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Unexpected field-induced phase transitions between ferrielectric and antiferroelectric liquid crystal structures

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Liquid crystals are intriguing electrically responsive soft matter systems. We report previously unexplored field-induced changes in the structures of some frustrated liquid crystal phases and describe them theoretically. Specifically, we have discovered using resonant x-ray scattering that the four-layer intermediate smectic phase can undergo either a transition to the ferrielectric (three-layer) phase or to the ferroelectric phase, depending on temperature. Our studies of intermediate phases using electric fields offer a way to test theories that describe ferroelectricity in self-assembling fluids.

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It is increasingly clear that a detailed understanding of the nature and origins of ferroelectricity, antiferroelectricity, and ferrielectricity in self-assembled fluid systems is required. For example, the fact that ferroelectric liquid crystal models have been shown to be responsible for some aspects of channel function in cell membranes [1,2] indicates that these complex fluid materials influence a wide range of physical systems. Such nonlinear systems are typically responsive to external stimuli, particularly to applied electric fields. The only fluids that exhibit ferroelectricity, antiferroelectricity and ferrielectricity are tilted smectic liquid crystals, which can readily undergo field-induced phase transitions, reorientation, and restructuring and provide an ideal model system for the study of self-assembled polar fluid structures.

Tilted smectic liquid crystals consist of a layered structure in which the average molecular orientation (the director) is tilted away from the layer normal by a fixed angle, the magnitude of which is both material and temperature dependent [3]. The phases are characterized by different arrangements of the azimuthal orientation of the director from one layer to the next, as shown in Fig. 1(a). The chirality of the system leads to an additional small modulation in the azimuthal director angle, producing a helical pitch of typically several hundred layers [4]. In the ferroelectric chiral smectic-C phase (Sm-C^*) the director is synclinic from layer to layer, whilst for anticlinic ordering the phase is denoted the Sm-C^*_A phase and is antiferroelectric [5]. Two intermediate phases between the low temperature Sm-C^*_A and higher temperature Sm-C^* phases have been confirmed, via resonant x-ray scattering [6], to have three- and four-layer repeat units, with structures as shown in Fig. 1(a) [7–10]. The three-layer phase is ferrielectric and polar, while the four-layer phase is antiferroelectric and therefore nonpolar. These intermediate phases, especially in their interaction with applied fields, allow the existing theoretical models of self-assembled polar fluids (none of which fully explains the formation of the rich variety of these phases) to be tested rigorously. Here we report the first observation of a field-induced transition between the four- and three-layer intermediate phases, together with a theoretical model which is in qualitative agreement with our results.

In a device geometry, the liquid crystal material is sandwiched between two substrates, allowing the application of large electric fields across the sample. There have been some previous studies of field-induced changes in the three-layer intermediate phase [11,12], hampered by typically narrow phase stability (1–2 K) [13,14]. Hiraoka *et al.* measured the apparent tilt angle in the three-layer phase as a function of applied field, observing helical unwinding followed by a field-induced transition to the Sm-C^* phase which occurred at lower fields as the Sm-C^* phase was approached [12]. There has only been a single study demonstrating that resonant x-ray scattering can directly detect the four-layer structure in devices [13], but no details of the effect of electric fields on the structure were revealed. In particular, the question remains as to how the nonpolar four-layer phase evolves into a polar phase under the application of a sufficiently large applied field. One possibility is that the polar four-layer structure described in Ref. [15] [shown in Fig. 1(b)] becomes stable. Resonant x-ray scattering provides a unique methodology to investigate this, and other, possibilities.

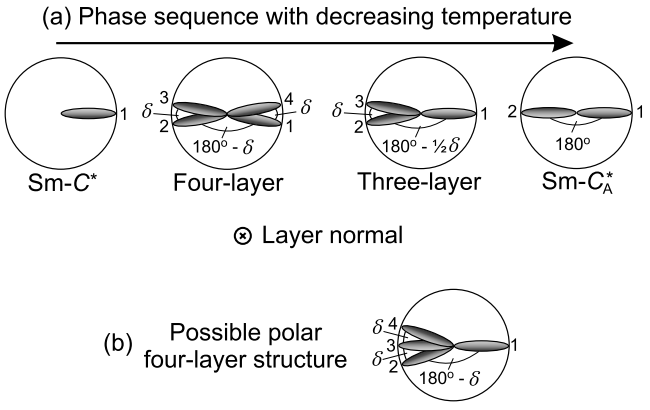

FIG. 1. (a) The repeating structures of the well-known tilted smectic phases as viewed along the layer normal (δ is the *distortion angle*). (b) The structure of a polar four-layer intermediate phase. In all cases, chirality induces a small additional azimuthal rotation of the director from one layer to the next, omitted for clarity.

