Surface-induced multiple reentrant transitions

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We have studied tilted surface layers in the bulk SmA temperature window of one liquid crystal using null transmission ellipsometry. Five distinct nonplanar surface structures were observed. We present analyses of the tilt and azimuthal profiles of the structures and examine the transitions between the structures. The transitions are identified as a double reentrant synclinic-anticlinic-synclinic-anticlinic transition. Meanwhile, the transitions also display reentrant ferroelectric-antiferroelectric-ferroelectric behavior.

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I. INTRODUCTION

Bulk liquid crystals (LCs) exhibit a rich array of phases depending on temperature, e.g., isotropic liquid, nematic, smectic A (SmA), and a variety of smectic C\(^\ast\) (SmC\(^\ast\)) variant phases. The smectic phases form a layered structure, which allows for stable free-standing films to be prepared using many compounds. In the SmA phase, the molecular long axis, described by the director \(\mathbf{n}\), is parallel to the layer normal. In the SmC\(^\ast\) variant phases, the molecules are tilted at an angle \(\theta\) with respect to the normal. In this case, the \(c\) director, defined by the projection of \(\mathbf{n}\) in the layer plane, is useful for discussing molecular orientations. Many experiments have observed the existence of tilted surface layers at temperatures well above the bulk SmA \(\rightarrow\) SmC\(^\ast\) transition temperature. For many LC compounds, surfaces tend to be more ordered than the bulk sample, in stark contrast to typical crystalline solids. This phenomenon, known as surface freezing, has been explained in terms of suppression of fluctuations at the surface due to surface tension [1]. Layers containing tilted molecules are optically biaxial. Thus, films consisting of bulk SmA with SmC\(^\ast\) surfaces are biaxial only at the surface. This allows for easy measurement of the surface properties with very little interference from the bulk using proper optical probes.

The structures of surface layers above the bulk SmA-SmC\(^\ast\) transition have attracted much interest in recent years. Each surface may contain several layers of tilted molecules. \(\theta\) decreases exponentially with distance away from the surface of the film; typical coherence lengths are on the order of a few smectic layers. Most previous experimental results are explained in terms of an Ising-like model, with coplanar \(c\) directors for all tilted layers. The molecular orientation may be either symmetric (anticlinic) or antisymmetric (synclinic) about the center of the film. One experiment observed nonplanar tilts [2]. Both synclinic [3,4] and anticlinic [4,5] structures have been observed when no electric field is present. By applying an electric field, transitions from synclinic to anticlinic structures [4,6] and from anticlinic to synclinic structures [4,7] have been observed. Transitions may also occur upon changing the temperature of a film. In two remarkable cases, a reentrant synclinic-anticlinic-synclinic transition [8] and a double reentrant synclinic-anticlinic-synclinic-anticlinic transition [9] were observed. Various models to explain the stability of the synclinic and anticlinic structures have included elastic energy due to spatial variations of \(\mathbf{n}\), coupling between the applied electric field and the polarization induced by the tilt [10], and polarization fluctuations at the two surfaces [4]. Synclinic structures have polarization perpendicular to the tilt plane and anticlinic structures have polarization parallel to the tilt plane.

If chiral compounds showing the antiferroelectric (SmC\(^\ast\)) phase are used, interactions beyond nearest neighbor layers give rise to new bulk structures like the SmC\(_{a}\), SmC\(_{\ast}\), and SmC\(_{\ast}\) phases [11–19]; these structures are not Ising-like. In SmC\(_{a}\), the \(c\) directors rotate by a constant angle between any two adjacent layers, creating an incommensurate helical superstructure. SmC\(_{\ast}\) (SmC\(_{\ast}\)) is best described by a three (four) layer structure in the distorted clock model [20]. The presence of these more complicated phases in the bulk sample suggests that surface structures may be more complex than Ising-like models under appropriate conditions. Reference [21] reported antiferroelectric coupling between adjacent surface layers, similar to the bulk SmC\(_{a}\) phase. The chiral compound (S)12OF1M7 was studied in this experiment. The molecular structure is given in Fig. 1. The bulk phase sequence for (S)12OF1M7 is SmC\(_{a}\) (78.4 °C) SmC\(_{\ast}\) (81.1 °C) SmC\(_{\ast}\) (84 °C) SmC\(_{\ast}\) (91.3 °C) SmC\(_{a}\) (92.4 °C) SmA. A rich sequence of surface transitions in the bulk SmA temperature window was obtained. We will discuss the observed surface structures and analyze the surface transitions. We observed a double reentrant synclinic-anticlinic-anticlinic transition and a simultaneous reentrant ferroelectric-antiferroelectric-ferroelectric transition.

