Polarization and Tilt-Angle Measurements near the Smectic-*A*–Chiral-Smectic-*C* Transition of *p*-(*n*-decyloxybenzylidene)-*p*-amino-(2-methyl-butyl)cinnamate (DOBAMBC)

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For a given temperature below the smectic-*A* (Sm*A*)–chiral-smectic-*C* (SmC^*) transition of DOBAMBC, polarization (P) and tilt angle (θ) have been measured almost simultaneously with high resolution. The ratio P/θ stays fairly constant for $T_c - T > 2$ K and shows a precipitous drop near the transition temperature (T_c). A calculation based on a generalized mean-field model, similar to the one proposed by Zeks, is in good agreement with our result. This generalized mean-field model also gives the prominent feature of the helical pitch anomaly just below the Sm*A*-SmC^* transition.

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Since 1975, when Meyer *et al.*[1] established the existence of and investigated the behavior of ferroelectric liquid crystals which showed a chiral smectic-*C* (SmC^*) phase in *p*-(*n*-decyloxybenzylidene)-*p*-amino-(2-methyl-butyl)cinnamate (DOBAMBC), considerable experiment and theoretical effort has been put into characterizing the bulk properties of SmC^*. In 1980, Clark and Lagerwall[2] demonstrated bistability and submicrosecond switching in thin SmC^* sample cells. Thus the problem of carefully characterizing the bulk properties of SmC^* is not just academic; it has important technological implications as well. Here we will report our high-resolution and almost simultaneous measurements on polarization (P) and tilt angle (θ) near the smectic-*A* (Sm*A*)–SmC^* transition of DOBAMBC. Striking behavior in P/θ is found near the transition and a phenomenological theory is given to explain our result.

The spontaneous polarization is determined from measurements of the displacement current through the field-reversal method. The well-aligned liquid-crystal sample in planar configuration was grown between a pair of glass slides which were coated with transparent and conducting indium-tin-oxide (ITO) films. To achieve high-quality alignment, the glass slides were spin-coated with nylon and then rubbed on cotton cloth.[3] The sample cell was driven by a triangular wave[4] instead of a square wave.[5] The linear background (triangular-wave method) instead of the exponential one (square-wave method) simplifies the data reduction a great deal.[4] Just below the Sm*A*-SmC^* transition, the displacement current resulting from the bulk spontaneous polarization is very small. A signal averager was employed to enhance the signal-to-noise ratio. At our operating frequency (10 Hz), the spontaneous polarization was measured as a function of applied electric field strength (E) for $T_c - T = 1.0$ and 20.2 K. The measured polarization remains fairly constant (within 1%) for $E > E_p$. Here E_p is approximately equal to twice the critical field (E_u) to unwind the helix. In the applied electrical field, the E_u was determined by observation of the disappearance of the helix under a polarizing microscope. Our measurements were carried out at $E = 2E_p(T_c - T = 20\text{ K}) = 2.5\times10^6$ V/m. A smaller polarization was obtained for $E < E_p$, because the helix is not fully unwound and/or the surface layers are not aligned. For $E > E_p$, the constancy of the measured polarization indicates that the electric-field–induced dipole moment will contribute to the background current instead of the displacement current peak which appears right after the value of E crosses the zero-field line.

The molecular tilt angle was measured by an electro-optical technique with a dc applied electric field. In the SmC^* phase the molecular director is switched by the changing of the polarity of an external applied field. Then the principal axes of the liquid-crystal sample cell could be determined from the measured angles as the cell was rotated between one pair of cross polarizers. A minimum amplitude of the electro-optical response would be detected when the molecular director was parallel or perpendicular to the principal optical axis of the polarizers. In order to reduce the finite-field effect on the tilt angle, at a given temperature the tilt angles were measured with at least four different applied electric fields. An extrapolation to the zero-field limit is our measured tilt angle. Thus far both spontaneous polarization P and tilt angle θ have been measured by several groups.[5-8] Large variances exist among the published data. In taking our experimental data, tilt angle and polarization were measured one after the other at each given sample temperature. This almost simultaneous measurement on P and θ is necessary because of the T_c shift (20 mK/h) and allows us to reveal a prominent and unexpected behavior in the ratio P/θ near T_c. All the data have been corrected for this T_c shift.

Here T_c is the SmA-SmC^* transition. Our DOBAMBC sample was purchased from Frinton Laboratories[9] and was recrystallized twice from methanol by us. The transition temperature is about 93.7 °C.

