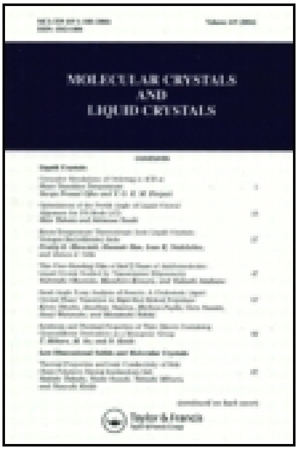

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STRUCTURES AND ELECTRIC FIELD EFFECTS IN FERRO-, FERRI- AND ANTIFERRO-ELECTRIC LIQUID CRYSTAL DEVICES

Helen F. Gleeson [a]
[a] Department of Physics and Astronomy, University of Manchester, M13 9PL, UK

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STRUCTURES AND ELECTRIC FIELD EFFECTS IN FERRO-, FERRI- AND ANTIFERRO-ELECTRIC LIQUID CRYSTAL DEVICES

Helen F. Gleeson
Department of Physics and Astronomy,
University of Manchester, M13 9PL, UK

This paper reviews several experimental studies of electric-field effects in liquid crystal devices containing ferroelectric, antiferroelectric and ferrielectric liquid crystals. Small-angle X-ray scattering has been employed to study both rapid, reversible layer flexing and irreversible, high-field deformations in surface stabilised ferroelectric devices. New antiferroelectric materials are also considered and the tilt angle and chevron angle adopted in devices are described. Generally, the chevron angle is found to compare well with the steric tilt angle (~20°) and is considerably lower than the optical tilt angle (~30°). Both conventional and resonant X-ray scattering experiments have been used to probe the layer and interlayer structure and field-induced deformations in antiferroelectric, ferrielectric and ferroelectric liquid crystal devices. It is found that the mechanism of the chevron to bookshelf transition is phase-dependant and is thresholdless in the ferroelectric phases of these materials. Further, resonant scattering reveals that the field-induced antiferroelectric or ferrielectric to ferroelectric transition can occur at field strengths that are similar to or higher than those required to deform the smectic layers.

Keywords: ferroelectric; antiferroelectric; liquid crystal devices; chevron structure; electric field effects

INTRODUCTION

The discovery of the chevron structure was a milestone in understanding the geometry and switching phenomena in ferroelectric devices since the layer structure adopted in smectic C* devices has a significant influence on their electro-optic properties. Cooling from the orthogonal smectic A

This work was carried out in collaboration with S J Watson, L S Matkin, L Baylis, G Bryant & A Morse, Manchester University; M Hird & J W Goodby Hull University; R Pindak, P Mach & J Pitney, Lucent Technologies Bell Labs; C C Huang & P Johnson, Univ. of Minnessota; Ph Barois, Univ. of Bordeaux; A-M Levelut, Univ. Paris Sud; G. Srajer & J. Pollmann, APS.

(SmA) phase into a tilted phase causes a reduction in the smectic layer spacing and the layers in a device frequently adopt a chevron structure [1] to accommodate this layer shrinkage. Soon after the discovery of the chevron structure in surface stabilised ferroelectric devices (SSFLC), it became clear that application of a sufficiently large field would induce a chevron to bookshelf transition, transforming the regular chevron structure to an in-plane chevron [2,3]. More recently it was observed that electric fields at strengths much lower than those required to reorganise the smectic layers permanently could cause significant layer flexing [4,5].

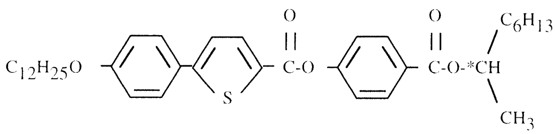
This paper reviews several aspects of the smectic layer structure in devices containing the SmC* sub-phases studied by conventional, time-resolved and resonant X-ray scattering. The first part of the paper gives a summary of the influence of low and high fields on SSFLC devices, providing a context for similar data presented on new materials containing antiferroelectric (AFE), ferroelectric (FE) and 3- and 4-layer intermediate phases. Such systems are generally not surface stabilised as materials exhibiting these phases have short pitch (typically sub-micron). The second section of the paper describes the evolution of the chevron to bookshelf transition in the AFE, FE and intermediate phases and contrasts it with the quite different behaviour observed in SSFLC devices. Finally, resonant X-ray scattering experiments are described that examine the interlayer structure and field-induced deformations in devices containing the AFE and 4-layer intermediate phases.