II. EXPERIMENTAL SETUP

Null transmission ellipsometry (NTE) is a technique particularly well-suited for studying optical properties of thin

\[
\text{H}(\text{CH}_2)_2 \begin{array}{c} \text{O} \end{array} \begin{array}{c} \text{C} \end{array} \begin{array}{c} \text{O} \end{array} \begin{array}{c} \text{C} \end{array} \begin{array}{c} \text{C} \end{array} \begin{array}{c} \text{C} \end{array} \begin{array}{c} \text{C} \end{array} \begin{array}{c} \text{H} \end{array} \begin{array}{c} \text{F} \end{array} \begin{array}{c} \text{C}_4\text{H}_9 \end{array}
\]

FIG. 1. Chemical structure of (S)12OF1M7.
surface layers. Elliptically polarized laser light is transmitted through a free-standing film with anisotropic optical properties. The sample introduces a phase lag between the $\hat{p}$ and $\hat{\delta}$ components of the polarization, causing a change in the ellipticity of the polarization state of the laser light. The phases of the components of the incident light are adjusted so that the transmitted light is linearly polarized. Two ellipsometric parameters are measured: $\Psi$ and $\Delta$. $\Psi$ measures the phase difference between the incident $\hat{p}$ and $\hat{\delta}$ components necessary to produce linearly polarized light and $\Delta$ is the polarization angle of the transmitted light. A detailed description of our NTE apparatus can be found in Ref. [22].

Inside a temperature-regulated two-stage oven, thin free-standing liquid crystal films are created by pulling the sample across a hole of radius 7 mm in a glass coverslip. The free-standing film geometry ensures that the smectic layers are parallel to the film plate. An electric field is applied using eight electrodes placed symmetrically about the hole in the coverslip. The electric field is in the plane of the film and uniform except for very near the electrodes. The spontaneous polarization of the film aligns with the electric field, producing a stable monodomain sample. The electric field is small enough that the film structure is not altered by the field. By varying the voltages on the electrodes, the electric field and molecular orientations can be controlled. In this paper, the orientation of the electric field will be denoted by $\alpha$, the angle between the electric field and the incident plane (see Fig. 2).

### III. EXPERIMENTAL DATA

The parameters $\Psi$ and $\Delta$ were measured for several 16-layer films as the temperature was ramped at a rate of 20 mK/min. Here we will only discuss $\Delta$; one can see in Fig. 3 that $\Psi$ shows similar features. Both heating and cooling ramps were performed to check for reproducibility. The electric field orientation was switched between 0° and 90° every 2.5 min during the temperature ramps. Figure 3 shows $\Delta$ as a function of temperature for both orientations ($\Delta_{0}$ and $\Delta_{90}$). Five distinct surface structures are evident. Above $T_{3}$ the bulk is uniaxial SmA, so the features of the curves in Fig. 3 are dominated by the biaxiality of the surface layers. Above $T_{1}$, $\Delta$ is nearly equal at the two orientations, suggesting a synclinic arrangement of the surface layers. As the film is cooled below $T_{1}$, a transition in the surface layer structure occurs as evidenced by the jump in $\Delta_{90}$. Upon further cooling, another transition occurs at $T_{2}$. The absolute value of $\Delta_{0} - \Delta_{90}$ remains nearly constant at $T_{2}$. The sign of $\Delta_{0} - \Delta_{90}$ changes at $T_{2}$, suggesting that the molecules rotate about the layer normal by 90° at the transition. Changes in the sign of $\Delta_{0} - \Delta_{90}$ are also evident at $T_{3}$ and $T_{4}$. Changes in the magnitude of $\Delta_{0} - \Delta_{90}$ show that the net biaxiality of the surface layers also changes at $T_{2}$, $T_{3}$, and $T_{4}$, illustrating a more subtle change in the structure than simple rotation of all molecules about the layer normal by 90°. The 90° rotations indicate a change in polarization of the film from longitudinal to transverse, as described in Ref. [10].

