The case of thresholdless antiferroelectricity: polarization-stabilized twisted SmC* liquid crystals give V-shaped electro-optic response

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[Inui et al., J. Mater. Chem., 1996, 6, 671]. We find that the thresholdless or V-shaped switching is obtained in the absence of antiferroelectricity. This analog electro-optic response is due to the field-induced switching of a twisted smectic C* structure stabilized by polar surface interactions and by electrostatic bulk polarization charges. Interactions. The latter confine the director twist to thin surface regions leaving the bulk of the cell uniform, which gives extinction at zero field. In sufficiently thin cells, such thresholdless switching can in fact be followed down to much lower temperatures, where the bulk would be antiferroelectric, but is maintained in the cells in the ferroelectric state by hysteresis from surface action.

I. Introduction

In 1995 Fukuda³ and later Inui et al.² reported a thresholdless electro-optic response in a three-component mixture of chiral smectic liquid crystals. V-shaped, hysteresis-free transmission–voltage curves were observed over a wide temperature range and were quite different from the behavior of both surface-stabilized ferroelectric liquid crystals (SSFLCs), which show a single hysteresis loop,³ and antiferroelectric liquid crystals (AFLCs), which have a double hysteresis loop.³ The effect was dubbed ‘thresholdless antiferroelectricity’, presumed to be a new kind of antiferroelectricity. The electro-optic response of this and similar materials is very attractive for active matrix liquid crystal displays.³

The Tokyo group’s first model of this effect suggested that in the relevant temperature range the interlayer tilt correlation is very weak, resulting in a ‘random smectic C-like’ phase.³ Later a ‘surface-induced randomization’ of the tilt directions in adjacent layers was proposed.³ However, neither of these models is able to explain satisfactorily all observed phenomena in this mixture. We have synthesized and investigated the same three-component mixture (cf. Fig. 1) as studied by the Tokyo group³ and we will refer to it simply as the Tokyo mixture. The phase sequence is Iso 69°C SmA* 64°C SmX* 43°C SmC* 43°C, with thresholdless switching occurring in the unidentified SmX* phase.³ The transition A* to X* is (at least nearly) second order and relatively sharp, while the other transitions are first order and subject to considerable variations due to coexistence and surface actions. In 2μm cells we could for instance follow the A* phase up to about 74°C while the 43°C transition (also reported to be broad by the Tokyo group) seems to take place in the region 45–47°C, and is accompanied by striking coexistence effects, cf. Fig. 2.

II. Identification of the phase

In order to determine the nature of the SmX* phase we performed dielectric spectroscopy measurements and depolarized total internal reflection measurements to probe the order in the bulk and at the surfaces, respectively. We supplemented these by studying the electro-optic behavior of freely suspended films as well as in bulk cells representing different geometries. These experiments, some of which will be described in more detail elsewhere, show conclusively that the so-called SmX* phase is in fact SmC*.

In Fig. 2 dielectric spectroscopy data are shown taken with a 2.3μm cell with ITO electrodes and evaporated S0 for planar alignment. On cooling in the A* phase the divergence-like rise of the relative permittivity on approaching the lower-temperature phase, combined with the slowing-down in frequency, is the expected characteristic for a soft mode which is a precursor to a phase with strongly collective polar order. The onset of this polar order at Tc is confirmed by the cusp after which the susceptibility falls down more slowly. In this Goldstone or phason mode the measured ϵ value is about 20 to 25 and the relaxation frequency about 1 kHz, because in a 2.3μm cell the smectic C*—as we may now identify the phase—is on the verge of being surface-stabilized. In a 25μm thick cell the corresponding measured ϵ value is about 500 and the frequency about ten times lower (±100 Hz) which confirms the identification of the mode as a Goldstone mode. On entering the antiferroelectric phase we then see how the branches characteristic of the C*, phase appear, both lying at ϵ=0, and with considerably higher relaxation frequencies. This shows the antipolar order of that state. However, we also see that the Goldstone mode, as evident both in relative permittivity and in relaxation frequency, continues and persists in the entire SmC* phase. The presence of the SmC* Goldstone

