Synchrotron studies of electric-field effects in smectic liquid crystals

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ABSTRACT

X-ray studies of liquid crystals can reveal a variety of information regarding their physical properties including structures, order parameters, configurations within devices and switching mechanisms. This Review describes the use of synchrotron radiation to examine electric-field effects in ferroelectric and antiferroelectric liquid crystal devices. Three general types of experiment are described. Firstly, static studies in which either no electric field is applied to the device of interest, or the field is changed sufficiently slowly to ensure that the equilibrium response is measured. Secondly, time-resolved studies are described, in which layer deformations are followed on a 10 μs time scale, providing detailed information about the switching mechanisms in ferroelectric devices. Finally, resonant X-ray scattering experiments are described in which the influence of electric fields on interlayer structure within devices containing antiferroelectric and intermediate (ferrielectric) phases is considered.

Introduction

X-rays provide an ideal probe of smectic liquid crystals. In such materials, molecules typically around 40Å in length are organised in layers that are more correctly considered as density waves. The layer spacing is usually close to the molecular length. The ordering of the molecules within the layers is determined by the phase type, as indicated in Figure 1. The simplest smectic phase is the smectic-A phase (SmA), in which the orientational order of the molecules (defined by a director, **n**) is coincident with the layer normal, **k**. In smectic-C (SmC) liquid crystals, the director adopts a temperature dependent tilt angle, θ, with respect to **k** and molecules in consecutive layers are oriented in the same direction (synclinic ordering). The chiral form of the SmC phase (chirality is indicated by an asterix, SmC*) is of particular interest as it has the potential to exhibit ferroelectricity [1] in surface-stabilised devices [2]. The details of this phenomenon are discussed in many excellent texts [3]. Antiferroelectricity was first observed in liquid crystals in 1989 [4] in a system closely related to the SmC* phase. In the SmC^*_{AF} phase, the molecules in consecutive layers adopt an anticlinic arrangement, modified by a macroscopic helix induced by the chirality which has a pitch typically several hundred smectic layers in length. Two final modifications of the tilted, chiral, smectic phases should be introduced; the

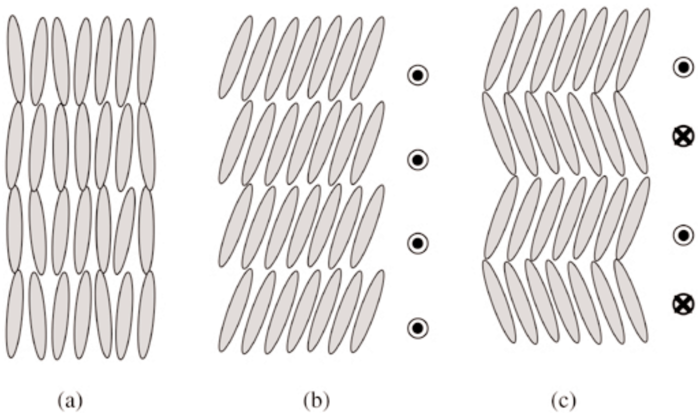
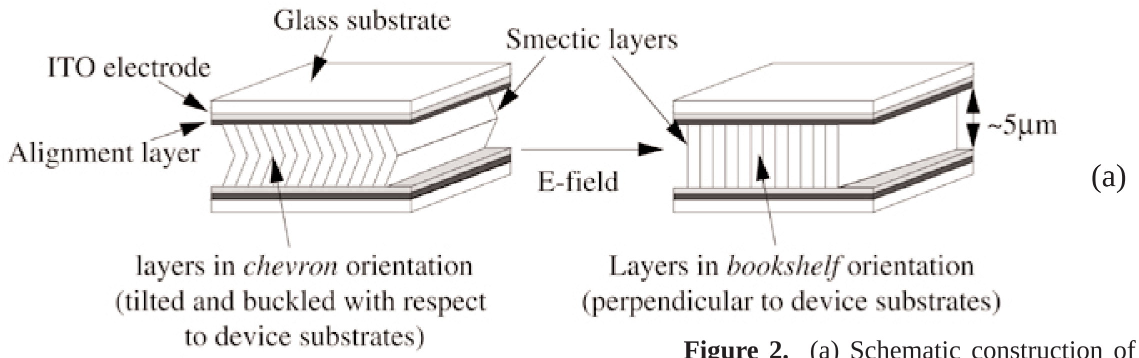