We can obtain more detail about the surface layer structure by rotating the direction of the electric field. The ellipsometric parameters were measured as a function of $\alpha$, with the temperature held constant. A typical data set included rotation of $\alpha$ from 0° to 360° in steps of 10° with several independent measurements of $\Psi$ and $\Delta$ at each step to monitor data quality. In order to characterize the surface structures, many rotations were performed at various temperatures. Typical rotation data are given in Figs. 4–8 for one temperature (marked by upward arrow in Fig. 3) in each of the five temperature regions (henceforth labeled SmST₁ through SmST₅, to denote smectic-surface tilt phases). The differences in these figures confirm that the surface structures change. Figure 4(a) shows rotation data for SmST₁. The $\Delta$ versus $\alpha$ curve has a pronounced minimum at $\alpha$=270°. This is a signature of a synclinic surface structure. Figure 5(a)
shows rotation data for SmST2. Both $\Psi$ and $\Delta$ are nearly symmetric in a $180^\circ$ rotation, which could indicate either antifluidic surface layers, or antiferroelectric ordering within each surface. SmST2 [Fig. 6(a)] again shows $180^\circ$ symmetry, but the maxima and minima are displaced by $90^\circ$ from Fig. 5(a). This illustrates the $90^\circ$ rotation of the film that was evident in Fig. 3. Figures 7(a) and 8(a) show the rotation data for SmST4 and SmST5.

IV. DATA ANALYSES

A more detailed analysis using Berreman’s $4 \times 4$ matrix method [23] is necessary to determine the surface structures.

FIG. 5. (Color online) (a) $\Delta$ and $\Psi$ versus $\alpha$ and (b) $\Psi$ versus $\Delta$ at $T=94.42$ °C (SmST2). (c) Shows directions of the components of the polarization. $P_{FE}$ is very small for this structure because the surfaces are nearly antiferroelectric, so a different scale has been used for the diagram. $e_2$ is the same for all diagrams, but $e_1 = 100e_2$ in this figure, in contrast to Figs. 4 and 6–8.

FIG. 6. (Color online) (a) $\Delta$ and $\Psi$ versus $\alpha$ and (b) $\Psi$ versus $\Delta$ at $T=93.48$ °C (SmST3). (c) Shows directions of the components of the polarization. $\Sigma P_{FL}$ (int) represents the net $P_{FL}$ from the interior layers.

Berreman’s method models each smectic layer as a uniaxial slab with indices of refraction $n_e$ along the long axis of the molecules and $n_o$ perpendicular to the long molecular axis. Maxwell’s equations are applied to each layer using an incident electromagnetic (EM) wave and appropriate boundary conditions to get the ellipsometric parameters for the transmitted light beam. $n_o$ and $n_e$ were obtained by spreading 71 films with different thicknesses at 103 °C, in the uniaxial SmA phase. A plot of $\Psi$ versus $\Delta$ for these films was compared to simulation using a uniaxial slab with $n_o$ and $n_e$ as free parameters [24]. In SmA, the indices of refraction for this compound are found to be $n_o = 1.496 \pm 0.003$ and $n_e = 1.658 \pm 0.003$. Quantizing the film thickness in the simulation gave a measure of the smectic layer spacing: $d = 3.66 \pm 0.05$ nm. This method also allows measurement of the thickness of films in number of layers. Simulations using the $4 \times 4$ matrix method are included in Figs. 4–8.

