Optical Reflectivity and Ellipsometry Studies of the Sm-C_α^* Phase

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(Received 6 July 1999)

Both optical reflectivity and ellipsometry data obtained from freestanding films in the Sm-C_α^* phase of one liquid-crystal compound display characteristic oscillations as a function of temperature. A model for the film consisting of surface anticlinic layers and an interior short-pitched azimuthal helix provides an excellent description of our data. Our results show a linear evolution with temperature of the relative interlayer azimuthal angle. The data enable us to place an upper bound on the degree of distortion in the short-pitched helix.

PACS numbers: 61.30.Eb, 77.84.Nh, 83.70.Jr

The surprising discoveries of ferroelectric and antiferroelectric behavior in liquid crystal Sm-C^* [1] and Sm-C_A^* [2] phases without long range positional order are fundamental to condensed matter physics. Three phases showing more complicated electric field responses (Sm-C_{FI1}^*, Sm-C_{FI2}^*, and Sm-C_α^*) have also been identified [3]. While the structure of the Sm-C^* and Sm-C_A^* phases are now well understood, the underlying structures of these intermediate phases is still the subject of debate. Recent resonant x-ray experiments [4] have for the first time resolved the structural periodicity of these phases. Furthermore, the polarization analysis [5] gives direct evidence for the clock model [6] unit cell in the Sm-C_{FI1}^* and Sm-C_{FI2}^* phases. In this paper we study the detailed structure of the Sm-C_α^* phase found in the 10OTBBB1M7 compound [7] (Fig. 1) using optical reflectivity and ellipsometry. The clock model with a continuously evolving helix is the only model that is consistent with our data. Our results also confirm the periodicity measured by x rays for this phase [4]. Alternative models, in particular, the proposed Ising model devil's staircase [3,8], conflict with even the gross features of our data. We also propose that surface anticlinic layers [9] coexist with the helical Sm-C_α^* phase in our freestanding films. Our results also allow us to place an upper bound on the degree of distortion in the short-pitched helix should such a distortion exist.

The Sm-C_α^* phase, like all of the Sm-C^* variant phases, is known to possess a tilted smectic structure. The average orientation of the long axis of the molecules (the director) within the ith layer may be described by the tilt angle (θ_i) with respect to the layer normal and the azimuthal angle (ϕ_i). Each layer possesses a net dipole, oriented perpendicular to the layer normal and the director. Our results allow us to model $[\theta_i]$ and $[\phi_i]$ as continuous functions of temperature in the Sm-C_α^* phase in freestanding films.

The liquid-crystal freestanding film is prepared in a double stage temperature controlled oven with a temperature resolution of 0.01 K. The film is drawn across a 7×5 mm rectangular hole in a horizontal glass coverslip [10]. Two gold electrodes produce an aligning electric field in the plane of the film The 10OTBBB1M7 compound studied is isolated in a $\frac{5}{6}$ atm argon environment. The ellipsometry optical components share this argon environment.

The reflectivity of the film is measured with a chopped He-Ne laser beam, either circularly or linearly polarized, that impinges on the film at 1° with respect to the film normal. While both the linearly and circularly polarized light are sensitive (to within 1 Å) to the overall optical thickness of the film [11] and thus the tilt angle, the linearly polarized light alone will also be sensitive to azimuthal orientation of the molecules. Employing both reflectivity probes allows for separation of these two effects.

The design of our polarizer-compensator-system-analyzer (PCSA) null ellipsometer has been inspired by a number of experiments on freestanding films. In particular, our experiment follows the extensive work of Bahr *et al.* [12,13]. The He-Ne laser beam is incident at 45° from the film normal and perpendicular to the electric field. At null, the measured quantity Δ is the phase lag between the p and s components of polarization as the

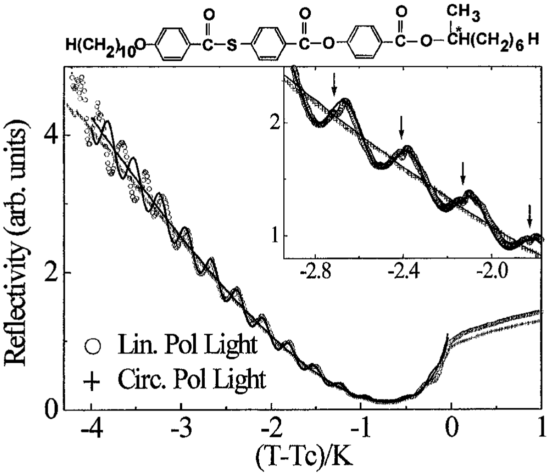

FIG. 1. Reflectivity vs temperature with fit (solid lines) to the proposed model for a 273-layer film. The inset highlights the quality of the fit and the observed helix reorientations (arrows).

beam enters the sample and Ψ is the orientation of the output linear polarization state. Note that because the transmission matrix of the sample is in general not diagonal for the proposed structures, the physical meaning of Δ and Ψ differs slightly from the common definition [14]. With the quarter wave plate fixed at 45° with respect to the incident plane, $\Delta = \frac{\pi}{2} - 2P$, and $\Psi = A$, where P and A are the orientations of the polarizer and analyzer, respectively, at null. By fitting a range of intensities about the null point, a resolution of 0.001° in Δ and Ψ is achievable at an acquisition rate of 1 point/min.

