Measurement of the Anticlinic Coupling Coefficient of an Antiferroelectric Liquid Crystal

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Abstract

In this paper, we report a novel way to evaluate the anticlinic interlayer coupling coefficient U between smectic layers of an antiferroelectric liquid crystal, by utilizing a small field-induced perturbation of the molecular orientation. U was found to exhibit an unusual "S-shaped" dependence on temperature, with values ranging between 0.4×10^4 and 0.4×10^4 erg cm^{-3} over a 10 °C temperature range below smectic A-smectic C_A phase transition temperature. The results are good agreement with estimates for U based upon the threshold field for the onset of solitary waves, and provide strong supporting the low-field regime for the single Fourier component model.

1. Introduction

Chandani, *et al.* first observed in 1989 [1] the antiferroelectric phase (sometimes known as the "anticlinic" phase) of chiral smectic C liquid crystals. This phase, also denoted as SmCA*, has polarizations in neighboring layers that are antiparallel. Under the surface-stabilized situation, it is experimentally revealed that the layer structure of these materials in the SmC_A* phase has anticlinic director ordering, viz., the molecules in neighboring layers have the same polar tilt angle qi with respect to the layer normal, but differ in azimuthal angle $|\varphi_i - \varphi_{i+1}|$ by approximately 180° [2](see Fig. 1). Here *i* corresponds to the layer index. For a sufficiently large electric field perpendicular to the molecular tilt plane, a transition to ferroelectric-like synclinic ordering is observed, where the azimuthal angle becomes the same for all layers and there exists a nonzero polarization Po perpendicular to the tilt plane. This switching from anticlinic to synclinic order is 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 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

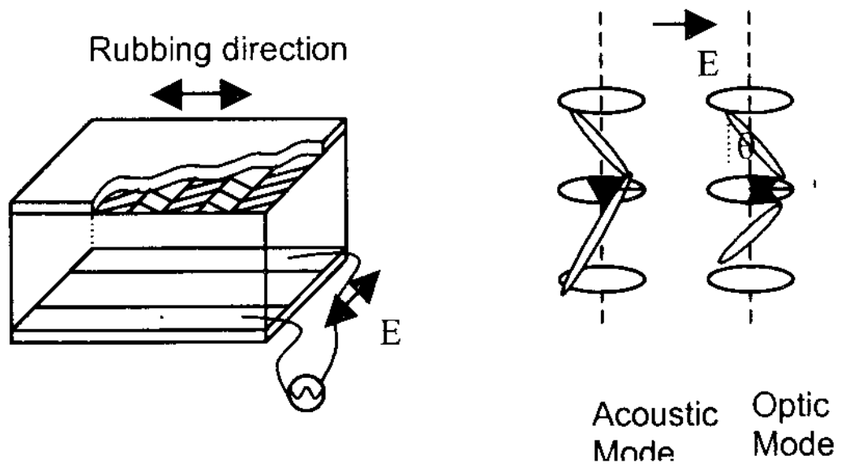

Fig. 1. Schematic representations of the sample cell and anticlinic ordering. θ and φ correspond to the polar and azimuthal molecular tilt angles.

significantly from 180°.

2. Theory

Let us consider the antiferroelectric cell in the bookshelf geometry as shown in Fig. 1. On applying an electric field along the y direction, the free energy expression introduced by Li, and Wang, et al [3, 7] is written as

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

Here f_i is the free energy density of the i-th smectic layer; φ_i is the azimuthal angle; P_o is the local polarization; and $\Delta\varepsilon$ is the dielectric anisotropy. The coupling between layers is expressed in terms of the 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 define φ as the field-induced azimuthal deviation from these values, Eq. (1) can be rewritten as

$$f_i = -P_o E \sin\varphi + \frac{\Delta\varepsilon \cdot \sin^2\theta}{8\pi} E^2 \cos^2\varphi + U\cos 2\varphi \quad (2)$$