EXPERIMENTAL

The device construction was similar for all of the experiments. The glass substrates were 170 μm thick, coated with a conductive indium tin oxide layer. The SSFLC devices were approximately 3 μm thick and were filled with the commercially available ferroelectric liquid crystal SCE13 (Merck Ltd.). Alignment was achieved by coating the surfaces of the device with a rubbed polyvinylalcohol (PVA) alignment layer. Polarising microscopy indicated that the SSFLC devices had a half-splayed director profile.

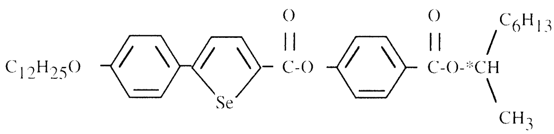
The devices containing the materials exhibiting AFE, FE and intermediate phases were filled with compounds 1–3 shown in Figure 1 and assembled to produce a liquid crystal sample approximately 15 μm in thickness. Compounds 1–3 all have short helical pitch and are not surface stabilised at this thickness. These samples were aligned in a planar geometry using a rubbed Nylon 6/6 alignment layer. In all of the X-ray experiments, the temperature of the devices was maintained with an absolute accuracy of $\pm 1°C$ and a relative accuracy of $\pm 0.1°C$ by use of a heating stage.

1



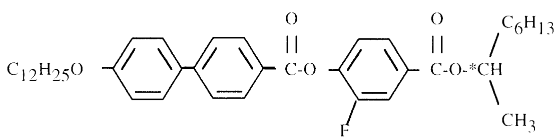
K 64.2 SmC^*_A 80.2 SmC^*_{FI1} 82.2 SmC* 92.6 SmA 97.9 I

2



K 67.7 (SmI* 33.3 SmI^*_A 42.2) SmC^*_A 97.8 SmC^*_{FI1} 99.0 SmC* 109.4 SmA 116.6 I

3



K 53.3 SmC^*_A 76.0 SmC^*_{FI1} 78.0 SmC^*_{FI2} 80.0 SmC^*_{AF} 85.0 SmC^*_β 90.0 SmA 106.0 I

FIGURE 1 The structures of compounds 1–3, synthesised at Hull University. Phase sequences were assigned by a combination of microscopy and resonant x-ray scattering [7].

The X-ray experiments have been described in detail elsewhere. The small-angle and time-resolved X-ray scattering experiments [4,5] were carried out at the SRS, Daresbury, UK using a wavelength of 1.5 Å and a beam size of approximately 1 mm × 1 mm.

An area detector was used, allowing layer deformations to be observed in both the plane and the depth of the device. The resonant X-ray scattering experiments [6] were performed at the Advanced Photon Source, Argonne, USA. In this case, the incident X-rays were tuned to the selenium K-edge absorption energy (12.66 keV).

FIELD EFFECTS IN THE SSFLC DEVICE

1. Irreversible Layer Motion: the Chevron to Bookshelf Transition

Patel [8] first demonstrated that the chevron structure in an SSFLC device could be eliminated by applying a large voltage for several hours, after which the smectic layers were perpendicular to the device substrates and rotated in the surface plane by an angle approximately equal to the chevron angle. The chevron to bookshelf transition, also known as Electric Field Treatment (EFT), has since been investigated extensively using a wide variety of waveforms, applied voltages, frequencies and field application times. The high fields (5–10 Vμm^{-1}) required to achieve the chevron to bookshelf transition are common to all the experiments reported.