Figure 1. Representations of the several types of smectic liquid crystals: (a) smectic-A, (b) smectic-C* and (c) smectic-C^*_{AF}

intermediate SmC^*_{FI1} and SmC^*_{FI2} phases. These occur between the ferroelectric SmC* phase and the antiferroelectric SmC^*_{AF} phase and were originally described as ferrielectric, though this is now known not to be strictly true. The structure of these phases has been elucidated recently by resonant scattering X-ray [5,6,7] and optical [8] experiments. It is the higher temperature SmC^*_{FI2} phase, which has a 4-layer repeat, that is of interest in this Review.

Ferroelectric and antiferroelectric liquid crystals are of significant interest, not just because they are the only known fluids that exhibit such properties (all



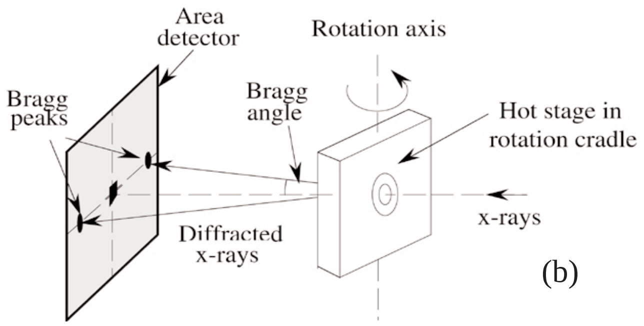


Figure 2. (a) Schematic construction of a liquid crystal device showing the geometry of the smectic layers. The left hand Figure depicts the layers in a chevron geometry, i.e. tilted with respect to the substrates with the apex of the layers in the centre of the device. The right hand Figure shows layers in the bookshelf configuration i.e. perpendicular to the device substrates. The chevron structure can be transformed to a bookshelf structure by applying a sufficiently large electric field. (b) The arrangement of the X-ray scattering experiments. The device is held within the hot stage with respect to the X-ray beam as depicted in Figure 3.

other materials in this class are solids), but because of their potential in electro-optic devices. Ferroelectric liquid crystal devices are characterised by bistability and switching that is a factor of 10^2-10^3 times faster than the millisecond switching exhibited by conventional (nematic) devices such as those used in lap-top computers. Antiferroelectric liquid crystal devices have the potential for tri-state switching and also exhibit rapid switching times of around 10^{-5}-10^{-6} seconds. Despite their clear advantages over nematic liquid crystals, ferroelectric and antiferroelectric liquid crystal devices are only just appearing in the market place, primarily because of the added complexity that the smectic layer structure adds to the device geometry and electric-field switching mechanisms. Synchrotron radiation has proven to be a powerful tool in studying these phenomena. This Review paper highlights some of the ways in which synchrotrons can be used to investigate the layer structure in devices and the ways in which electric-fields deform this layer structure.

Experimental

All of the conventional X-ray scattering experiments described within this Review were carried out at station 2.1 of the SLS at Daresbury Laboratory. The resonant scattering experiments were carried out at the Advanced Photon Source (APS) at Argonne National Laboratories, Il.. The liquid crystal devices were constructed as indicated in Figure 2(a). Parallel glass plates of thickness 150μs were used to encapsulate a thin layer of liquid crystalline material, usually between 3μs and 25μs thick, depending on the type of material to be studied. The glass had a conductive Indium Tin Oxide (ITO) coating on the inner surfaces to allow fields to be applied perpendicular to the glass plates. An alignment layer (usually rubbed nylon) was also added to the inner surfaces to ensure good, uniform alignment of the liquid crystal film.