On expanding f_i to order φ^2, and minimizing, we find

$$\varphi \approx \frac{P_o E}{4U + \frac{\Delta\varepsilon \sin^2\theta}{4\pi} E^2} \quad (3)$$

In the case of an anticlinic to synclinic transition via a solitary wave, as discussed in the previous section, the threshold electric field leads to a prediction of the interlayer coupling energy coefficient U_s [5]: $U_s = \frac{P_o E_{th}}{2}$. Here, E_{th} is the threshold field for the onset of synclinic fingers invading the anticlinic phase. In order to distinguish the interlayer coupling energy U that is obtained from the direct measurement of φ, we denote U_s as a coupling coefficient obtained from the threshold field.

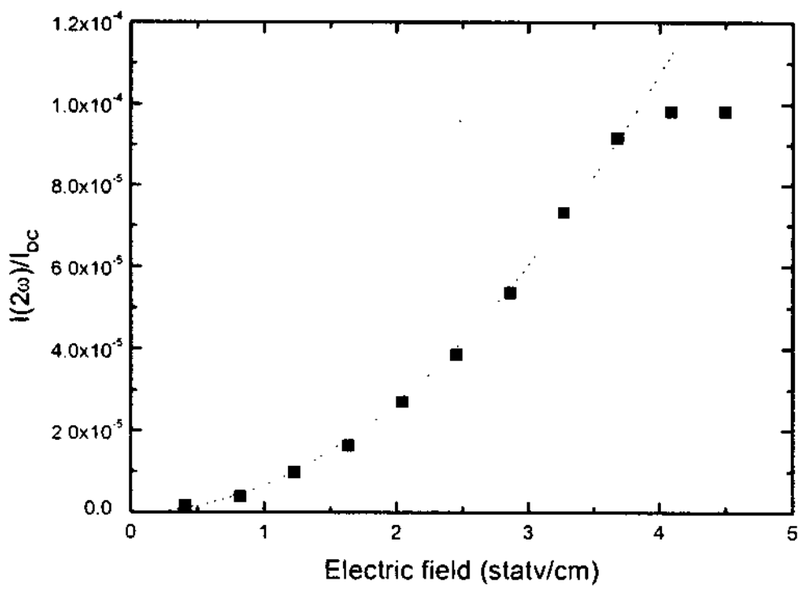

Fig.2. Experimental result of the electric field dependence of the $2f$ intensity components, I(E).

3. Experiments

In order to generate an in-plane electric field, one side of the glass plate was coated with electrically conducting ITO and etched to form an 800 μm gap. To achieve homogeneous 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 was separated by Mylar spacers of nominal thickness d = 3μm, and cemented together with the rubbing directions parallel to each other. A schematic representation of the sample cell is shown in Fig. 1. The thickness of cell was measured by the interference method. Because the cell thickness d 800 μm, the resulting electric field was nearly parallel to the substrates, especially in the mid-region 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 two antiferroelectric liquid crystals: (R)TFMHPOBC and (R)MHPOBC. The polarizations of these materials add, but their helices wind in opposite directions. We found that for temperatures just below the smectic A – smectic CA* (anticlinic) phase transition temperature, a 70:30 wt.% mixture of (R)TFMHPOBC and (R)MHPOBC provides a very long pitch (> 10 μm) that easily could be surface-stabilized in the bookshelf geometry [2, 10]. The phase sequence of this mixture is Isotropic – 138°C – Smectic A – 120°C – Smectic C_A*

The cell was mounted in a temperature-controlled oven and filled with the mixture above the isotropic – smectic A phase transition temperature. The sample was then gradually cooled from the isotropic phase (cooling rate is 0.04 °C/min) into smectic C_A*phase. Because of the long chiral pitch the anticlinic smectic C_A* phase was aligned in the bookshelf geometry.

The sample cell was placed between crossed polarizers, where the angle between the two polarizers and the z-axis was 45°. Light from a 5 mW He-Ne laser was focused on an aperture of diameter ~50 μm 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 f = 100 Hz was applied to the sample, and the optical signal from the detector at frequency $2f$, along with the d.c. signal, were measured with a lock-in amplifier.