Our spontaneous polarization P and tilt-angle θ data and their ratio P/θ are shown in Figs. 1(a) and 1(b) as a function of $T_c - T$ for a sample with thickness 25 μm. The same results were obtained for the sample with thickness 75 μm. Qualitatively, our tilt-angle data agree with those obtained by Ostrovskii *et al.*[7] and the polarization data are consistent with those measured by Hoffmann, Kuczynski, and Malecki.[8] However, we have much higher resolution in the measurements of temperature (3 mK), tilt angle (1.7×10^{-3} rad), and polarization ($\pm 0.5\%$). Comparison with all the existing data will be made in a future publication. While a simple power-law fitting to the tilt angle, i.e., $\theta = \theta_0 |t|^{\beta}$, fails to account for all the data, the tilt-angle expression derived from the extended mean-field free energy as suggested by Huang and coworkers[10,11] gives a much better fitting result. Our almost simultaneous measurements on both polarization and tilt angle reveal one striking feature. While the ratio P/θ remains fairly constant for $T_c - T \gtrsim 2$ K, this quantity drops precipitously in the region $T_c - T \lesssim 2$ K. Here we will offer a phenomenological free-energy expansion to explain this unusual behavior.

The most commonly cited mean-field free-energy expression for the SmC^* phase is[12]

$$G_1 = \tfrac{1}{2} a t \theta^2 + \tfrac{1}{4} b \theta^4 - \Lambda \theta^2 q + \tfrac{1}{2} K \theta^2 q^2 + \tfrac{1}{2} \epsilon^{-1} P^2 - f P \theta q - z P \theta. \tag{1}$$

Here q is the wave vector of the SmC^* helix, K the elastic modulus, Λ the coefficient of the Lifshitz-invariant term responsible for the modulation, and f and z the coefficients of the flexoelectric and piezoelectric coupling between the tilt angle θ and the polarization P. The coefficients a and b are positive constants and the temperature difference is $t = T - T_0$. Here T_0 is the "unrenormalized" transition temperature. Three major predictions result from this free-energy expansion. First, the SmA-SmC^* transition temperature (T_c^c) is higher than the SmA–smectic-C (SmC) transition temperature (T_c^r) of the corresponding racemic liquid crystal which does not have macroscopic spontaneous polarization ($P = 0$) and helix ($q = 0$). Experimentally, it has been found that the difference $T_c^c - T_c^r$ is only a few tenths of a degree.[1,13] Secondly, q is temperature independent. This prediction is at variance with experimental results which show a minimum in q just below T_c.[6,14,15] Far below T_c, q is decreasing slowly with temperature. Thirdly, the polarization is proportional to the tilt angle. In the light of our experimental result, this theoretical prediction fails again in the region just below T_c and agrees reasonably well with our data for $T_c - T \gtrsim 2$ K.

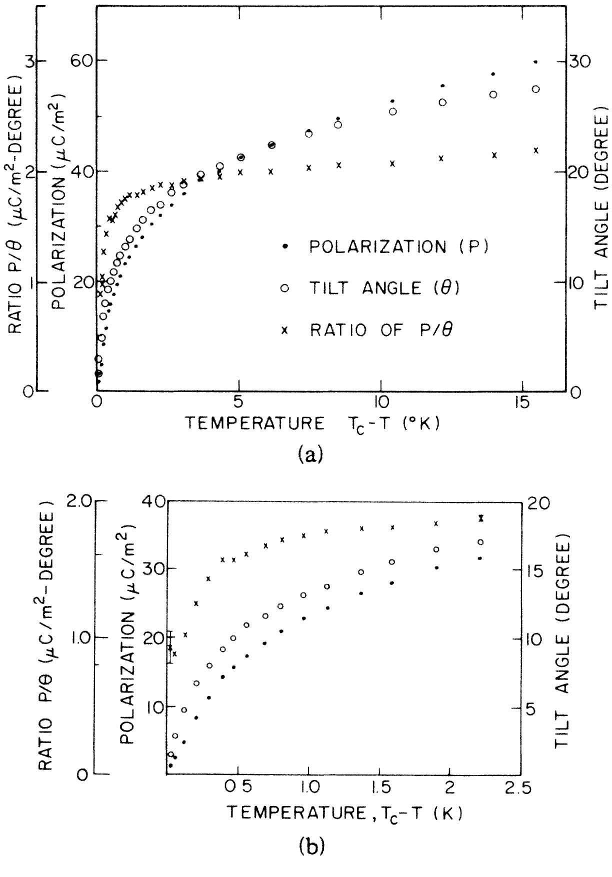

FIG. 1. Spontaneous polarization, tilt angle, and their ratio (P/θ) vs $T_c - T$ for DOBAMBC, (a) in a large temperature range and (b) in the vicinity of the transition. Two typical errors in the ratio P/θ are shown in (b).