The liquid crystal devices were held in a temperature-controlled environment in a cradle as shown in Figure 2(b). The liquid crystal phases of interest were exhibited at well-defined temperatures. Rotation of the sample about an axis perpendicular to the direction of incident X-rays allowed the layer structure within the device to be deduced; diffraction maxima occur when the geometry is such that the smectic layers satisfy the Bragg condition. Electric fields were applied to the samples via the transparent electrodes and the electrical signal was synchronised with the detector where necessary. The time-resolved facility at station 2.1 of the SRS allows a minimum time frame of 10μs to be selected which provides reasonably good time resolution in the study of switching mechanisms for ferroelectric liquid crystals.

Smectic layer structures in ferroelectric and antiferroelectric devices and static field effects.

The structure adopted by smectic layers within a device depends on many features, but most significantly the phase sequence of the material studied, the way in which the layer spacing changes with temperature, the alignment layers used within the device and the electric-field history. Most commonly, ferroelectric and antiferroelectric liquid crystals adopt a so-called chevron structure, first observed by Reiker *et al* [9] (see Fig. 3). The chevron structure is a consequence of the layer shrinkage that occurs as the material cools from an untilted SmA phase to the tilted SmC* phase and the chevron angle is around 0.85 of the tilt angle, θ [3]. Chevron structures have also been observed in devices containing achiral SmC [10] and SmA [11] materials where there is also layer shrinkage, but in which the geometrical considerations differ from the ferroelectric case.

The electric torque produced when a sufficiently large field is applied to the device can cause the chevron structure to transform irreversibly to a so-called bookshelf structure in which the layers are largely perpendicular to the device substrates. This transition is usually accompanied by the formation of a chevron structure in the plane of the device, a consequence of geometric considerations. Figure 3 indicates how the diffraction pattern and experimental geometry can facilitate the study of the layer structure within a device, defining the chevron angle for both types of chevron. The chevron to book-shelf transition has been studied extensively within ferroelectric liquid crystals [12,13]. For conventional, surface-stabilised devices it occurs at relatively high fields (typically between 5 and 10 $V\mu m^{-1}$) and usually has a distinct threshold. The response time of the transition depends on the field applied, but it is slow compared to the ferroelectric switching, occurring over seconds rather than microseconds [13]. This is as expected since the transition is associated with gross reorganisation of the layer structure, rather than switching of the molecular directions within the layers. If the field is removed before the reorganisation is complete, a distorted bookshelf structure results, indicating that the transition is both field- and time-dependent.

There are rather few studies of the chevron structure within antiferroelectric devices [14], or of the nature of the chevron to bookshelf transition [15,16,17, 18,19]. It is important to note that such devices are generally not surface-stabilised in contrast to those discussed above, since the helicoidal pitch of materials that exhibit antiferroelectric phases is generally too small to allow surface stabilisation. Further, the chevron angle differs significantly from the tilt angle θ deduced optically with ratios of around 0.6 quoted for some materials [20]. The chevron to bookshelf transition takes a different form

