1). From this quadratic dependence we can deduce the interlayer coupling, which will be given below. At somewhat higher fields we found that  $I_{2\omega}$  tends to increase less rapidly than  $E^2$ , most likely due to the not-perfectly-in-plane field and higher-order ( $E^2$ ) couplings to the field. This is particularly noticeable near the electrodes, where there is a large component of field perpendicular to the substrate. For the region of small field shown in Fig. 3, however, the deviation from quadratic behavior is not observed.

The starting point of our analysis is the expression for the free energy  $F = \sum_i \int f_i d^2x$  used in Refs. [3] and [14]:

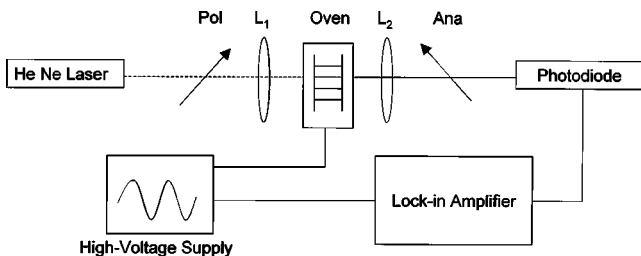


FIG. 2. Schematic diagram of the electro-optic setup. ‘‘Pol’’ is the polarizer, ‘‘Ana’’ is the analyzer,  $L_1$  is the focusing lens, and  $L_2$  is the recollimation lens.

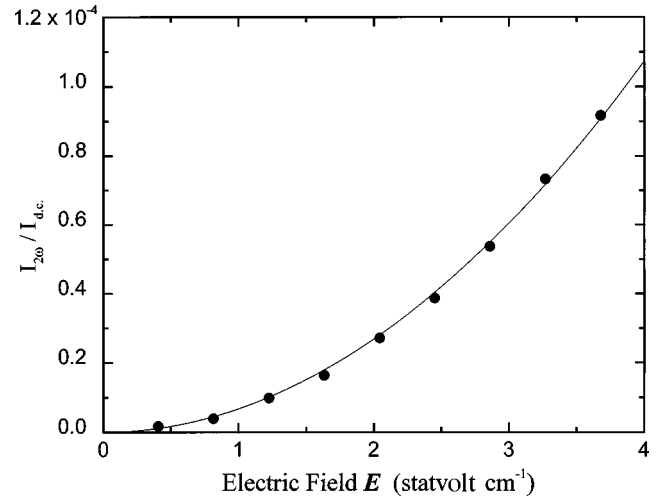


FIG. 3. Representative set of data at  $T_{\text{SmA-SmCA}^*} - T = 7^\circ\text{C}$  for the  $2\omega$  intensity component divided by the dc intensity vs applied electric field. The error bar is approximately the size of the data point.

$$f_i = -P_0 E \sin \varphi_i + \frac{\Delta \varepsilon \sin^2 \theta}{8\pi} E^2 \cos^2 \varphi_i + \frac{U}{2} \{ \cos(\varphi_{i+1} - \varphi_i) + \cos(\varphi_i - \varphi_{i-1}) \}. \quad (1)$$

Here,  $f_i$  is the free-energy density of the  $i$ th smectic layer,  $\varphi_i$  is the azimuthal angle,  $P_0$  is the local polarization, and  $\Delta \varepsilon$  is the dielectric anisotropy. The coupling between layers is expressed in terms of the lowest Fourier coupling coefficient  $U$ , which has dimensions of energy per volume, and represents a local interaction involving dipoles and possibly steric effects. To minimize the free energy, we note that for the unwound helices  $\varphi_i(E=0) = 0$  and  $\varphi_{i+1}(E=0) = \pi$ . If we account for symmetry and define  $\varphi$  as the field-induced azimuthal deviation from the equilibrium anticlinic orientation, the average free-energy density for a given layer depends only on  $\varphi$  and is given by

$$\langle f \rangle = -P_0 E \sin \varphi + \frac{\Delta \varepsilon \sin^2 \theta}{8\pi} E^2 \cos^2 \varphi - U \cos 2\varphi.$$

On expanding  $\langle f \rangle$  to order  $\varphi^2$  and minimizing, we find

$$\varphi \approx \frac{P_0 E}{4U - \frac{\Delta \varepsilon \sin^2 \theta}{4\pi} E^2}. \quad (2)$$