Data showing the evolution of the chevron to bookshelf transition in an SSFLC device containing SCE13 at room temperature (~40°C below the SmA to SmC* transition) are presented in Figure 2. The device is rocked initially to the chevron angle, where the intensity of the Bragg peak is high. On increasing the voltage, the layers ultimately adopt a bookshelf geometry, resulting in almost zero intensity of Bragg reflection for the device held at the chevron angle. The waveform applied is a 10 Hz triangular wave and each voltage is held for approximately 30 seconds before being increased step-wise. For the device shown, the chevron to bookshelf transition begins at around 22 V (~7 V/μm). Prior to the transition, there is an increase in the intensity of the Bragg peak attributed to improved alignment or enhancement of the chevron arm under investigation, a consequence of the initial half-splayed structure. On removal of the

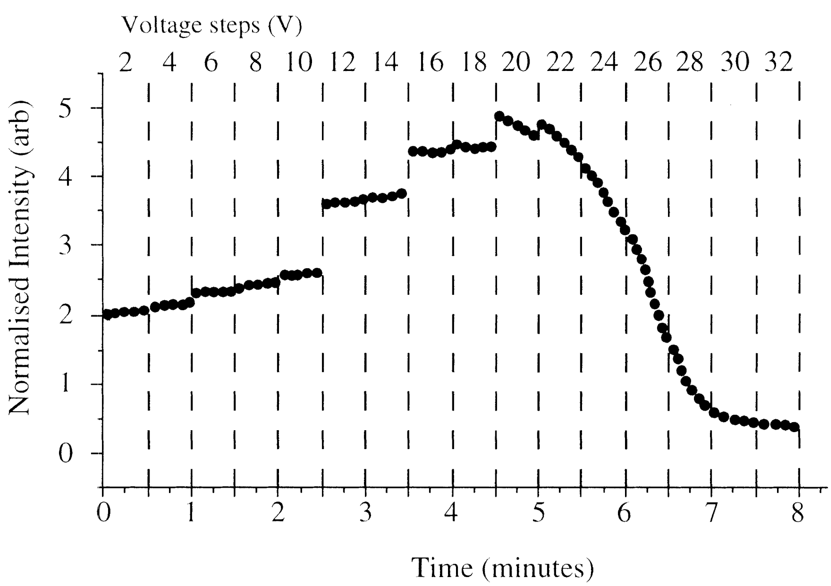


FIGURE 2 The change in the intensity of the Bragg peak of the SSFLC device on application of a stepwise increased voltage.

voltage, the structure relaxes to a distorted bookshelf structure implying that process of layer reorganization is both voltage and time-dependent.

Figure 3 shows the intensity of the Bragg peak as a function of time with the device held at the chevron angle and $55\,V_{rms}$ applied for 40 seconds. This voltage is above the chevron to bookshelf transition, though rocking curve experiments before and after the EFT show that the transition is not complete, but an obtuse layer structure results [9]. These data (and data for other rocking angles and voltages) fit well to the double experimental function in Eq. (1),

$$I = I_f + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \qquad (1)$$

implying that at least two and possibly three physical processes are relevant during the chevron to bookshelf transition.

1. Movement of the chevron interface in a plane perpendicular to the device substrates. One arm of the chevron is enhanced, moving towards a tilted bookshelf structure, as seen by other authors [10].
2. Deformation of the initial structure into a complex, three-dimensional structure, also in agreement with the findings of other workers [11,12]. This is a slower time scale process.
3. Bulk co-operative layer rotation which occurs on a longer time scale than either of the above processes. Evidence for this is provided from data obtained at rocking angles lower than the chevron angle [9]. However, this is not the dominating mechanism as the maximum intensity measured at such angles is an order of magnitude lower than that measured at the chevron angle.

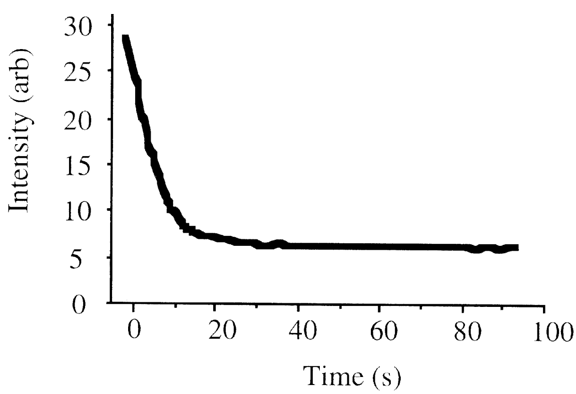


FIGURE 3 The intensity of the Bragg peak at the chevron angle following the application of $55\,V_{rms}$ for 40 seconds.