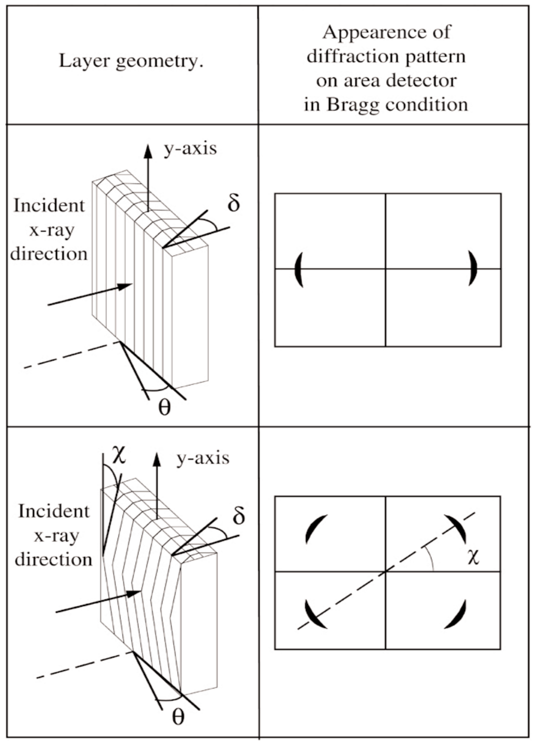
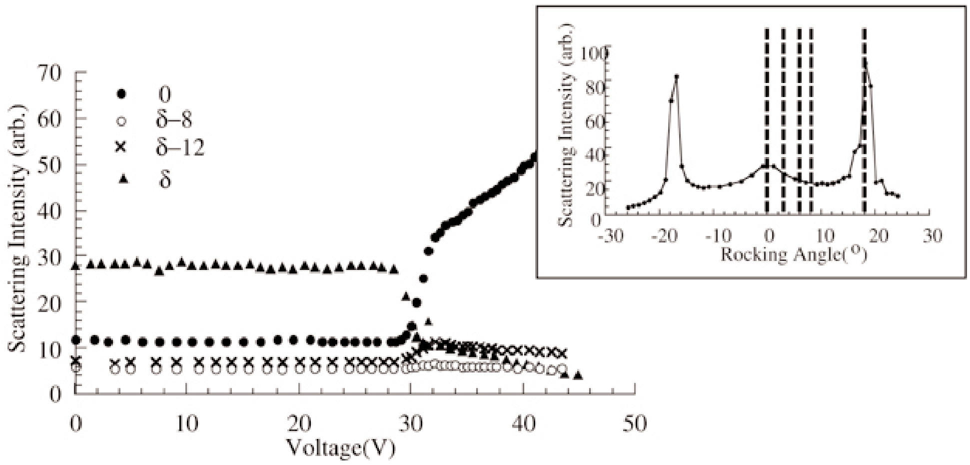


Figure 3. Idealised layer structures adopted within smectic devices and the associated idealised diffraction patterns observed in the Bragg condition. The devices on the left depict the geometry of the smectic layers. In both cases the layers adopt a configuration that combines a chevron structure adjacent to the substrates with bookshelf layers in the centre of the device. The chevron angle is defined as the angle subtended at the glass substrate,δ, so in the bookshelf geometry δ= 0. In the lower diagram, the layers have also buckled in the plane of the device, forming a so-called 'in-plane' chevron at an angle χ to the rotation axis.

in the SmC^*_{AF}, intermediate and SmC* phases, as can be seen from the data shown in Figure 4. In this experiment, an initial rocking curve (inset) shows the original chevron structure adopted within the device, in each case with some residual bookshelf layers, probably situated at the apex of the chevron. The device was held at specific rocking angles and the electric field incremented gradually. The Bragg peak intensity indicates the presence or absence of layers at a specific rocking angle for a particular value of applied field. Once the layers were deformed irreversibly (at voltages higher than around 40 Vrms, 100Hz), the device was subjected to a heating and cooling cycle to ensure that the original layer structure was reformed prior to changing angle and repeating the electric-field experiment. The data show that the chevron to bookshelf transition occurs differently in each phase. In the SmC^*_{AF} phase, a distinct threshold is observed and this has been noted in separate experiments to occur at fields higher than are required to induce an antiferroelectric to ferroelectric transition. Such a result is unsurprising

(a)