The fact that the difference $T_c^c - T_c^r$ is small and the chiral-smectic-C helical pitch ($= 2\pi/q \simeq$ a few microns) is much larger than the typical molecular length ($\simeq 30$ Å) suggests that coupling coefficients, i.e., Λ f, and z, are very small and one has to include some higher-order terms. Here we will include the following four terms

$$G_2 = -\tfrac{1}{2} e P^2 \theta^2 + \tfrac{1}{4} g P^4 - d q \theta^4 + \tfrac{1}{6} c \theta^6. \tag{2}$$

The first term is the lowest nonchiral P-θ biquadratic coupling term. The third term is equivalent to replacement of Λ in G_1 by $\Lambda + d\theta^2$ and should describe the monotonic increase of the pitch with temperature at low temperature. These three terms are suggested by Zeks.[16] From our work on SmA-SmC (or SmC^*) we found that the last term is essential to describe this transition.[10]

Now minimizing the total free energy G ($= G_1$

$+G_2$) with respect to q, one has

$$q=K^{-1}(\Lambda+d\theta^2+fP/\theta). \tag{3}$$

Substituting this expression for q in G, one obtains

$$G_A=G_B(\theta)+G_c(\theta,P). \tag{4}$$

Here

$$G_B(\theta)=\tfrac{1}{2}(at-\Lambda^2/K)\theta^2+\tfrac{1}{4}(b-4\Lambda d/K)\theta^4+\tfrac{1}{6}(c-3d^2/K)\theta^6=\tfrac{1}{2}a_2(T-T_c)\theta^2+\tfrac{1}{4}a_4\theta^4+\tfrac{1}{6}a_6\theta^6 \tag{5}$$

and

$$G_c(\theta,P)=\tfrac{1}{2}(1/\epsilon-e\theta^2-f^2/K)P^2+\tfrac{1}{4}gP^4-[(z+\Lambda f/K)\theta+(df/K)\theta^3]P=\tfrac{1}{2}\alpha P^2+\tfrac{1}{4}gP^4-\beta P. \tag{6}$$

Again minimizing G_A with respect to P, one gets

$$gP^3+\alpha P-\beta=0. \tag{7}$$

Here $a_2=a$, $T_c=T_0+\Lambda^2/Ka$, $a_4=b-4\Lambda d/K$, and $a_6=c-3d^2/K$; $\beta=(z+\Lambda f/K)\theta+(df/K)\theta^3$ and $\alpha=1/\epsilon-f^2/K-e\theta^2=e(\theta_1^2-\theta^2)$, where $\theta_1^2=(1/\epsilon-f^2/K)/e$. The solution for Eq. (7) can be written as[17]

$$P=[2/(3g)^{1/2}]|\alpha|^{1/2}Y(x), \tag{8}$$

where

$$x=(27g)^{1/2}\beta/(2|\alpha|^{3/2})$$

and

$$Y(x)=\begin{cases}\sinh(\frac{1}{3}\sinh^{-1}x) \text{ for } \theta^2<\theta_1^2,\\ \cosh(\frac{1}{3}\cosh^{-1}x) \text{ for } \theta^2>\theta_1^2 \text{ and } x>1,\\ \cos(\frac{1}{3}\cos^{-1}x) \text{ for } \theta^2>\theta_1^2 \text{ and } x<1.\end{cases}$$

The equation for θ can be obtained by minimizing G_A with respect to θ:

$$a_2(T-T_c)\theta+a_4\theta^3+a_6\theta^5-[(\beta/\theta)+(2fd/K)\theta^2]P-e\theta P^2=0. \tag{9}$$

Choosing the following set of parameters,

$$(27g)^{1/2}(z+\Lambda f/K)/2e^{3/2}\theta_1^2=1,\quad gd^2\theta_1^2/e^2K=0.001,$$

$$(27g)^{1/2}fd/2Ke^{3/2}=-0.04,\quad (27g)^{1/2}\Lambda/2e^{1/2}f=-2.3,$$

$$ga_6\theta_1^2/4e^2=207,\quad ga_4/4e^2=333,$$

we have solved Eq. (9) numerically. The (arbitrary) temperature scale is defined so that $T_c-T=1$ when $\theta/\theta_1=1$. This determines the coefficient of the first term in Eq. (9) and $ga_2/4e^2\theta_1^2=538$.