2. Reversible Layer Flexing

The question of whether the smectic layers in a chevron structure flex during the normal (low field) switching process in SSFLCs has been considered by several authors. It is clear from simple geometric arguments that the motion of the director around the cone must be accommodated in some way at the chevron interface. Hartmann *et al.* [13] proposed that the layer tilt varies during director reorientation such that the director is uniform and planar everywhere within the device. Switching occurs via reversible bending of the layers to slightly higher tilt near the chevron interface. Alternatively, Gießelmann and Zugenmaier [14] suggested a model that incorporates bend for tilted layers with an initially splayed director profile. During switching the director is uniformly oriented in the bulk and the layers reduce in tilt. There is evidence for layer flexing and reorganisation from both optical [14,15] and X-ray [4,5] measurements. Figure 4 shows time-resolved X-ray scattering data for a SSFLC device across a bipolar switching cycle. The applied field was 3 V/μm, well below that required to induce a chevron to bookshelf transition.

The data show directly that layer flexing occurs as part of the switching process. It is particularly marked on field reversal and occurs on the same microsecond time scale as the director motion. Further, the layers flex reversibly towards smaller angles during switching, supporting Gießelmann's model. The smaller relative change in intensity at the lower angle shown in the figure implies that the layers *bend* co-operatively on field reversal; if no bend occurred the intensity at the lower angle would

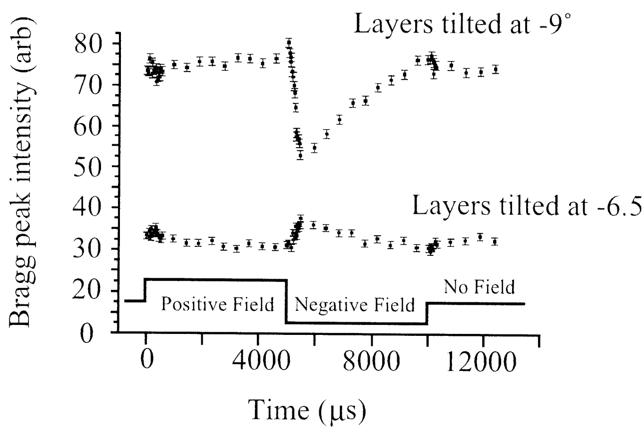


FIGURE 4 Variation of the Bragg peak intensity at the chevron angle (–9°) and at –6.5° over a bipolar switching pulse. The SSFLC device was ~5°C below the SmC*-SmA transition.

achieve the maximum value observed for the chevron structure at some point in the switching cycle. Further experiments are required to determine whether the layers move to the bookshelf geometry at the point where the director is parallel to the rubbing direction.

FIELD EFFECTS IN ANTIFERRO-, FERRI- AND FERROELECTRIC DEVICES

1. The Chevron to Bookshelf Transition

The structure adopted by the smectic layers in devices containing new materials exhibiting antiferroelectric and ferrielectric phases is of interest for similar reasons to those discussed in the previous section. It has been known for some time [16] that the optical tilt angle measured in materials such as those shown in Figure 1 is higher than the steric tilt angle (calculated from the layer spacing) by a factor between 1.4–1.6. The difference is a consequence of the molecular structure; the polarisability and mass axes do not coincide. Figure 5 compares the optical and steric tilt angles of compounds 1–3 with the chevron angle adopted in devices. It is clear that the chevron angle for compounds 1–3 is comparable to the steric tilt angle and hence is much lower than the optical tilt.

The evolution of the chevron to bookshelf transition in these systems depends on the phase under consideration. Typical data are shown in Figures 6(a) to (c) for the antiferroelectric, ferrielectric and ferroelectric phases. Other compounds show the same variation with phase [7,17] which can be summarised as follows:

1. The antiferroelectric phase shows a distinct threshold for the chevron to bookshelf transition. The threshold is relatively low (under 1 V/μm, compared with 5–10 V/μm in SSFLC devices). There is no evidence of layer curvature during the transition.
2. The intermediate (ferrielectric) phases have a very low threshold to the chevron to bookshelf transition (typically under 0.5 V/μm). Just above the threshold there is contribution to Bragg scattering at all angles considered, providing strong evidence of layer curvature.
3. There is no threshold to the chevron to bookshelf transition in the ferroelectric phases of these materials. Rather, the proportion of layers in the bookshelf geometry increases at the expense of the chevron. Further, there is no evidence of layer curvature.