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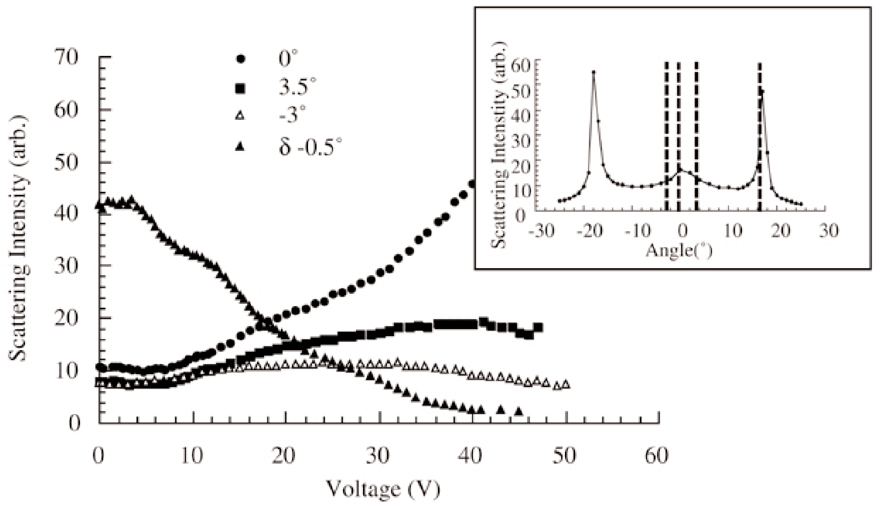

(c)

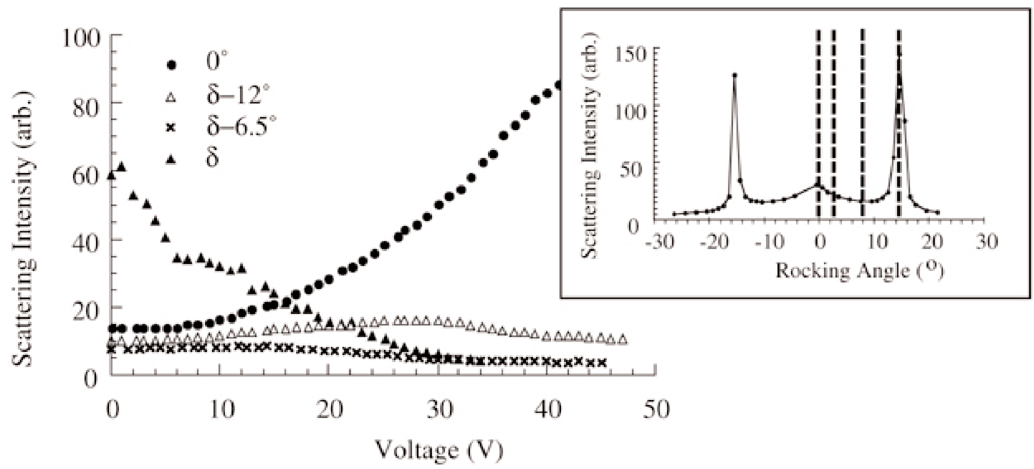

Figure 4. Bragg peak intensities as a function of applied voltage for specific rocking angles in a device containing material exhibiting **(a)** antiferroelectric, **(b)** intermediate and **(c)** ferroelectric phases. The inserts show the field-free rocking curves with distinct peaks at around ±20° indicating that the majority of the original structure was in a chevron configuration. Each of the inserts also shows a broad peak around a rocking angle of 0°, indicating that a small proportion of the layers were in a bookshelf configuration. The angles at which the intensity of the Bragg peak was monitored as a function of applied voltage (main Figures) are indicated by lines on the inserts.

since in the antiferroelectric phase there is no electric torque and the system must thus be switched to a ferroelectric structure before an electric field can influence the layer structure. In the intermediate phases, the threshold is low and there is evidence of layer curvature just above threshold (Bragg scattering is observed for all rocking angles). This is a surprising result and theoreticians are currently examining possible mechanisms for this type of deformation [21]. Finally, in the ferroelectric phase, there is a continuous growth of the residual bookshelf structure at the expense of the chevron layers and no threshold. Again, theoreticians are currently developing models that explain this feature [22].