The ordinary and extraordinary indices of refraction of the sample, n_o and n_e, and the layer thickness d are determined by spreading ~40 films ($1\ \mathrm{L} < N < 400\ \mathrm{L}$) in the Sm-$A$ phase [12]. Here N is the film thickness in number of layers (L). $\Psi(N)$ vs $\Delta(N)$ may then be fit to a uniaxial slab model [14]. This procedure yields $n_o = 1.470$, $n_e = 1.612$, and $d = 4.00$ nm for 10OTBBB1M7 [15]. With this information, we are able to determine the number of layers even in thick films to within one or two layers.

In the experimental runs described here, the temperature was ramped (20 mK/min) through the Sm-C_α^* phase window with a constant aligning field (5 V/cm). This field does not noticeably modify the zero field film structure [12]. The field direction is usually set in the Sm-A temperature range. Then the sample is cooled and heated. This process is repeated for both field orientations. We also performed ramps in which the electric field was reversed every 5 min to double-check the switching properties. In the Sm-C_α^* phase, we consistently observed no change in Ψ under field reversal. In the data presented in Fig. 2, the raw data (Ψ) showed an irreproducible offset that very slowly drifted with time. We have thus presented Ψ offset by 0.1° to represent the true switching properties of the phase.

Both the reflectivity and ellipsometric data shown in Figs. 1 and 2 may be described as a large-scale trend with superimposed oscillations. The large-scale trend in the data allows for the modeling of the average tilt angle θ vs temperature (T). The reflectivity shows a decrease to a minimum at $T - T_c = -0.7°$ and then a monotonic increase. Here T_c is the Sm-A-Sm-C_α^* transition temperature. Δ and Ψ both exhibit monotonic increases (Fig. 2). These trends are attributed to the monotonic decrease in the optical thickness of the film as it is cooled due to the increasing θ. To obtain θ vs T in the Sm-C_α^* phase range, we fit the reflectivity, Δ, and Ψ vs T to a simple uniaxial slab model [14]. The optical thickness of the slab is determined by the tilt angle and the indices of refraction. The tilt angle is described by a power law function of temperature $\theta = A[(T_c - T)/T_c]^\beta$. These fits yield $T_c = 396.8 \pm 0.1$ K, $\beta = 0.31 \pm 0.01$, and $A = 42° \pm 4°$. This value of the β is consistent with the commonly applied extended mean field model for the variation of tilt in the smectic phases [16]. The expression yields a reasonable tilt of 10° at the low end of the phase window. The error bars reflect the spread of values obtained for three different film thicknesses. Thus we have a reasonable and consistent expression for the tilt with which to begin modeling the more detailed azimuthal structure.

The oscillations in temperature space show four key characteristics. (1) The frequency in temperature space, f, is roughly constant. (2) f decreases linearly with N. Films of thickness $N = 349$, 273, 226, 59, and 17 layers give $f = 5.3$, 4.0, 3.0, 0.76, and 0 oscillations/K, respectively. A linear fit to f vs N yields an $f = 0$ intercept of 18 L. (3) The amplitude of the Δ and Ψ oscillations is roughly independent of N. (4) The basic features of Δ and Ψ show little change under field reversal (Fig. 2). The relevance of these four characteristics shall now be addressed.

The qualitative features of the data immediately rule out an Ising-like devil's staircase structure [8]. In an Ising structure with an aligning field the director sits in the plane of incidence and only changes in ϕ_i of 180° are allowed. Both vertically incident linear polarized light and Ψ are insensitive to such reorientations. This insensitivity of the