From the electrooptical measurement we can evaluate the field dependence of the azimuthal angle φ(E) by classic optical analysis, provided that the dominant motion under the electric field is optic mode. The light intensity $I(\varphi)$ at the detector is ,

$$I(\varphi) \approx I_o \sin^2\left(\frac{kd\Delta n(0)}{2}\right) + I_o \sin\left(kd\Delta n(0)\right)\frac{kd\delta\Delta n}{2} \qquad (4)$$

The first term of Eq.(4) corresponds to d.c. component of intensity $I_{dc}(=I(\varphi=0))$ and second one to $2f$ component δI [$= I(2f)$]. The coefficient U was then obtained by numerically fitting the ratio $I(2f)/I(\varphi=0)$.

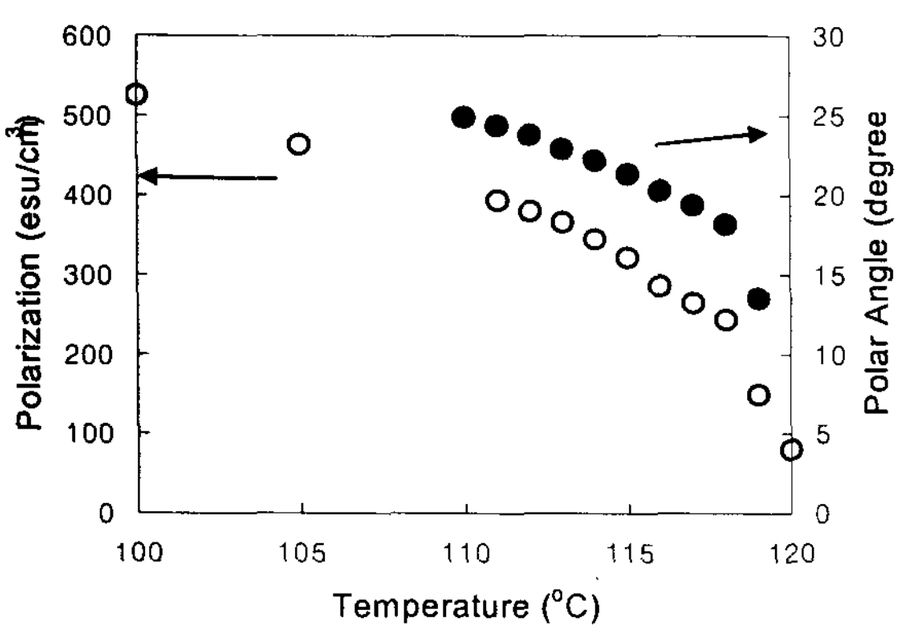

Fig.3. Temperature dependence of polarization (open) and polar tilt angle (solid).

4. Results

Fig. 2 shows a typical experimental result of the in-plane electric field dependence of the $2f$ intensity components, I(E) at T=113 °C. Up to an electric field of about 4 statv cm-1, the $2f$ intensity exhibits a quadratic dependence that corresponds to the optic mode in the anticlinic phase. From this quadratic dependence we can deduce the interlayer coupling. The physical parameters needed for these equations were measured separately by using conventional planar and wedged cells.

Fig. 3 presents the temperature dependence of tilt angle θ and macroscopic polarization P_s. Because of a paucity of data points, we interpolated the data with the form $(T\text{-}T_c)^{\beta}$, β 0.24 for tilt angle and β 0.5 for polarization, respectively. In Eq. (3) we assumed that $\Delta\varepsilon$ -1.1. It should be pointed out that the value $\Delta\varepsilon$ above is taken from pure TFMHPOBC [5], and that the term proportional to E^2 in the denominator of Eq. (2) is negligibly small. Any value $|\Delta\varepsilon| < 10$ will have negligible effect on determining U. The refractive indices that were measured by the wedged cell in the smectic A phase are n_o 1.48 and n_e 1.61. From these data, the coupling energy was then evaluated