The temperature dependence of the pitch ($=2\pi/q$) and of the ratio of polarization to tilt angle $(P/P_0)/(\theta/\theta_1)$, where $P_0=2\theta_1(e/3g)^{1/2}$ are shown in Fig. 2. The unit of pitch is its value at T_c. From our high-resolution heat-capacity work near the Sm*A*-Sm*C** and Sm*A*-Sm*C* transitions of the chiral and racemic versions of 2-methylbutyl-4′-*n*-pentyloxy-biphenyl-4-carboxylate, we have found that $(T_c^c-T_c^r)/T_c^c$ is only about 0.1%. So we choose the parameters associated with the first three terms in Eq. (9) to be about 1000 times larger than the last three terms. With this criterion, we eliminate the "S"-shaped kink reported by Zeks.[16] Our experimental results on P and θ displayed in Fig. 1(b) do not have "S"-shaped kinks. Another way to justify our choice of the parameters is to consider the relative size of various terms in Eq. (1). From our heat-capacity and tilt-angle measurements,[18] we obtained $a=4.6\times10^4$ J/m^3-K. At $T_c-T=5$ K, $\theta=0.3$ rad and $P=40$ μC/m^2. Employing available data[19] for K ($\sim5\times10^{-12}$ N), f ($=4\times10^{-1}$ V), z ($=4\times10^6$ V/m), and q ($=3\times10^6$ m^{-1}), we obtain that the leading term at θ^2 is about 1000 times larger than the rest of the terms with q and/or P in Eq. (1). Zeks has chosen $ga_4/4e^2=0.27$ such that $ga_2/4e^2\theta_1^2=0.07$, which is too small. The major difference between our parameters and the ones chosen by Zeks is that much more realistic values have been chosen

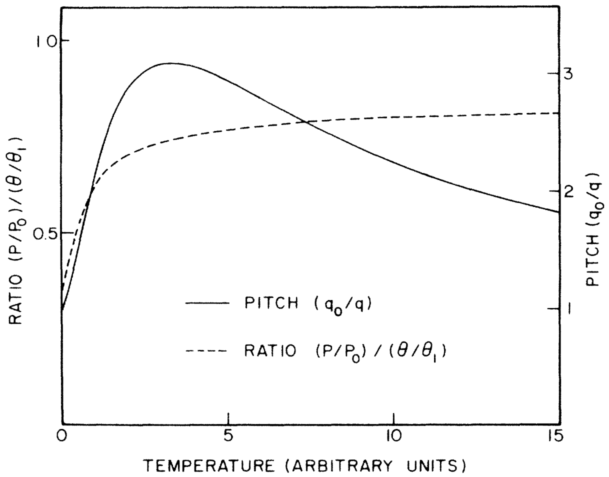

FIG. 2. Calculated $(P/P_0)/(\theta/\theta_1)$ and q_0/q vs t in arbitrary units.

for coefficients a and b. Also we need the θ^6 term to give the proper account of the temperature behavior of θ and p.

In conclusion, experimentally we have found anomalous behavior in the ratio P/θ near the SmA-SmC^* transition of DOBAMBC. Measurement on another chiral-smectic-C compound shows a similar anomaly in P/θ. Consequently, this anomaly in P/θ may be a general one. Provided that this generalized mean-field model is sufficient to describe the SmA-SmC^* transition, Eq. (3) indicates that any anomaly in q requires an anomaly in P/θ except for the θ^2 dependence. Anomalous temperature variation of the helical pitch seems to be very common in the SmC^* phase. Thus an anomaly in P/θ seems to be unavoidable and should be very common in the SmC^* phase. Theoretically, a much more realistic mean-field free energy has been proposed which gives a very good account of the anomalous behavior in P/θ and the helical pitch in the chiral smectic-C phase.

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[17] We have found a mistake in the solution for Eq. (7) reported in Ref. 16. Instead of our Eq. (8) for the parameter x, Zeks used $x = (27g)^{1/2}|\beta|/(2|\alpha|^{3/2})$. Once β changes from being positive for small θ to negative for large θ, this will produce a discontinuity in the slope of x. Consequently, both P and θ will have a discontinuity in the slope. In the expression for β, df/K usually is a negative quantity.

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