Thus, from the electro-optical measurement we can evaluate the field dependence of the azimuthal angle  $\varphi(E)$  by classic optical analysis [15], provided that the dominant motion under the electric field is the optic mode. We may simplify the model by assuming that the system is uniaxial within each smectic layer. For our geometry the optical intensity  $I(\varphi)$  is given by  $I(\varphi) = I_0 \sin^2(\frac{1}{2}kd\Delta n(\varphi))$ , where  $k$  is the wave vector of the light,  $I_0$  is the maximum intensity, and  $\Delta n(\varphi)$  is the effective birefringence, which may be shown to be  $\Delta n(\varphi) = (n_o^2 + \delta \varepsilon \cos^2 \theta)^{1/2} - (n_o^2 + \delta \varepsilon \sin^2 \theta \cos^2 \varphi)^{1/2}$ . For this expression we have assumed that  $n_e$  and  $n_o$  are the extraordinary and ordinary refractive indices, respectively, that

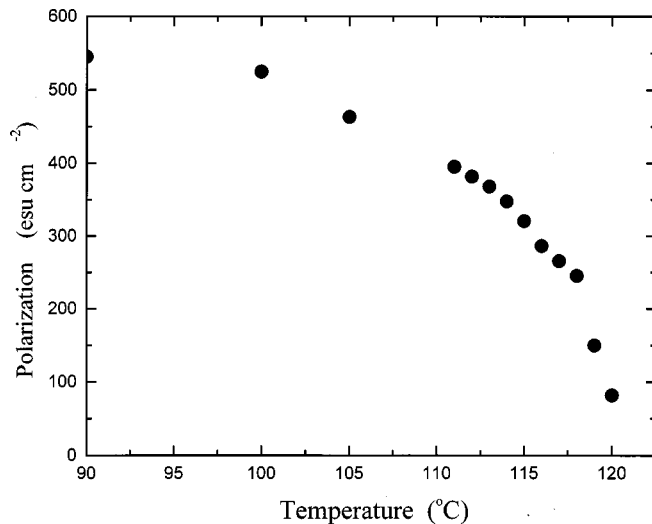


FIG. 4. Polarization vs temperature. Phase transition occurs slightly above 120 °C.

are associated with a given (tilted uniaxial) smectic layer, and that  $\delta\varepsilon = n_e^2 - n_o^2$ . Note that  $I_{dc}$  corresponds to  $I(E = \varphi = 0)$ . The temperature-dependent physical parameters needed to evaluate these equations were obtained separately by using conventional planar and/or wedged cells. Using the triangular wave method [16] we determined the polarization versus temperature; data are shown in Fig. 4. We also measured the polar tilt angle  $\theta$  by means of polarizing optical microscopy. Using a capacitance cell (electric field perpendicular to the slides) with the sample in the bookshelf geometry, we determined the angle for optical extinction in both zero electric field and in a field that was sufficiently large to switch the liquid crystal to a uniform smectic-C alignment. The resulting data for  $\theta$  versus temperature are shown in Fig. 5. Finally, the refractive indices were obtained from the wedge cell method [17]. Measurements were made at several temperatures in the smectic-A phase, where it was found that both  $n_e$  and  $n_o$  are very insensitive to temperature, having values  $n_e = 1.61$  and  $n_o = 1.48$ . These values were adopted for  $n_e$  and  $n_o$  throughout the smectic- $C_A^*$  phase as well. The coefficient  $U$  was then obtained by numerically fitting the

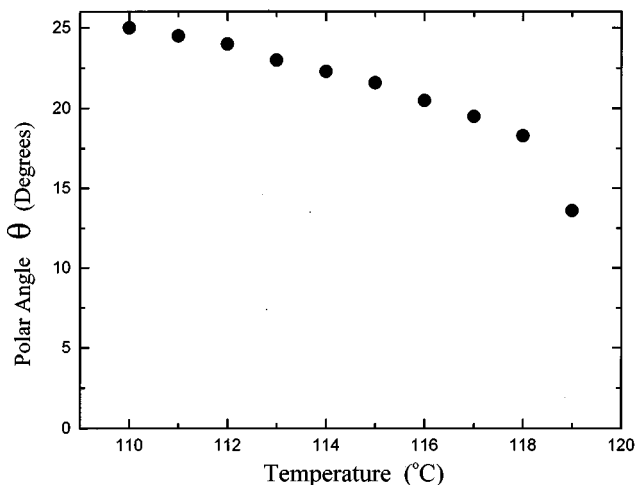


FIG. 5. Polar tilt angle vs temperature.