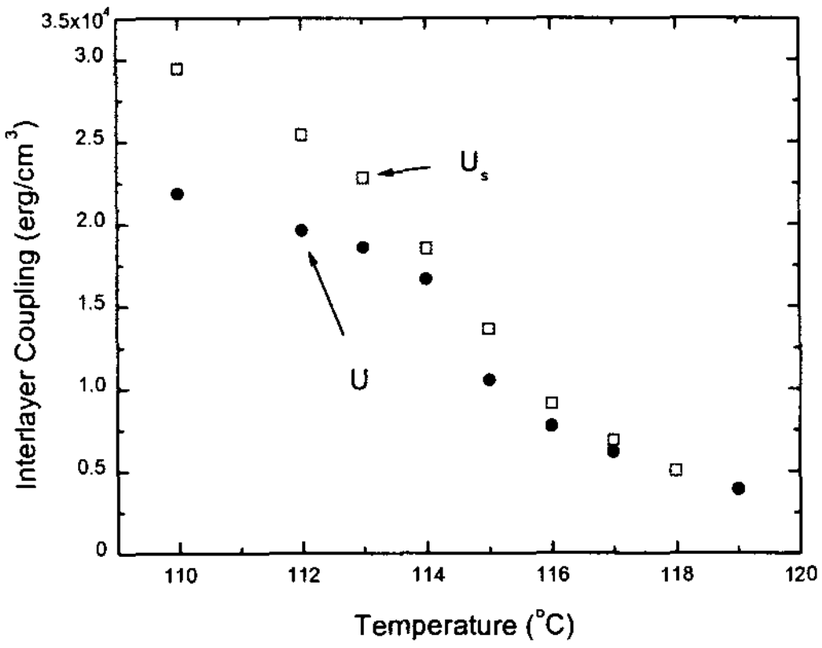

Fig. 4. Experimental results of interlayer coupling U evaluated by our low field perturbative technique (solid) and U_s by threshold measurements of field-induced solitary waves (open).

using the Eq. (3), and was presented in Fig. 4.

As Fig. 4 indicates, the magnitudes of interlayer coupling energy in both experiments are very similar. The values U_s(T) from the threshold field are slightly larger. A small discrepancy may be due to a different technique we used. However, in the lower temperature regime, the difference between the two becomes larger as the temperature is lowered.

Now consider the magnitude of the interlayer coupling coefficient. 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 100~500 erg cm^{-3} for the case of MHPOBC. This value, however, depends critically on the spacing between and magnitudes of the dipoles. For example, in their estimation, the spacing of a molecule was inferred from the layer spacing measured by the X-ray diffraction. However, according to the schematic explanation and illustration (Fig.1 in Ref.6) suggested by Miyachi [6], the net spacing which contribute effectively to the interlayer coupling seems to be much smaller than that of the layer spacing. Furthermore, the interlayer coupling should include beyond nearest neighbor interactions in three dimension, rather than solely pair interactions. Therefore it is no wonder that the experimentally measured U is up to two orders of magnitude bigger than the upper limit. U, in fact, has been estimated experimentally.

From the anticlinic-to-synclinic switching threshold, Fornier and Verweire [12] estimated U = 5.15×10^4 erg cm^{-3} for mixture compound CS-4000(Chisso). Li, et al. [3] also deduced U = 2.8×10^4 erg cm^{-3} for optically pure TFMHPOBC at 3.5 °C below smectic A to smectic C_A* phase transition. Although both values are estimated in different samples and at different temperatures, they are inconsistent from our value in the limit of small fields.

Finally, an "S"-shaped behavior (Fig. 4) for U(T) [and U_s(T)] was observed. This may be due to the nascent smectic C phase at lower concentrations in the neighborhood of phase transition temperature, which will soften the layer interaction.

5. Conclusions

We have experimentally estimated the anticlinic 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 φ^2 even out to moderately large values of φ, and that the free energy expression used to predict the onset of switching by means of solitary waves is a physically realistic model.

6. Acknowledgements

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