The chevron to bookshelf transition appears to be voltage and time-dependent in all of the phases, in common with the SSFLC devices, though

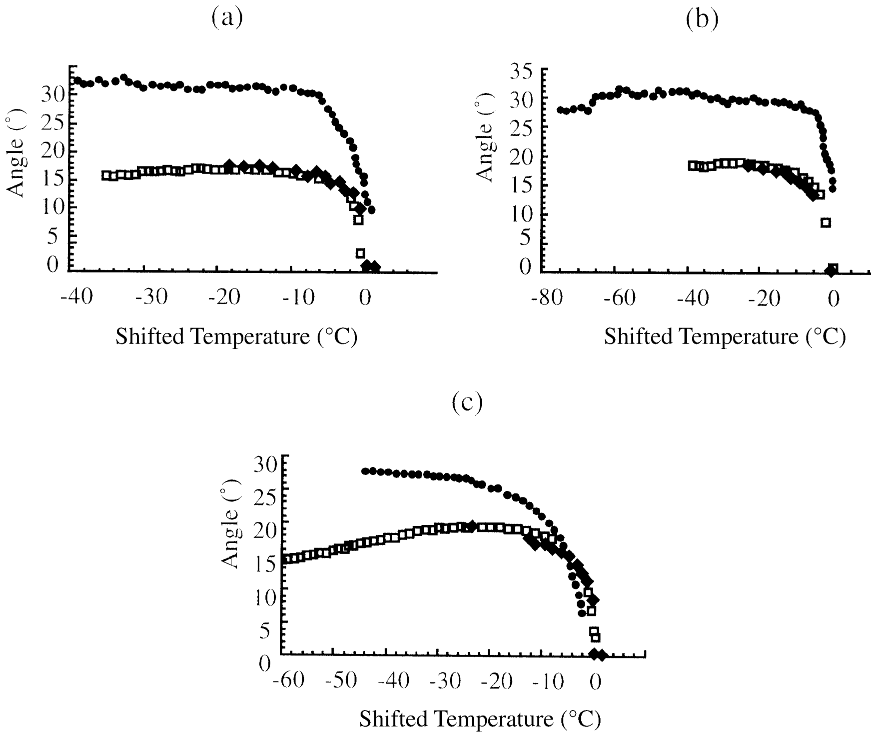


FIGURE 5 A comparison of the chevron (◆), optical (●) and steric (❑) tilt angles of compounds 1–3 (figures (a) to (c)). ferroelectric phases of compound 2 respectively.

to date there have been no investigations of the time constants of the process which might give some insight into the mechanisms involved. The local layer structure and field effects have also been examined in the antiferroelectric phase of (S)-TFMHPOBC by Takahashi *et al.* [18] using microbeam synchrotron techniques. Their investigations were time-resolved and considered the formation of horizontal from vertical chevron structures during the application of an electric field at different points in the field cycle. Prior to the experiments, the sample was field-treated and the resulting texture was striped. The spatial resolution of the microbeam allowed the local layer structure across the stripes to be considered. Their data show that the horizontal chevron angle is smaller than that measured vertically in the device (~17°, similar to that for compounds 1–3), indicating that gross layer reorganisation must occur following the chevron to bookshelf transition.