FIG. 7. (Color online) (a) $\Delta$ and $\Psi$ versus $\alpha$ and (b) $\Psi$ versus $\Delta$ at $T=92.14$ °C (SmST4). (c) Shows directions of the components of the polarization.
Experiments using differential optical reflectivity [25] indicate that in SmC$_x$ not more than six surface layers are present in (S)120F1M7, therefore three tilted layers for each surface were considered. $\theta_j$ and $\varphi_j$ are the tilt and azimuthal angles for the jth layer when $\alpha=0^\circ$ (electric field in the incident plane), as defined in Fig. 2. $j=1$ denotes the first layer on the side of the film from which the laser light is incident. The 32 angles $\theta_j$ and $\varphi_j$ for $j=1–16$ were varied to determine the surface layer structure. The tilt profile was calculated from the mean-field theory result [26]

$$\theta_j = \theta_{\text{surf}} \frac{\cosh \left( \frac{2j - 1}{2} - N \right)}{\cosh \left( \frac{N - 1}{2} \right)} \cdot \xi.$$  \hspace{1cm} (1)

Here N and $\xi$ are the film thickness and correlation length in number of smectic layers. Because the inner layers have small tilt angles, the simulations are not sensitive to their azimuthal orientations, so for convenience we assumed $\varphi_j = \varphi_{j=1}$ for $j=4–8$ and $\varphi_j = \varphi_{j=14}$ for $j=9–13$. $\varphi_{14}$ and $\varphi_{16}$ were determined by the symmetry of the $\Psi$ and $\Delta$ versus $\alpha$ curves. Symmetry about the vertical center of the film further constrains the azimuthal orientations for the surface layers, so that only the parameters $\varphi_2$ and $\varphi_3$ needed to be varied to determine each structure, along with increases of $\theta_{\text{surf}}$ and $\xi$ with decreasing temperature.

Before discussing the structures, some comments on polarization in chiral smectic LCs are necessary. Two types of polarization are possible due to molecular orientations in smectic layers: ferroelectric polarization ($P_{FE}$) and flexoelectric polarization ($P_{FL}$). The ferroelectric polarization density in each layer is a result of chiral symmetry breaking when molecules are tilted. $P_{FE}$ is perpendicular to the $c$ director for each layer and approximately proportional to the tilt angle

$$\vec{P}_{FE} = e_1 (\sin \varphi_2 - \cos \varphi_0, 0).$$  \hspace{1cm} (2)

$P_{FL}$ results from gradients of $n$. In a continuum description, the flexoelectric polarization density is given by

$$\vec{P}_{FL} = e_2 \mathbf{n} \times (\nabla \times \mathbf{n}),$$  \hspace{1cm} (3)

where $e_2$ is a flexoelectric coefficient [27]. Other flexoelectric terms have been neglected because they yield qualitatively similar results. For smectic LCs, Eq. (2) can be discretized to find the flexoelectric polarization between two adjacent layers. The direction of $P_{FL}$ is easily calculated from the tilt and azimuthal angle of adjacent layers.

$$\vec{P}_{FL}(j,j+1) = e_2 \left( \mathbf{n}_j + \mathbf{n}_{j+1} \right) \times (- \mathbf{n}_{j,y} + \mathbf{n}_{j+1,y}, \mathbf{n}_{j,x} - \mathbf{n}_{j+1,x}, 0).$$  \hspace{1cm} (4)

In bulk samples, net $P_{FL}$ vanishes, but in thin films, $P_{FL}$ may be comparable to $P_{FE}$ [10]. The parameters for the best fits to all data shown in Figs. 4–8 are listed in Table I along with estimated uncertainties. The uncertainty given for each parameter was chosen by holding the other parameters constant while varying the parameter in question to determine the range of acceptable values. In addition to the experimental data and fitting curves, Figs. 4–8 also give the directions of various polarization contributions. Currently we do not have a good estimate of their magnitudes. First, within SmST$_1$ (see Fig. 4), the structure consists primarily of two layers at each surface. The coupling between the first and second layers is ferroelectric