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Fig. 1 Chemical structures and concentrations (by weight) of the three-component Tokyo mixture.
mode (‘hereditary peaks’) was already found in previous dielectric work over the entire SmC* temperature interval and reveals a coexistence of ferroelectric and antiferroelectric order in the low-temperature phase conventionally looked upon as just SmC*. In addition, studies on the Tokyo mixture as well as on some similar materials have now clearly revealed the importance of surface effects. In sufficiently thin cells, where the surfaces have a dominating influence, the whole phase behavior will be affected. Then, not only is there coexistence, but certain thermodynamic phases may be completely suppressed. Specifically, we have found that ferroelectric order tends to displace and suppress antiferroelectricity in thin cells. The smectic C* interval (roughly between 47°C and 64°C) is the temperature range of the Tokyo mixture which is characterized by thresholdless switching. An example of the electro-optic response of a 2 µm bookshelf-aligned cell taken in the middle of that interval, at 57°C, is shown in Fig. 3a. However, as will be discussed in more detail below, this switching can also be pursued far down into the C* phase. An example of this is shown in Fig. 3b.

The phase designations from dielectric spectroscopy were corroborated by monitoring the depolarized light obliquely reflected off freely suspended films with a controlled number of smectic layers when an electric field was applied in the plane of the film. In these films, the SmX* phase behaves like a typical SmC*, with the spontaneous polarization normal to the tilt plane for both odd and even numbers of smectic layers. The complete lack of odd–even effects argues strongly against antiferroelectricity. At lower temperatures, below the SmC* phase, the films show behavior typical of an antiferroelectric phase with polarization normal to the tilt plane for odd number of layers and in the tilt plane for even number.

Depolarized total internal reflection is a sensitive probe of the liquid crystal orientation at the surfaces of cells. Our studies of the Tokyo mixture on aligning surfaces showed that in the smectic C* phase the molecular order at the surface is synclinic and monostable, with the director preferentially on one side of the tilt cone and in the plane of the cell. In the antiferroelectric C* phase, at zero-field the surface regions have the optic axis along the smectic layer normal and in the plane of the cell, suggesting antclinic molecular order at the surface. This fully supports the previous results. Having established that we are not dealing with some exotic liquid crystal phase above 45°C, but with the SmC*, the question now is what director configuration gives thresholdless switching in thin planar-aligned cells.

III. Electro-optic behavior

Electro-optic measurements by themselves are not reliable for identifying the order or structure in the samples but they contribute important clues. We first studied the behavior of the two smectic phases below the SmX* in homeotropically-aligned cells, where the layers are parallel to the glass plates. These cells were about 10 µm thick and incorporated copper electrodes for applying electric fields parallel to the glass plates. The distance between the electrodes was about 0.2 mm. The chosen configuration means that the SmX* phase is no longer surface-stabilized. In a triangular applied field the optic axis swings around without threshold in the SmX* phase as the local polarization adjusts to the field. Grandjean lines were visible during switching.
at all temperatures, indicating the presence of a helix in both phases.

In the (more usual) bookshelf geometry the electro-optic properties of planar-aligned cells subjected to a triangular applied voltage were studied in considerable detail using transmission microscopy. The appearance of V-shaped switching is known to depend on frequency and to be very sensitive to the properties of the alignment layer. It may require a thick polymer layer, but a thin layer seems to work if combined with an insulating layer next to the ITO. We have made cells with and without insulating layers and found the ‘best’ V-shaped switching in a thin (d ≈ 2 μm) cell with SiO2 insulating layers (thickness 1000 Å, evaporated at normal incidence) between the ITO electrodes and the nylon alignment layers.

In this cell, ideal V-shaped switching was observed in the entire Sm* temperature range for driving frequencies up to about 25 Hz (Fig. 3a). At higher frequencies some hysteresis occurred, although even at 300 Hz the hysteresis was quite small and the transmission-voltage curves were only slightly ‘W-shaped’.