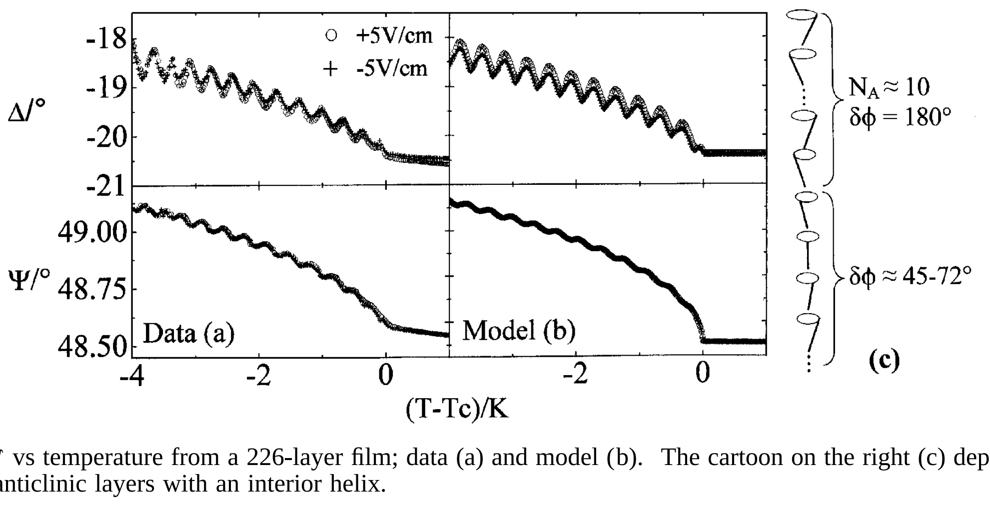

FIG. 2. Δ and Ψ vs temperature from a 226-layer film; data (a) and model (b). The cartoon on the right (c) depicts our proposed model of surface anticlinic layers with an interior helix.

reflected light arises from the 2-fold rotational symmetry of the linear polarizer in this geometry. The insensitivity of Ψ to such reorientations is seen both in simple slab models for tilted smectic films and in 4×4 matrix calculations [14,17–19] for stratified tilted smectic structures. Hence the oscillations in the linear polarized reflectivity and in Ψ cannot be caused by Ising-like changes in structure. The Ising model also predicts a large net polarization at certain periodicities. Such structures would cause large changes in Δ under field reversal contrary to the observations. Since an Ising-like structure could not produce the qualitative features of the data we instead consider an evolving short-pitched helical structure.

To model the details of the data quantitatively we use the 4×4 matrix approach to determine the reflection and transmission matrices for stratified uniaxial media [14,17–19]. The reflectivity under incident polarized light is directly calculable from the reflectivity matrix. The Jones matrix equations for the PCSA arrangement can be solved for Δ and Ψ as analytical functions of the transmission matrix. The model is adjusted manually to fit with both the reflectivity and ellipsometric data.

A film with a short pitch that evolves with temperature does produce oscillations [20] in the data. This can be understood by considering the helix total length to pitch ratio L_h/L_p. When L_h/L_p is an integer, the structure is uniaxial to first order at optical wavelengths. For noninteger L_h/L_p, while most of the structure is still uniaxial, there are now extra layers that add biaxiality. As the pitch decreases from $L_h/L_p = j$ to $L_h/L_p = j - 1$, one oscillation in the degree of biaxiality occurs. From the x-ray results [5], we expect the pitch to decrease from eight to five layers on cooling. This pitch change is roughly consistent with the observed number of oscillations found in thick films. However, the modeled oscillation amplitudes are roughly a factor of 5 smaller than seen in both the reflectivity and ellipsometric data. Furthermore, the switching properties of a simple helix structure are not those observed. A helix model shows oscillations in Δ and Ψ that invert under field reversal, a feature that is qualitatively different from the data.

To account for nonswitching, large amplitude oscillations we propose that an anticlinic surface phase coexists with an internal short-pitched helical structure [Fig. 2(c)]. The orientation of the surface anticlinic layers are set by the ends of the helix. Thus as the helix unwinds, the surface layers rotate. Their rate of rotation increases with pitch evolution rate and film thickness. The polarization state of the light is affected more strongly by the rotation of the biaxial surface structure than the nearly uniaxial interior short-pitched helix. Thus the amplitude of the oscillations in the optical data is determined by the degree of biaxiality (tilt and thickness) in these surface structures. Because of the symmetry of the anticlinic surface structures, this model predicts only a slight change in Δ and Ψ under field inversion. This prediction agrees with the data. Further empirical support for this model is seen above T_c in the Sm-A phase where the switching properties of a surface Sm-C^* phase change to those of a nonswitching phase upon cooling. Also, for a thickness independent pitch evolution, one expects f vs N to be linear as is observed. The $f = 0$ intercept of $N = 18$ L determined by the fit suggests the presence of a nine-layer surface phase. This estimate of the surface phase thickness is consistent with the fact that no oscillations are observed at $N = 17$. These arguments elucidate some of the intuitive features of the data and the model.