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Our experiment takes advantage of materials that exhibit remarkably wide (>10 K) intermediate phases [8,16] formed from binary mixtures that include a selenium-containing liquid crystal host and the highly chiral dopant S1011 (Merck). The molecular structures of both components are given elsewhere [8]. This report is concerned with mixtures including concentrations of 2% and 4% (w/w) of S1011, which exhibit phase transition temperatures of I, 98 °C; Sm-*A*, 87 °C; Sm-C^*, 83 °C; Sm-C^*_{FI2}, 78 °C; Sm-C^*_{FI1}, 76 °C; Sm-C^*_{A} and I, 96 °C; Sm-*A*, 78 °C; Sm-C^*, 68 °C; Sm-C^*_{FI2}, 55 °C; Sm-C^*_{FI1}, 38 °C; Sm-C^*_{A}, respectively. The samples were contained in parallel devices constructed from 150-μm-thick glass, with gap thicknesses between 19 μm and 28 μm. The inner glass surfaces include indium tin-oxide electrodes to allow application of electric fields and nylon alignment layers, rubbed on one surface, to promote monodomain planar alignment of the liquid crystals.

The experiment was carried out on beamline X6B at the National Synchrotron Light Source, Brookhaven National Laboratory, using an arrangement similar to our earlier work [13]. The x-ray energy was tuned to the K-absorption edge of the selenium atom in the core of the host material, then further optimized to 12.6611 keV through observation of the resonant scattering signal. At the resonant energy, superlattice peaks appear in Q space due to the periodicity in the azimuthal orientation of the director across the smectic layers. Such peaks occur at positions given by $Q_z/Q_0=l+m(1/\nu\pm\varepsilon)$, where l and m are integers with $m=0, \pm1, \pm2$; $\nu=3$ and 4 for the three- and four-layer phases, respectively; and ε is the ratio of the layer spacing to the helical pitch. Therefore, superlattice peaks occur around $Q_z/Q_0=2/3$ and 3/4 for the three- and four-layer intermediate phases, respectively, with the helical superstructure resulting in the splitting of the peaks [17,10].

A 10-Hz-square wave form was applied to the samples, with the data acquisition triggered to collect x-ray scattering data from the last two-thirds of each positive half of the cycle, eliminating any transient effects (measured electro-optically to occur in under 200 μs). The samples were mounted in the Bragg condition on a heating stage connected to a temperature controller providing temperature stability of ±0.1 K.

A resonant peak is observed at $Q_z/Q_0=2/3$ (the solid line in Fig. 2) in a 27.1-μm-thick device containing the 2% mixture at 77.2 °C, confirming a stable three-layer phase in the device at this temperature. The smectic layers exhibit a chevron structure [18] because of strong surface anchoring and layer shrinkage on cooling from the smectic-*A* phase, which can be rearranged by a sufficiently large electric field into a bookshelf structure [19,20]. The phase was observed to switch using polarized microscopy in response to any field above 0 V/μm, an observation consistent with the fact that the phase is polar. Increasingly large-amplitude electric fields were applied stepwise to the device and x-ray scans repeated. The resonant peak is retained at fields of 0.11 V/μm and 0.22 V/μm, where the peak becomes narrower and more intense (dashed line in Fig. 2). The narrowing is attributed to field-induced helical unwinding of the phase, causing the split resonant peaks that result from the helicoidal structure at zero field [8,10] to merge. Detailed analysis of the peaks, such as has been carried out previously [7,8], is not possible because the number of counts is too low (a result of absorption by the glass substrates), even though the experimental resolution is as good as in previous experiments. As the field is increased further, the $Q_z/Q_0=2/3$ peak remains visible, even when the bookshelf structure is formed at fields between 0.92 and 1.18 V/μm (dotted line in Fig. 2, with 1.47 V/μm). The three-layer resonant peak finally disappears as the field is increased from 1.84 V/μm to 2.05 V/μm and x-ray scans at other positions in Q space revealed no resonant peaks corresponding to four-, five-, or six-layer intermediate structures. We therefore conclude that the Sm-C^* phase is induced by the large external field, consistent with previous results [12]. On removal of the field, the three-layer peak is recovered and the bookshelf structure is largely retained.