At low frequencies (f ≈ 1 Hz) a characteristic reversed W-hysteresis can then be observed: the V splits symmetrically around E=0, but now in the opposite sense as compared to normal hysteresis. Very likely this is due to ions sticking at the cell surfaces. The ions build up a counteracting electric field in the cell and make the total internal electric field change sign before the applied external field. In thicker cells (d ≈ 4 μm) the switching was accompanied by the appearance of thin lines parallel to the smectic layers that could be related to the material’s tendency to form a helix at E=0 in these cells.

The Tokyo group has also reported V-shaped switching at 25°C, corresponding to the SmC* temperature range of the mixture. Our observations confirm that while the d.c. response is antiferroelectric, dynamic switching occurs with no threshold. In the absence of electric fields, the apparent optic axis lines up parallel to the smectic layer normal, in both 4 μm and 2 μm cells. The transition from SmC* to SmC's is slow and the two phases may coexist for several hours after cooling from SmC* to room temperature. The transition seems to occur more slowly in 2 μm cells than in 4 μm cells. In the SmC's phase, there is a distinct field threshold above which the cell switches into the ferroelectric state for the first time, indicating that the ‘virgin’ state is indeed antiferroelectric.

On slowly reversing the field, however, the switching to the opposite ferroelectric state is continuous and ‘thresholdless’. In fact, V-shaped switching was achieved in an applied a.c. field f = 0.5 Hz as long as the field amplitude exceeded the value corresponding to the virgin antiferroelectric-to-ferroelectric threshold (see Fig. 3b). For lower amplitudes, the sample slowly relaxes back towards the virgin state and a threshold for switching to either of the ferroelectric states reappears.

For very low frequencies (f = 0.02 Hz) the sample has time to relax during field reversal and typical tri-state antiferroelectric switching is achieved with distinct thresholds and two hysteresis loops. For somewhat higher frequencies (f ≈ 1 Hz) the response becomes W-shaped.

IV. Interpretation of the results

From the experimental observations we may draw the following conclusions:

(1) The presence of a helix indicates that the material has a well-defined periodicity (pitch) and, therefore, that neither of the two phases studied is ‘random’.

(2) The distinct threshold in both homostropic and planar cells shows that the antiferroelectric phase is not intrinsically ‘thresholdless’.

(3) The dielectric spectroscopy and freely suspended film experiments show that the mysterious SmX* phase is identical to SmC*.

(4) The total internal reflection experiments show that the director order is synclinic at the surfaces, not only in the bulk. They also suggest that this order generally, with the exception of hysteretic effects, is antclinic in the C* phase.

(5) The monostable synclinic order at the surfaces is characteristic of cells with symmetric, strong polar boundary conditions that induce a twisted smectic C* structure in which the macroscopic polarization of the cell is initially perpendicular to the applied electric field. The useful effect is therefore based on a surface-stabilized ferroelectric liquid crystal working in dielectric mode. The structure is indeed ferroelectric since it has a macroscopic polarization in the absence of external fields and could be switched in a bistable mode if we applied the electric field differently. This is because the polarization is directed in the plane of the cell and in order to switch it to the opposite ferroelectric state we would also have to apply the field in the plane of the cell. The two ferroelectric states then correspond to the director lying on the top or bottom of the smectic tilt cone in the bookshelf geometry. In the V-shaped switching case we apply the field, as usual, normal to the cell plane and hence also normal to the macroscopic polarization.

A direct result of this is that there is a torque density in the bulk. If we apply the electric field, as usual, normal to the cell plane and hence also normal to the macroscopic polarization.

(6) The V-shaped switching of the Tokyo mixture is the electro-optic response of this twisted smectic C* phase.

The twisted smectic C* is a rather special case of an SSFLC structure in which the macroscopic polarization of the cell is initially perpendicular to the applied electric field. The useful effect is therefore based on a surface-stabilized ferroelectric liquid crystal working in dielectric mode. The structure is indeed ferroelectric since it has a macroscopic polarization in the absence of external fields and could be switched in a bistable mode if we applied the electric field differently. This is because the polarization is directed in the plane of the cell and in order to switch it to the opposite ferroelectric state we would also have to apply the field in the plane of the cell. The two ferroelectric states then correspond to the director lying on the top or bottom of the smectic tilt cone in the bookshelf geometry. In the V-shaped switching case we apply the field, as usual, normal to the cell plane and hence also normal to the macroscopic polarization. A direct result of this is that there is a torque density in the bulk. If we apply the electric field, as usual, normal to the cell plane and hence also normal to the macroscopic polarization.