**TABLE I.** This table summarizes the parameters for the best fits to Figs. 4–8.

<table>
<thead>
<tr>
<th></th>
<th>SmST$_1$</th>
<th>SmST$_2$</th>
<th>SmST$_3$</th>
<th>SmST$_4$</th>
<th>SmST$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{\text{surf}}$ (deg)</td>
<td>18.4±0.2</td>
<td>25.3±0.3</td>
<td>26.5±0.4</td>
<td>27.3±0.3</td>
<td>29.5±0.5</td>
</tr>
<tr>
<td>$\xi$ (layers)</td>
<td>0.95±0.05</td>
<td>1.45±0.02</td>
<td>1.60±0.05</td>
<td>1.96±0.05</td>
<td>2.31±0.1</td>
</tr>
<tr>
<td>$\varphi_1$ (deg)</td>
<td>270±1</td>
<td>270±2.5</td>
<td>0±2.5</td>
<td>270±3</td>
<td>0±5</td>
</tr>
<tr>
<td>$\varphi_2$ (deg)</td>
<td>270±7</td>
<td>102±3</td>
<td>193±3</td>
<td>270±5</td>
<td>0±10</td>
</tr>
<tr>
<td>$\varphi_3$ (deg)</td>
<td>120±15</td>
<td>102±7</td>
<td>193±5</td>
<td>103±6</td>
<td>216±5</td>
</tr>
<tr>
<td>$\varphi_{14}$ (deg)</td>
<td>60±15</td>
<td>78±7</td>
<td>347±5</td>
<td>77±6</td>
<td>324±5</td>
</tr>
<tr>
<td>$\varphi_{15}$ (deg)</td>
<td>270±7</td>
<td>78±3</td>
<td>347±3</td>
<td>270±5</td>
<td>180±10</td>
</tr>
<tr>
<td>$\varphi_{16}$ (deg)</td>
<td>270±1</td>
<td>270±2.5</td>
<td>180±2.5</td>
<td>270±3</td>
<td>180±5</td>
</tr>
</tbody>
</table>
and the two surfaces are in a synclinic arrangement. Here we use ferroelectric (antiferroelectric) to mean that the \( c \) directors for the first and second layers are parallel (antiparallel) and synclinic (antclinic) to mean that the \( c \) directors for the first and 16th layers are parallel (antiparallel). \( \theta_{\text{surf}} \) and \( \xi \) are determined by the amplitudes of the \( \Psi \) and \( \Delta \) versus \( \alpha \) curves. The tilts for the third and 14th layers must be nonplanar in order to produce the sizable difference between \( \Psi_{90} \) and \( \Psi_{270} \). \( \Psi_{90} - \Psi_{270} > 0 \) requires that \( \phi_3 \) be in the second quadrant; by symmetry, \( \phi_{14} \) is in the 1st quadrant. The shape of the \( \Psi \) versus \( \Delta \) curve determines the magnitude of the nonplanar angle. Fits at different temperatures in SmST1 indicate that the nonplanar angle varies with temperature. For example, just above \( T_1 \), \( \phi_{14} \) is in the fourth quadrant and \( \phi_3 \) is in the third quadrant. Figure 4(c) shows a polarization diagram for the structure at \( T=102.60 \degree C \). Net \( P_{\text{FE}} \) and \( P_{\text{FL}} \) are both perpendicular to the tilt plane of the outermost layers, in the direction of the electric field.