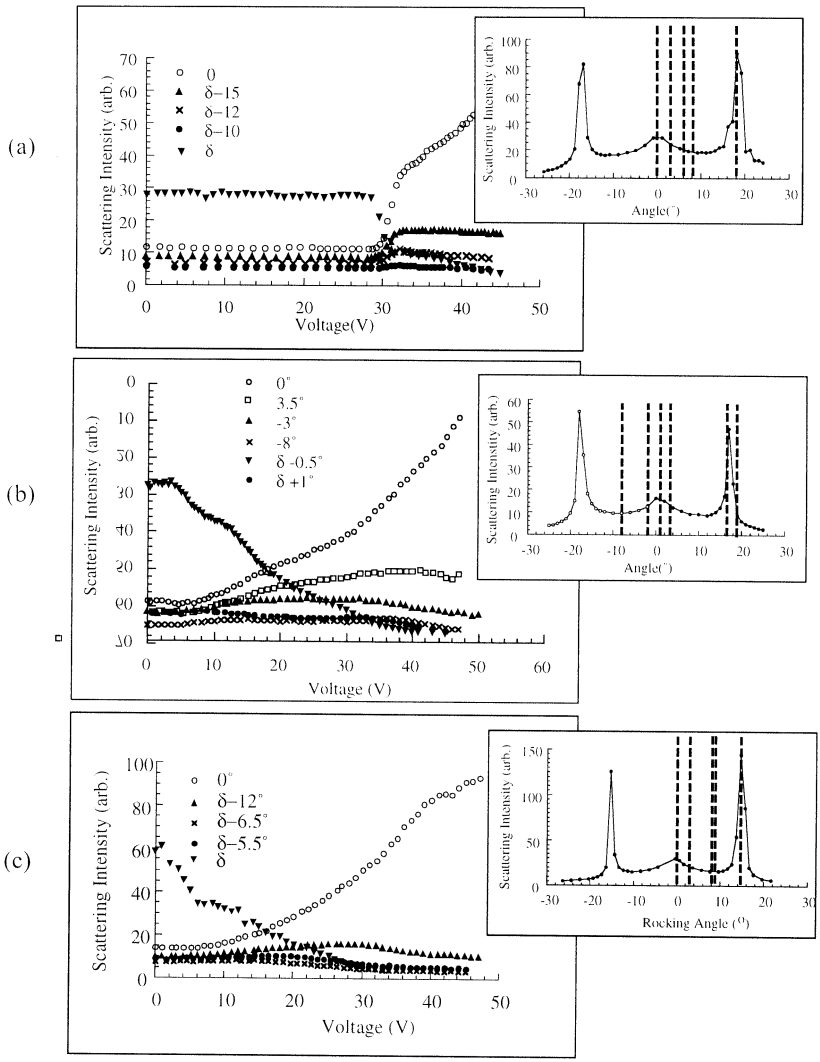


FIGURE 6 The evolution of the chevron to bookshelf transition in (a) the antiferroelectric, (b) the intermediate and (c) the ferroelectric phase of compound 2. The insets show the relevant rocking curves.

2. Inter-layer Field Effects

Resonant X-ray scattering has proven to be invaluable in elucidating the inter-layer smectic structure in antiferroelectric, ferroelectric and intermediate phases [19,20]. It is possible to carry out the experiment in a device geometry [6], as well as on free-standing films, allowing the influence of electric fields on the interlayer structure to be observed directly. Materials such as compound 2 can be studied by this technique since it contains selenium–glass is largely transparent to the X-rays at the Se-edge energy. Improvement in sample alignment and experimental resolution have allowed resonant signals associated with the 2-layer antiferroelectric phase and the 4-layer intermediate phase to be detected [21].

Figure 7 shows the resonant signal measured in the antiferroelectric phase of a device containing compound 2 as the amplitude of the applied electric field is increased. The characteristic signal around $Q/Q_0 = 1.5$ is

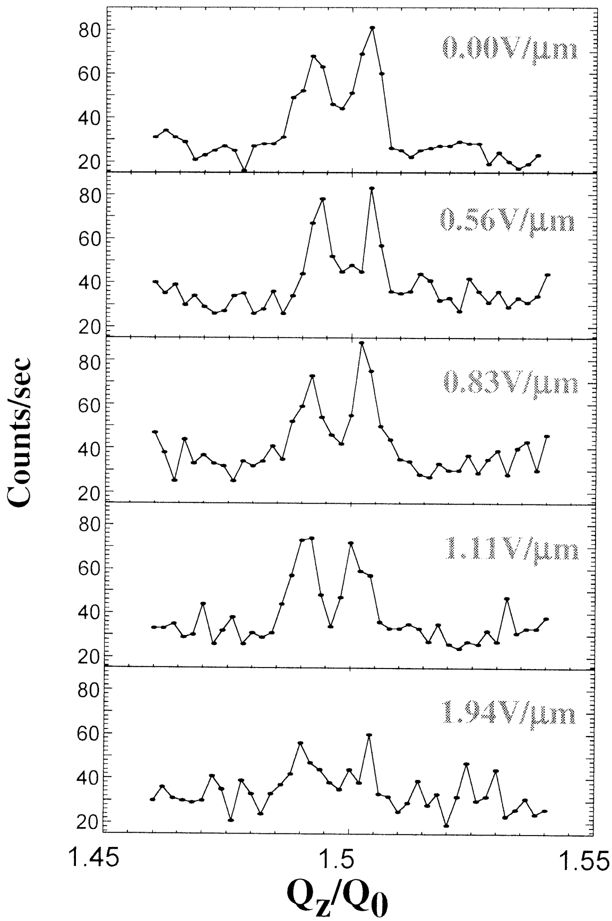


FIGURE 7 Resonant scattering signals as a function of applied field in the antiferroelectric phase.