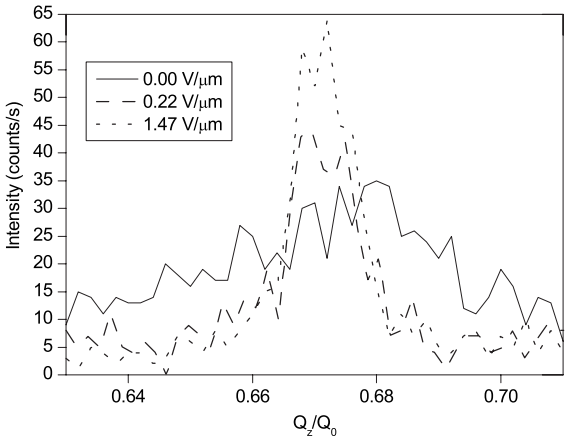

FIG. 2. Three-layer resonant peaks at different applied fields from a device at 77.2 °C containing the 2% mixture. The typical error in each data point is $\sqrt{N}$ where N is the number of counts (error bars are not shown for clarity). Data points are connected by lines as a guide to the eye. Equivalent behavior, though at different applied fields, was observed at different temperatures and in the three-layer intermediate phase of the 4% mixture.

The field-induced evolution of the four-layer intermediate phase was investigated in a 19.1-μm-thick device containing the 4% mixture. At 60 °C with no applied field, a resonant peak was obtained at $Q_z/Q_0=3/4$ (solid line in Fig. 3). Since this phase is nonpolar, there is a field threshold below which no director realignment is observed, found to be around 0.5 V/μm via polarizing microscopy. No change in the phase structure is expected below this threshold, while a polar phase must form above it. The four-layer peak is thus retained at 0.16 V/μm (dashed line in Fig. 3) but disappears when the field is increased to 0.62 V/μm. Surprisingly, it is replaced by a resonant peak at $Q_z/Q_0=2/3$ (dotted line in Fig. 3), indicating that the four-layer intermediate phase is transformed into the three-layer phase. This result confirms that, where the field-induced transition is to another intermediate phase structure, it is more favorable for the (polar) three-layer structure to form than the four-layer polar structure shown in Fig. 1(b). This occurs even though the latter structure is perhaps the more intuitive possibility, as suggested by Marcerou *et al.* [21] who studied a similar system

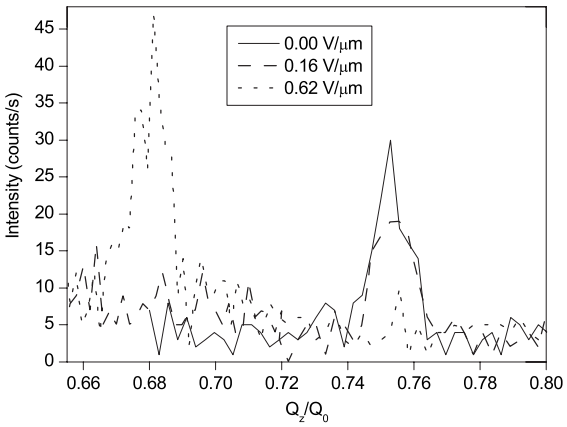

FIG. 3. Resonant peaks from a device containing the 4% mixture, at 60 °C, subject to different applied electric fields. In the absence of a field the sample is in the four-layer phase.

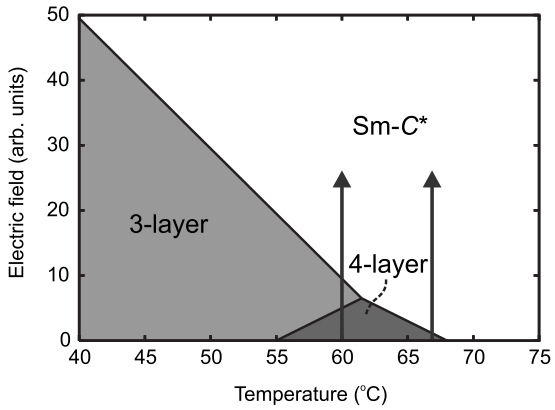

FIG. 4. Predicted phase diagram across the intermediate phase temperature range with increasing external field (equivalent to the vertical axis) for the 4% mixture. The arrows indicate two temperatures at which experiments were carried out.

without the benefit of resonant x-ray scattering. In our experiment, when the field is increased further to 1.07 V/μm, the peak at $Q_z/Q_0=2/3$ disappears and ferroelectric switching is observed. Subsequently, on removal of the field the $Q_z/Q_0=3/4$ peak is again visible with a signal-to-noise ratio comparable to the four-layer peak prior to the application of the field, confirming that beam damage did not affect our observations. Finally, we note that a direct field-induced transition from the four-layer phase to the ferroelectric state is observed under some conditions. Indeed, in the 4% mixture at 67 °C only this transition was observed, with a threshold of 0.39 V/μm.