Both \( \theta_{\text{surf}} \) and \( \xi \) in SmST2 increased from those found in SmST1. The shape of the \( \Psi \) versus \( \Delta \) curve places a tight constraint on the value of \( \xi \). The two outermost surfaces are still in a synclinic arrangement, but the coupling between the first and second layers is now nearly antiferroelectric. The opening of the two leaves of the \( \Psi \) versus \( \Delta \) curve depends on the nonplanar angle. If the assumption that \( \phi_3 = \phi_{14} \) is relaxed, satisfactory fits can also be obtained provided that the sum of the \( c \) directors for \( j=2-15 \) remains the same. Because the surfaces are nearly antiferroelectric, the net \( P_{\text{FE}} \) nearly cancels. \( P_{\text{FE}} \) is small and parallel to the electric field. The net \( P_{\text{FL}} \) is larger than for the structure in SmST1 and antiparallel to the electric field [see Fig. 5(c)]. This implies that \( P_{\text{FE}} \) is still the dominant contribution to the net polarization of the film.

The tilt plane of the outermost layers in SmST3 is perpendicular to that in SmST2. The outermost layers are antclinic. The angles between the \( c \) directors for the first and second layers and the 15th and 16th layers are nearly equal to the previous structure. This structure can be obtained by rotating the surface on the incident side of the film clockwise by \( 90^\circ \) and rotating the opposite surface counterclockwise by \( 90^\circ \). The net \( P_{\text{FE}} \) has magnitude larger than \( P_{\text{FE}} \) for SmST2, but smaller than \( P_{\text{FE}} \) for SmST1. The net \( P_{\text{FE}} \) for SmST3 is in the direction of the electric field. The dominant contributions to \( P_{\text{FL}} \) are nearly aligned for this structure, so there is a large net \( P_{\text{FL}} \) in the direction of the electric field. See Fig. 6.

Our simulation results from the data in SmST4 show that the coupling between the first and second layers is ferroelectric and that the two surfaces are synclinic. The \( \Psi \) versus \( \Delta \) and \( \Psi \) versus \( \alpha \) curves are similar to those for SmST2, while the \( \Delta \) versus \( \alpha \) curve is shifted by \( 180^\circ \). The structure for SmST2 cannot produce this different behavior in \( \Delta \) versus \( \alpha \) for any value of the angle between the \( c \) directors for the first and second layers. The data for SmST1 shows similar features in both the \( \Psi \) and \( \Delta \) versus \( \alpha \) curves. The minimum at \( \alpha=90^\circ \) in the \( \Delta \) versus \( \alpha \) curve for SmST1 is a result of the nonplanar tilt of the third layer. As the tilt of the third layer increases, the minimum in the \( \Delta \) versus \( \alpha \) curve at \( \alpha=90^\circ \) becomes more pronounced. Simulations using a structure qualitatively identical to the structure for SmST1 fit the data quite well when \( \theta_{\text{surf}} \) and \( \xi \) are increased to account for the decrease in temperature and \( \phi_3 \) is adjusted to fit the maxima and minima of the \( \Psi \) and \( \Delta \) versus \( \alpha \) curves. The net \( P_{\text{FE}} \) is in the direction of the electric field. \( P_{\text{FL}} \) is small for this structure and dominated by the interior layers. The net \( P_{\text{FL}} \) is antiparallel to the electric field.

In SmST5, the coupling between the first and second layers is ferroelectric, but the two surfaces are in an antclinic arrangement. This structure can be obtained by rotating the two surfaces in opposite directions as described previously for the SmST1→SmST transition. This fit is less satisfactory than the fits for SmST1→SmST4. With increasing \( \xi \), the interior layers play a larger role and the assumption that \( \phi_j = \phi_3 \) for \( j=4-8 \) and \( \phi_j = \phi_{14} \) for \( j=9-13 \) may no longer be appropriate. The net \( P_{\text{FE}} \) for this structure is in the tilt plane of the outermost layers, parallel to the electric field. The net \( P_{\text{FL}} \) for this structure is relatively large and also in the direction of the electric field.