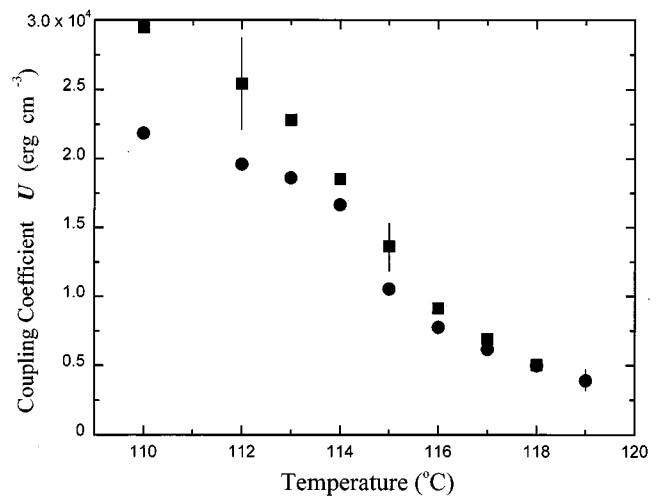


FIG. 6. Temperature dependence of  $U$  evaluated by our low field perturbative technique (●) and by threshold measurements of field-induced solitary waves (■). Typical error bars are shown.

ratio  $I_{2\omega}(\varphi)/I_{dc}$ , an example of which is shown in Fig. 3. Note that for  $|\Delta\varepsilon| < 10$ , which is certainly the case for these materials [3], the term proportional to  $E^2$  in the denominator of Eq. (2) is tiny and may be neglected. Two or more sets of experimental data were fitted at each temperature, all with consistent results for  $U$ . For example, at 113 °C we obtained a value  $U = (2.1 \pm 0.3) \times 10^4 \text{ erg cm}^{-3}$ . Results for  $U$  versus temperature, as obtained by this perturbative technique, are shown by the circles in Fig. 6.

Before continuing, let us examine the issue of terms beyond order  $\varphi^2$  in the free-energy expansion. Terms of order  $\varphi^4$ , for example, would contribute not only to the  $2\omega$  component of the intensity, but would have a significant  $4\omega$  component as well. Thus, in addition to the  $2\omega$  signal, we also examined the  $4\omega$  and  $6\omega$  signals. We found that for the applied fields used in this experiment, the  $6\omega$  signal was not measurable and the  $4\omega$  signal was very small. Thus, in our experiment we may conclude that the  $2\omega$  signal arose primarily from the  $\varphi^2$  terms in the free energy, with only a very small contribution from higher-order ( $\varphi^4$  and beyond) terms. Therefore it is physically valid that Eq. (2) may be based on an expansion to order  $\varphi^2$ .

Based on estimates of dipole-dipole interactions and omitting steric and entropic effects, Wang *et al.* suggested an upper limit of  $U$  to be of order  $100\text{--}500 \text{ erg cm}^{-3}$  for the case of (*R*)-MHPOBC [18]. This value, however, depends critically on the spacing between, and the magnitudes estimated for the dipoles. For example, they inferred the spacing between dipoles from the layer spacing measured by the x-ray diffraction. However, according to the schematic explanation and illustration suggested by Miyachi (Fig. 1 in Ref. [6]), the effective spacing that contributes to the interlayer coupling is apparently much smaller than that of the layer spacing. Furthermore, the interlayer coupling should also include beyond-nearest-neighbor interactions in three dimensions, rather than solely pair interactions. Therefore, it is not surprising that our experimentally measured value for  $U$  is nearly two orders of magnitude larger than the upper limit estimated in Ref. [18].