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Figure 4 shows uniform twisted smectic C* structure formed when polarization charge effects are negligible. The elastic deformation in the director field is a combined twist-bend-splay and the polarization is directed in the plane of the cell and make the total internal electric field change sign before the applied external field.
polarizers. Indeed, the good extinction of the zero-field state led Seo et al. specifically to exclude the possibility of a twisted configuration. However, as shown earlier by Nakagawa et al. and Zhuang et al., in materials with high spontaneous polarization $P_s$, polarization charge effects become important. In the Tokyo mixture we have found the value of $P_s$ to be about 170 nC cm$^{-2}$. Such twisted SmC* cells adopt a characteristic configuration with the director in the bulk homogeneous (with the projection of the director onto the cell plane parallel to the layer normal) and the twist confined to thin regions close to the surfaces. Off Fig. 4b. The thin surface regions do not significantly influence the polarization state of the transmitted light and the cell appears dark between crossed polarizers. In contrast, the uniformly twisted SmC* structure obtained when polarization charge effects can be neglected would give very poor extinction in this geometry, with a rather bluish transmission for $E=0$. The dynamic response of the director field in the twisted Sm* model can be computed using molecular dynamics simulations. The equation of motion is approximated using the semi-implicit Crank-Nicolson finite difference scheme. Elastooptic boundary conditions are imposed which combine both non-polar (nematic-like) and polar anchoring at the cell surfaces.

V. The polarization coherence length

Including the polarization charge has a remarkable stiffening effect, stabilizing a thick slab of uniform orientation in the middle of the cell. In a slowly varying applied electric field, this region reorients homogeneously as found in earlier simulations, and shown in Fig. 5a. The electro-optic response, computed using the Berreman $4 \times 4$ matrix method and assuming He–Ne laser illumination, is V-shaped and qualitatively reproduces the experimental observations (Fig. 5b). The extinction at zero field is virtually complete and the homogeneous switching of the bulk of the cell produces a linear optical response at low voltages. Optical saturation is achieved at higher voltages even without the cell surfaces switching.

Minimization of the sum of the electrostatic energy $-\langle W(P)\rangle$ and the elastic energy reveals that near each surface there exists a splayed region of thickness $\xi=(K/\rho)^{1/4}$ (in SI units), where $K$ is the elastic constant in the one-constant approximation. Assuming that there are no charged impurities, $\xi=\xi_0$ where $\xi_0$ is the relative permittivity in the case corresponding to a racemic mixture. If $\xi=\xi_0$, the cell thickness, the global cell structure is splayed, giving the characteristic bluish appearance between crossed polarizers. For $\xi<\xi_0$, however, the bulk is homogeneous, giving good extinction. It is illuminating to consider typical numerical values for the parameters involved in $\xi$. With $P=1 \text{ nC cm}^{-2}$, $K=5 \times 10^{-10}$ erg cm$^{-1}$, $\xi=5 \times 10^{-12}$ N and $\epsilon=9$ we get $\xi=2 \mu$m which is equal to $d$. Hence for $P=1 \text{ nC cm}^{-2}$ there would be no stiffening effect, but already for $P=10 \text{ nC cm}^{-2}$, $\xi$ is one tenth of $d$. Experimentally, the stiffening effect does not seem to appear until $P$ approaches 100 nC cm$^{-2}$. This could be explained by ionic impurities screening the polarization charge. Alternatively one could phenomenologically account for these space charges by introducing a relative permittivity (being a complex number) having a much higher value than $\epsilon_0$. This observation indicates that with FLC materials which have been subject to extreme purification, V-shaped switching may be achieved with substances having considerably lower $P_s$ values, which would be of eminent importance for applications in TFT devices.