V. DISCUSSION

Two distinct types of reentrant behavior are evident in these data. The molecular arrangements in the outermost two layers in SmST1, SmST2, and SmST4 are synclinic, while those in SmST3 and SmST5 are antclinic. There is a double reentrant synclinic-antclinic-synclinic-antclinic transition similar to the transition observed in Ref. [9]. Under some circumstances single reentrant behavior may be explained by the coupling between the electric field and \( P_{\text{FE}} \), while ignoring \( P_{\text{FL}} \) [5], by using a phenomenological model to calculate the elastic energies of the synclinic and antclinic structures when no applied field is present. In Ref. [5], a term is added to the free energy of the synclinic state to account for the coupling of \( P_{\text{FE}} \) to the electric field. Adding a free energy term that couples \( P_{\text{FL}} \) to the electric field in a similar manner can in principle account for a double reentrant transition. This model requires an electric field to produce the reentrant transition and the transition temperatures are dependent on the magnitude of the electric field. We have performed temperature ramps similar to Fig. 3 with two different electric field strengths: \( E=0.143 \text{ V/cm} \) and \( E=14.3 \text{ V/cm} \). Measurements with \( E=0 \text{ V/cm} \) are not feasible because we require an electric field to orient the molecules. All five surface structures appeared for each electric field strength and the transition temperatures were equal within our resolution. This implies that the transitions are not driven by the electric field. The antclinic and synclinic structures are stabilized by some long-range interaction that is not well understood. Both the SmST2→SmST3 and SmST2→SmST5 transitions show dramatic increases in the net \( P_{\text{FL}} \), while the coupling between adjacent layers remains the same. This suggests that \( P_{\text{FL}} \) plays some role in the transitions.

Each of the structures observed contains nonplanar tilts within each surface, in contrast to the Ising-like models considered in previous experiments. Nonplanar tilts are present in bulk samples in the SmC*\( _{\alpha} \), SmC*\( _{FI1} \), and SmC*\( _{FI2} \) phases. The structures SmST1→5 can be viewed as precursors of these bulk SmC*\( ^{\alpha} \) variant phases. The SmC* \( ^{\alpha} \) variant phases are predicted by a phenomenological model including third nearest neighbor coupling terms, in which interlayer interactions...
vary with temperature [11,12]. Nonplanar structures occur when nearest neighbor (nn) interactions are ferroelectric and next nearest neighbor (nnn) interactions are antiferroelectric. In SmST$_1$, the first and second c directors are nearly parallel so the nn interaction dominates. In SmST$_2$ and SmST$_3$, the first and second c directors are nearly antiparallel and the second and third c directors are parallel. The nonplanar angles in SmST$_2$ and SmST$_3$ are small, so these structures can be viewed as precursors of the bulk antiferroelectric or ferroelectric phases. In SmST$_4$ and SmST$_5$, the first and second c directors are parallel and the third c director is nearly antiparallel. nn interactions dominate at the surface and nnn interactions play a larger role further away from the surface. The structures exhibited in this compound are rather complicated, making it difficult to glean concrete information about the relative strengths of the nn and nnn interactions. Compounds with surface structures intermediate in complexity between (S)12OF1M7 and the compounds that gave Ising-like structures may be useful for exploring the effects of tilt and temperature on the nn and nnn interactions. The second type of reentrant transition alluded to earlier is evident in the relative orientations of the molecules in the first and second layers. There is a ferroelectric-antiferroelectric-ferroelectric transition. To the best of our knowledge, no other LC systems exhibit ferroelectric-antiferroelectric-ferroelectric transitions and such transitions are rare in other systems as well. At this time, we have no explanation for this phenomenon.

In conclusion, we have determined the surface structures for a complicated set of surface transitions using NTE. Five nonplanar structures were observed, showing that typical Ising-like models of surface structures are inadequate for this compound. The complicated sequence of transitions is driven simultaneously by long-range and short-range interactions. Current theoretical models cannot explain the double reentrant synclinic-anticaclinic-synclinic-anticaclinic transition or the reentrant ferroelectric-antiferroelectric-ferroelectric transition.

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