To implement our model the following parameters are required: the relative interlayer azimuthal angle in the helix as a function of temperature $\delta\phi(T) = \phi_i - \phi_{i-1}$, number of surface anticlinic layers N_A, tilt angle at the surface θ_s, and the tilt penetration depth ξ. In our model, the tilt angle is assumed to decay exponentially to the bulk value over ξ. The surface structure determines the amplitude of the oscillations, with the oscillation size increasing with N_A, ξ, and θ_s. The frequency and the phase of the oscillations are determined by $\delta\phi(T)$. The constant oscillation frequency with temperature implies a linear growth in the relative azimuth as a function of temperature, i.e., $\delta\phi = B(T_c - T)$, where $B = d(\delta\phi)/dT$ is a constant. The modeling of the data as shown in Figs. 1 and 2(b) yields the following values for the above parameters: $B = 5.7 \pm 0.4°/\mathrm{K}$, $N_A = 10$, $\xi = 5$, and $\theta_s = 12°$. The error in B reflects the range of values obtained for different film thicknesses. The surface parameters are correlated and should be interpreted as a rough approximation of the surface structure. However, the same surface parameters are successfully used to model the reflectivity, Δ, and Ψ for all of the film thicknesses studied.

Our model also explains the small discrete steps in our data (Fig. 3). In the model, these singularities mark a sudden 180° rotation in the helix. As the net polarization of the helix passes through zero, it reverses its orientation by 180°. Thus the helix must rotate in order to align its net dipole with the field. The model, which gives the predicted optical signals for equilibrium orientations

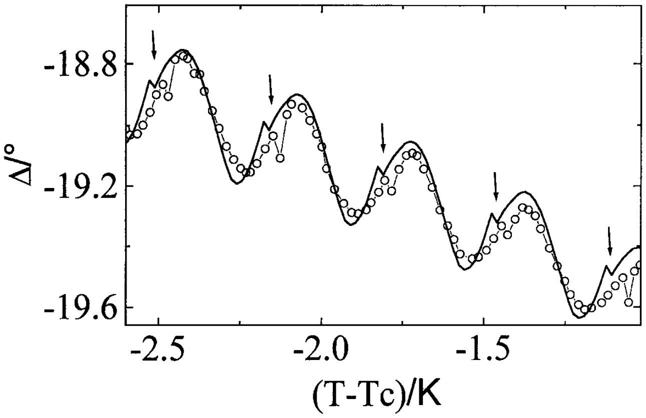

FIG. 3. Δ vs temperature from the 226-layer film (circles) with fit to the model (solid line). The arrows mark points at which the net polarization of the film rotates by 180°.

only, shows no such features in the reflectivity. However, the data density in time of our reflectivity measurement (1 pt/5 s) is sufficient to track the helix as it passes through its nonequilibrium orientations. This explains the small features in Fig. 1. The width of the features in the reflectivity data suggests that the helix takes about 1 min to reorient itself.

One other model was attempted for comparison. It has been speculated that in order to account for recent light scattering data [21], a biaxial unit cell for the Sm-C_α^* superlattice period is required. Within the clock model, this would require a distorted helix. We have attempted to model the data in terms of such a distorted clock unsuccessfully. Helical structures containing a polar unit cell predict oscillation frequencies and switching properties that are incompatible with the data. Models with a nonpolar unit cell come closer to reproducing the data for the thicker films but predict that the amplitude of the oscillations decrease in proportion to film thickness. By contrast, the observed thickness independent amplitude intuitively suggests that a surface structure accounts for the oscillations. While distortions in the helix alone cannot account for the data, models that include both a distorted helix and a surface anticlinic structure allow for an upper bound to be placed on the degree of distortion. Results from this type of modeling predict upper bounds of 1° and 5° for the average deviation in ϕ_i from the undistorted clock in helices with polar and nonpolar unit cells, respectively.

To conclude, the Sm-C_α^* phase for 10OTBBB1M7 in freestanding films can be modeled as a short-pitched helix with coexistent surface anticlinic layers. There is qualitative, intuitive, and quantitative justification for the observed optical reflectivity and ellipsometric data. The results give a direct argument for the necessity of an underlying helical structure. Our data are entirely incompatible with the Ising-like devil's staircase model. The oscillations are also not well modeled by a distorted clock. Our results may be compared and contrasted with one recent result [20]. Both support the clock model but suggest a radically different evolution behavior of the pitch. Also, the presence of surface induced anticlinic layers in the C_α phase is unique to this compound [22]. To test the general features of this phase, further study of the Sm-C_α^* phase using our optical system is in order.

We gratefully acknowledge R. Pindak, N. Clark, P. Barois, and S. Sprunt for detailed and thought-provoking discussions. We are extremely grateful for the extensive help of Ch. Bahr in the construction and implementation of our ellipsometer. The research was supported in part by the National Science Foundation, Solid State Chemistry Program under Grant No. DMR-9703898 and NATO International Scientific Exchange Programme.

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