A schematic representation of how the director field changes in response to an applied field is shown in Fig. 6. For $E=0$ the bulk is homogeneous with the director oriented on the bottom of the tilt cone so that its projection onto the glass plates is along the layer normal. When all the local dipoles are aligned along the upward field direction (in principle, once the lower surface switches) the transmission-voltage curve flattens out. On decreasing $E$ the lower surface relaxes back first, followed by the smooth relaxation of the bulk. As $E$ becomes negative, the transmission goes up in the same way, as the bulk polarization follows the field, until eventually the upper surface switches and the transmission-voltage curve flattens out again.
The bulk orientation of the director at $E=0$ was confirmed by studying the change in the effective birefringence of the cell when it was tilted about an axis parallel to the cell plane and to the smectic layers as shown in Fig. 7. With the cell oriented normal to the transmitted light ($\theta=0$) and with the smectic layer normal making an angle of 45$^\circ$ to the crossed polarizers, the sample appeared yellow. When tilted one way ($2\theta \approx 30^\circ$) the cell appeared yellow–white (lower birefringence), when tilted the other way $2\theta \approx −30^\circ$ orange (higher birefringence). This is consistent with an SSFLC having a bulk optic axis tilted 30$^\circ$ down from the plane of the cell, but is not consistent with antiferroelectric order.

VI. Conclusions

We have shown that the V-shaped switching reported in the Tokyo mixture is not an example of ‘thresholdless antiferroelectricity’. Rather, this analog electro-optic effect occurs in a surface-stabilized smectic C$^*$ liquid crystal in the absence of antiferroelectricity. The particular structure giving rise to the V-shaped switching is the experimental confirmation of theoretical predictions that the polarization charge makes the bulk homogeneous in twisted smectic C$^*$ cells when the spontaneous polarization is large. In fact, the homogeneous bulk has a spontaneous polarization directed parallel to the plane of the cell, thereby explaining the second harmonic generation at normal incidence and zero applied field reported by Seomun et al.\(^1\) This SHG signal manifestly contradicts the model suggested in refs. 1, 2 and 6 or any other ad hoc model discussed so far. We furthermore find that the V-shaped switching at $T=23$–25$^\circ$C described in early papers is a result of the field-induced smectic C$^*$ state being maintained by the large hysteresis associated with switching between synclinic and antclinic molecular order. As this hysteresis is quite different from the one relating the ferroelectric and antiferroelectric states in the bulk, there seems to be a substantial potential barrier between synclinic and antclinic order promoting the former as a result of surface effects. This is contrary to the preconditions for the random tilt directions in adjacent layers suggested by Fukuda,\(^1\) which would require a very low or even non-existent energy barrier between synclinic and antclinic order. Moreover, this ‘randomization’ was supposedly caused by the surfaces, whereas all evidence suggests that surfaces have just the opposite effect. Our findings also explain the recent observations of thresholdless switching and ‘learned ferroelectricity’ made by Gorecka et al.\(^5\) Our results suggest that thresholdless V-shaped switching in twisted smectic C$^*$ cells should occur in all SmC$^*$ materials with sufficiently large spontaneous polarization (which promotes a homogeneous bulk orientation and good extinction at $E=0$) in combination with strong polar interactions with the cell surfaces (promoting the twisted state). In order to test these assumptions we made a 2$\mu$m thick cell with the liquid crystal W415, which is known to exhibit a strong surface-electroclinic effect ($\approx 20^\circ$) in the SmA$^*$ phase\(^3\) and has high spontaneous polarization ($P_s \approx 300$ mC cm$^{-2}$). Both cell surfaces were rubbed and the cell was assembled with the rubbing directions at an angle of about 40$^\circ$, corresponding to twice the angle of the surface-electroclinic effect. This produced a twisted smectic C$^*$ structure similar to the one spontaneously adopted by the Tokyo mixture, i.e. with the apparent optic axis parallel to the smectic layer normal at zero field. Experiments confirmed that the W415 cell also exhibits thresholdless switching with good extinction at zero field.

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