Our experimental findings can be understood in light of a simple discrete model based on a generalized expression in terms of couplings between tilt order parameters in different smectic layers (see Ref. [15] and references therein). Taking into account interactions up to the next-to-next-nearest smectic layers, the free energy includes contributions from the linear coupling coefficients between any smectic layer and the layers nearest to it (Δ), next nearest (J_2), and next-to-next nearest (J_3), as well as a biquadratic coupling coefficient for adjacent layers (b_Q) and the chiral coupling coefficient (λ). In our approximation, we assume $\delta=0°$ (see Fig. 1), so b_Q and λ become negligible. The free energy densities of the Sm-C^* phase (F_C), the Sm-C_A^* phase (F_{CA}), the three-layer phase (F_3), the four-layer phase (F_4), and the polar four-layer phase (F_4^p) in the external electric field E are then expressed as $F_C=\Delta+J_2+J_3-P_SE$; $F_{CA}=-\Delta+J_2-J_3$, $F_3=(-\Delta-J_2)/3+J_3-P_SE/3$, $F_4=-J_2$; and $F_4^p=-P_SE/2$, where P_S is the spontaneous polarization of one layer (assumed to be constant over the temperature range [22]). The model describes all conventional phases presented in Fig. 1(a), which appear in the correct order with decreasing Δ (at $E=0$). Since in this system the three-layer phase has $\delta\gg 0°$ [8], its free energy is significantly lower than that described in our model. However, δ in the four-layer phase is small ($\sim 10°$ in this system [7]) and therefore its energy will be similar to that of the case of $\delta=0°$. Assuming $\Delta=\Delta_0(T^*-T)$, where the coefficient Δ must change sign at the synclinic-anticlinic transition temperature in the absence of subphases (T^*), the transition temperatures (at zero field) between the four phases are given by $T_{C-4}-T^*=2J_2'+J_3'$, $T_{4-3}-T^*=-2J_2'-3J_3'$, and $T_{3-CA}-T^*=-2J_2'+3J_3'$, where $J_2'=J_2/\Delta_0$ and $J_3'=J_3/\Delta_0$. The model could be improved by assuming that the rate of change of Δ is smaller at lower temperatures, but this does not change the topology of the phase diagram, and this modification will be addressed elsewhere. We note that, to our knowledge, the only other model that considers application of fields in intermediate phases assumes that they are incommensurate [23], and therefore we have not considered it here.

For the 4% mixture one obtains the values $J_2'=23/4$, $J_3'=-5/2$, and $T^*=59$ °C from the equations above using the actual transition temperatures. The phase diagram for the intermediate and Sm-C^* phase regimes in an applied electric field, obtained without using any additional fitting parameters, is shown in Fig. 4. The diagram qualitatively describes our experiment; upon application of a field, two temperature regimes appear in the four-layer phase, while only one regime exists for the three-layer phase. The higher-temperature regime of the four-layer phase directly transforms into the Sm-C^* phase above a threshold field, while in the lower regime it first transforms into the three-layer phase and then, above a second threshold, to the Sm-C^* phase. At $T=60$ °C we reproduce directly our experimental observations. It can be shown that for any values of the parameters, the polar four-layer phase in the external field is always higher in free energy than either the three-layer phase or the Sm-C^* phase, and thus does not appear.

In conclusion, we have employed resonant x-ray scattering to confirm unequivocally that the nonpolar four-layer phase transforms either to the three-layer phase or the ferroelectric phase rather than a polar arrangement of the four-layer structure under the effect of external electric fields. This previously unobserved transition could provide interesting electro-optic possibilities for devices. Further, the application of fields demonstrates how such an experiment offers a way to test the theories that describe self-assembling ferroelectric, ferrielectric, and antiferroelectric fluids. Our data also reveal that the three-layer intermediate phase exists over

a wide range in devices and is remarkably stable to applied electric fields. We present a theoretical argument suggesting that, under the effect of external fields, the four-layer phase temperature regime can generally split into two regions: one at higher temperatures where the ferroelectric Sm-C^* structure becomes stable and another at lower temperatures where the ferrielectric three-layer structure is more favorable.

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