Time-resolved X-ray studies of ferroelectric switching mechanisms.

The layer structure and field-evolution of the chevron to bookshelf structure are important features of antiferroelectric and ferroelectric devices. The layer structure has a huge influence on the optical properties of a device [3] and it is advantageous to operate a device below the chevron to bookshelf transition since an in-plane chevron causes large degrees of scattering (and hence loss in contrast and light transmission) in a device. However, a key question that challenged the liquid crystal community for some years was how the layer structure facilitated normal ferroelectric switching. The problem is simple; during switching of a ferroelectric device, the molecules move from one stable state at, say, $+\theta$, to the other at $-\theta$. In doing so, either the layer spacing must change (as the molecules go through $\theta = 0$) or they must flex to accommodate the switching. There are considerable technological difficulties in studying this directly via X-ray scattering since the weakly scattering liquid crystal layer is extremely thin (~ 5μs) and the switching occurs on a microsecond time scale. Station 2.1 at the SRS can be used to study time-dependent scattering on such a time scale and has been used to provide direct evidence of layer flexing during switching [23,24].

The experiment is carefully timed with the field applied to the ferroelectric liquid crystal device triggered by the detector system. The detection is arranged so that the X-ray scattering pattern is recorded at different times along the bipolar switching pulse, with an extremely short integration time of 30μs. The temperature and switching voltages are selected so that the device has an optical response time of around 150μs, ensuring that sufficient detail is obtained across the switching cycle. Naturally, 10μs time frames are of insufficient length to obtain any reliable signal, so the experiment was gated and repeated until the equivalent of 2 seconds of data collection time was accumulated in each diffraction pattern recorded. An area detector was used which afforded two distinct advantages. Firstly, it was possible to obtain information on any layer motion in the *plane* of the device through the switching cycle that might occur concurrently with layer flex through the depth of the device. The former would be apparent through an angular shift in the position in the Bragg peak on the detector, while the latter can be deduced from a change in the Bragg scattering intensity during switching which indicates that the layers have moved from the Bragg position. Further, any change in layer spacing would be apparent through a radial change in the position of the Bragg peak. Secondly, the area detector allowed both of the Bragg peaks in a Friedel pair to be measured at the same time, providing information on the layers at the angle of investigation and at a lower angle, shifted by