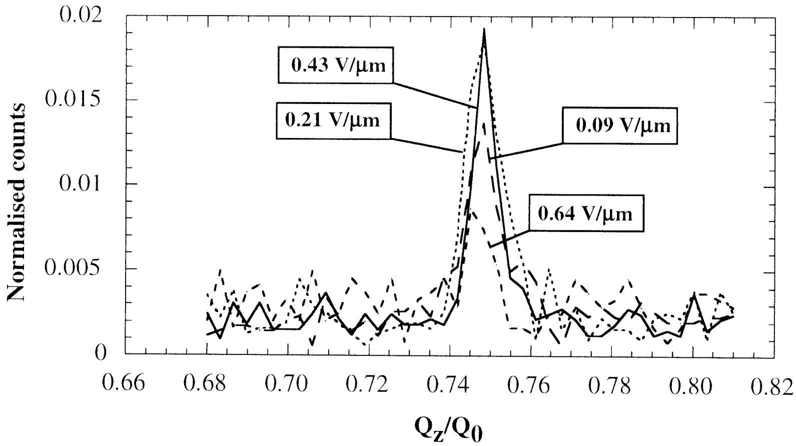


FIGURE 8 Resonant scattering signals as a function of applied field in the intermediate 4-layer phase.

apparent until after the chevron to bookshelf transition has occurred. Further, the splitting of the peaks, a measure of the helicoidal pitch of the system, does not change as the field is varied. These data show that for this material at the temperature considered, the field-induced chevron to bookshelf transition is coincident with the antiferroelectric to ferroelectric transition and that there is no field-induced change in pitch [6]. This observation is in agreement with that of Takahishi *et al.* [18] lending credence to the suggestion that the field-induced antiferroelectric to ferroelectric transition occurs in conjuction with layer reorganisation in this material.

The field-dependent resonant signal detected from the 4-layer intermediate phase of a fluorinated version of compound 2 is shown in Figure 8. In this case the characteristic signature is still visible after the chevron to bookshelf transition, indicating somewhat surprisingly that the layers move before director switching begins. This is the only material for which such data have been obtained to date and it will be interesting to see if this result is universal.

CONCLUSIONS

Gaining an understanding of layer motion in chiral smectic-C and related phases is vital if field-induced phenomena are to be fully understood. X-ray scattering provides a direct method of studying layer-related phenomena. It is clear that high fields can induce a chevron to bookshelf transition in all types of device and all phases. However, the mechanism of this irreversible layer motion depends not only on the type of device studied, but also on the phase under consideration. In SSFLC devices the chevron to bookshelf transition occurs at relatively high fields and the reorientation mechanism exhibits several time constants. At fields below those necessary to induce irreversible layer motion, the director switching process is mediated by rapid, reversible layer flexing to angles lower than the chevron angle.

The origin of the different evolution of the chevron to bookshelf transitions in the antiferroelectric, intermediate and ferroelectric phases is still a matter of debate. There is no significant difference in the tilt angles or bulk spontaneous polarisation across the phase regime, ruling out these parameters as reasons for the variation. There is, of course, no nett polarisation in the antiferroelectric phase and the resonant scattering data together with electro-optic measurements [22] imply that irreversible layer motion occurs only after the field-induced antiferroelectric to ferroelectric transition. This is in contrast to observations in the 4-layer intermediate phase where the chevron to bookshelf transition begins at fields lower than those required for ferroelectric switching. Layer curvature occurs readily perhaps as a consequence of the inter-layer structure. It has been proposed that there must be considerable strain at the chevron interface in accommodating the 4-layer structure [23]. The other factor it seems prudent to consider is that the elastic constants associated with the layers are different in the different phases, something as yet not examined by theoreticians.

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