The coefficient  $U$  also may be inferred by measuring the

threshold field  $E_{\text{th}}$  for the onset of synclonic solitary waves that invade the smectic- $C_A^*$  phase. This technique, however, involves a specific model for the analysis [3], large fields  $\sim 250$  statvolt  $\text{cm}^{-1}$  (applied *perpendicular* to the molecular tilt plane), and an azimuthal angle  $\varphi$  that is changing rapidly with  $E$  [3]. Using the free energy of Eq. (1), Li *et al.* predicted that  $U = \frac{1}{2}P_0E_{\text{th}}$  [3], and experimentally determined a value  $U = 2.8 \times 10^4 \text{ erg cm}^{-3}$  at  $3.5^\circ$  below  $T_{\text{SmA-SmA}^*}$  for (*R*)-TFMHPOBC [3]. Similarly, Fournier and Verweire estimated  $U = 5.15 \times 10^4 \text{ erg cm}^{-3}$  for the mixture CS-4000 (Chisso) [19]. In order to compare the values of  $U$  deduced indirectly from the solitary wave threshold field with our direct perturbative measurements for  $U$ , we measured the threshold  $E_{\text{th}}$  versus temperature for our material using a polarizing microscope and capacitance cell.  $U(T)$  was extracted from  $U = \frac{1}{2}P_0E_{\text{th}}$  (squares in Fig. 6).

As seen in Fig. 6, the coupling coefficients that are measured by the two techniques both exhibit an unusual ‘‘S-shaped’’ temperature dependence. To understand this S-shape, we note that at higher temperatures  $U$  tends to rise slowly with decreasing temperature. Although the phase diagram for our mixture does not show a smectic- $C^*$  phase for weight fractions  $x$  of (*R*)-TFHMPOBC in the range  $0.4 < x < 1.0$ , a similar mixture of (*R*)-TFMHPBC [4-(1-trifluoromethylhexyloxy-carbonyl)phenyl 4'-octylbiphenyl 4-carboxylate] and (*R*)-MHPBC [4-(1-methylheptyloxy-carbonyl)phenyl 4'-octylbiphenyl-4-carboxylate] is found to exhibit a narrow smectic- $C^*$  region between the smectic-*A* and smectic- $C_A^*$  phases [20]. Thus, our small values of  $U$  at higher temperatures may be due to an incipient smectic- $C^*$  phase that, by necessity, would require a *weak* interlayer coupling. In the middle temperature region both sets of mixtures are completely in the smectic- $C_A^*$  phase with no incipient smectic- $C^*$  phase nearby, and thus a rapid rise of  $U$  with decreasing temperature obtains. Finally, at the lowest temperatures, the polar tilt angle, polarization, etc. have saturated, and  $U$  therefore varies weakly with temperature.

Perhaps even more remarkable than the shape of the curve is the apparent quantitative similarity [21] of the two sets of

data (Fig. 6): The techniques used to measure  $U$  are very different, and probe entirely different ranges of electric field and  $\varphi$ . Let us examine the consequences of this result. If, in fact, beyond-first-Fourier components were required in the free-energy expression in Ref. [3] and Eq. (1) above, these terms would have given rise to an additional contribution to the perturbative expression for  $\varphi$  in Eq. (2). Experimentally, our perturbatively measured values for  $U$  would therefore have been considerably different from those actually obtained. On the other hand, higher harmonics would not have altered the expression for the solitary wave threshold field, but instead would have affected only the solitary wave dynamics [3]. *However*, the fact that the perturbatively obtained values for  $U$  are so similar to the values obtained from the solitary wave threshold field measurements argues that the correct free energy can be modeled quite accurately with only the leading Fourier component; higher components are not necessary. Therefore, we conclude that the solitary wave model of Ref. [3] and Eq. (1) above, which involves only the lowest Fourier component, is physically accurate, *at least up to and slightly beyond the threshold field  $E_{\text{th}}$* .

To summarize, we have experimentally estimated the antclinic interlayer coupling between smectic layers by a technique involving a small field-induced perturbation of the molecular orientation. Our value is consistent with estimates deduced from field-induced switching thresholds at much larger electric fields. We conclude that the interaction potential scales as  $\varphi^2$  even out to moderately large values of  $\varphi$ , and that the single Fourier component free-energy expression used to predict the onset of switching by means of solitary waves is a physically realistic model.

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