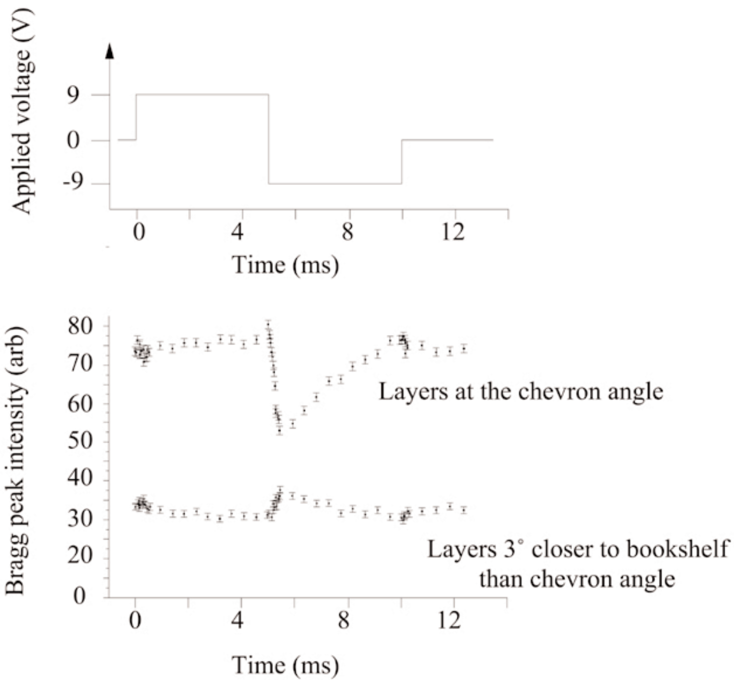

Figure 5. Time resolved data showing the intensity of the Bragg peak at different times along a bipolar switching pulse. Data are shown for an angle corresponding to the chevron angle and one approximately 3° lower. The Bragg peak intensity is a measure of the layers at a particular angle within a device.

twice the Bragg angle.

Typical time-resolved data are shown in Figure 5. It can be seen that as the field is reversed, the intensity of the Bragg peak reduces for layers at the original chevron angle, with a concurrent increase in scattering intensity at lower angles. Thus, layer flexing occurs on a ms time scale and towards lower angles, agreeing with the predictions of Gieβelmann and Zugenmaier [25]. No change in layer spacing was observed throughout the switching cycle in any of the experiments so far reported. The observation of in-plane motion is somewhat inconclusive but appears [23] to be small (around 1°) if indeed it occurs. It appears that switching between the two stable ferroelectric states is mediated in some cases at least by flexing of the layers to lower angles. It is of course interesting to consider whether the layers always flex by the same amount, whether this is a mechanism that is particularly easy relatively close to the SmC* to SmA transition (where our experiments were conducted to allow all the conditions required by the apparatus at station 2.1 to be met) or indeed whether similar phenomena occur in other phases. To date, no further information has been published, probably due to the technical difficulty associated with the experiments. However, preliminary data obtained in very recent experiments indicate that reversible, rapid, layer flexing also occurs to some extent in switching in the antiferroelectric phase [26] . Certainly future experiments will investigate this further.

Resonant X-ray studies of liquid crystal devices.

The previous Sections have indicated the value of X-ray scattering to the study of layer structures and switching mechanisms in ferroelectric and antiferroelectric devices. However, the experiments described can provide no information on the inter-layer structures in the SmC*, SmC^*_{AF} and intermediate phases, how they might be modified within devices, or indeed in what way they are influenced by electric fields. Resonant scattering experiments present a powerful probe of interlayer structure in smectic liquid crystals. Briefly, the X-ray energy is tuned to the absorption edge of one of the atoms contained within the liquid crystal molecule, typically either sulphur or selenium. In the resonant scattering experiments, forbidden reflections occur at positions corresponding to:

$$\frac{Q_z}{Q_o} = l + m\left(\frac{1}{\nu} + \varepsilon\right)$$

where *l* is an integer, *m* can take integer values between ±2, ν is the super-lattice periodicity and ε is the ratio of the smectic layer spacing to the helicoidal pitch of the structure. The super-lattice periodicity takes values of 1, 2, 3 and 4 in the SmC*, SmC^*_{AF}, SmC^*_{FI1} and SmC^*_{FI2} phases respectively. The SmC* phases were first studied using this technique by Mach *et al* [5,27] in free-standing films (the sample is suspended across a hole with no glass substrates), confirming details of the interlayer structures. The technique has been used extensively on films [7] and was later adapted to study devices, though it is has so far proven possible only to examine materials containing a selenium atom in such a geometry since glass is insufficiently transparent at the energies corresponding to the sulphur absorption edge.

Resonant scattering peaks have been obtained for all the SmC* related phases in a device configuration apart from the 3-layer SmC^*_{FI1} phase. The resonant scattering signal obtained from a device containing an antiferroelectric liquid crystal [28, 29] , is shown in Figure 6. The resonant peaks are positioned around Q_z/Q_o = 0.5 and the splitting corresponds to the helicoidal pitch adopted by the material at the temperature of the experiment. Application of an electric field leaves the spacing of the resonant peaks largely unchanged until they effectively disappear at the field-induced transition from the antiferroelectric to ferroelectric state, indicating that the pitch is unaffected by the field prior to that transition. The chevron to bookshelf transition occurs almost coincident with the loss of the resonant peaks characteristic of the SmC^*_{AF} phase, in agreement with the discussion above. Resonant peaks associated with the 4-layer SmC^*_{FI2} phase [29] are shown in Figure 7 at the Q_z/Q_o = 0.75 position. Interestingly, these peaks remain on application of fields beyond that necessary to induce the chevron to bookshelf transition. Since the SmC^*_{FI2} phase is strictly antiferroelectric in the absence of a field, it can be concluded that there must be some field-induced deformation of the structure prior to the chevron to bookshelf transition, allowing an electrical torque to be experienced by the layers. It is possible to speculate that this low-field induced

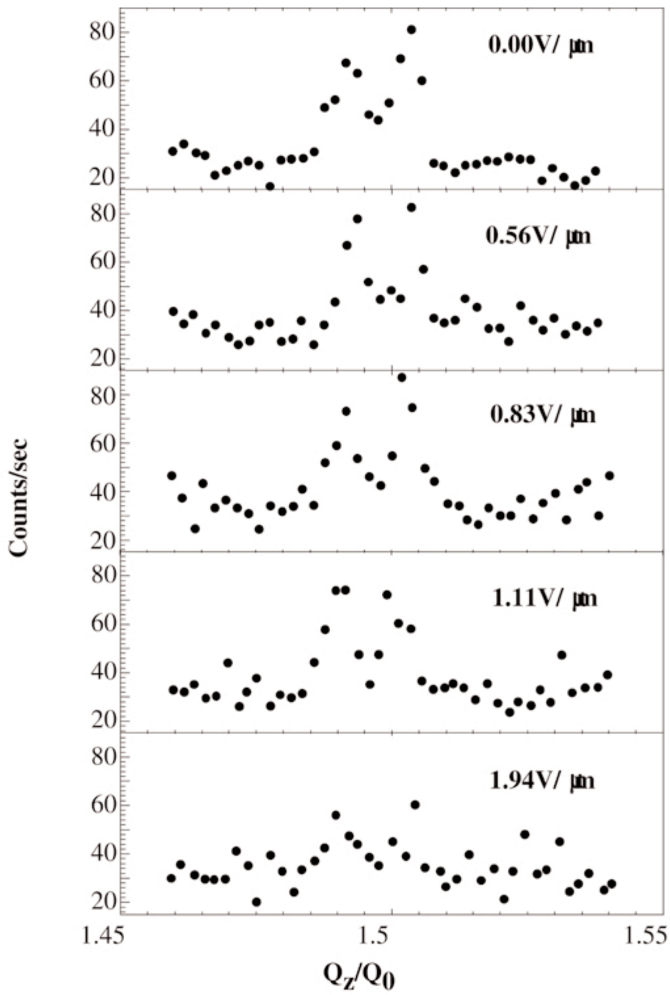

Figure 6. Resonant scattering data for the antiferroelectric phase showing the dependence of the resonant peaks on applied field. It can be seen that the peaks become indistinct for the highest voltage applied, indicating a loss of the 2-layer structure.

deformation is linked to the layer curvature observed at the chevron to bookshelf transition in other experiments. Unfortunately, to date, the resonant scattering data are insufficiently clear to allow detailed study of the 4-layer structure, they are sufficient only to indicate that such a repeat exists.

Summary

It is clear from this Review that a wealth of information can be obtained via synchrotron studies of smectic liquid crystal devices. The value of such experiments lies in the fact that they study layers *directly*. X-ray scattering is an invaluable tool in the study of liquid crystals and liquid crystal devices. It is certain, as synchrotron sources improve, providing microbeam sources, higher flux etc. that more sophisticated experiments will be carried out, providing yet more information about these systems.

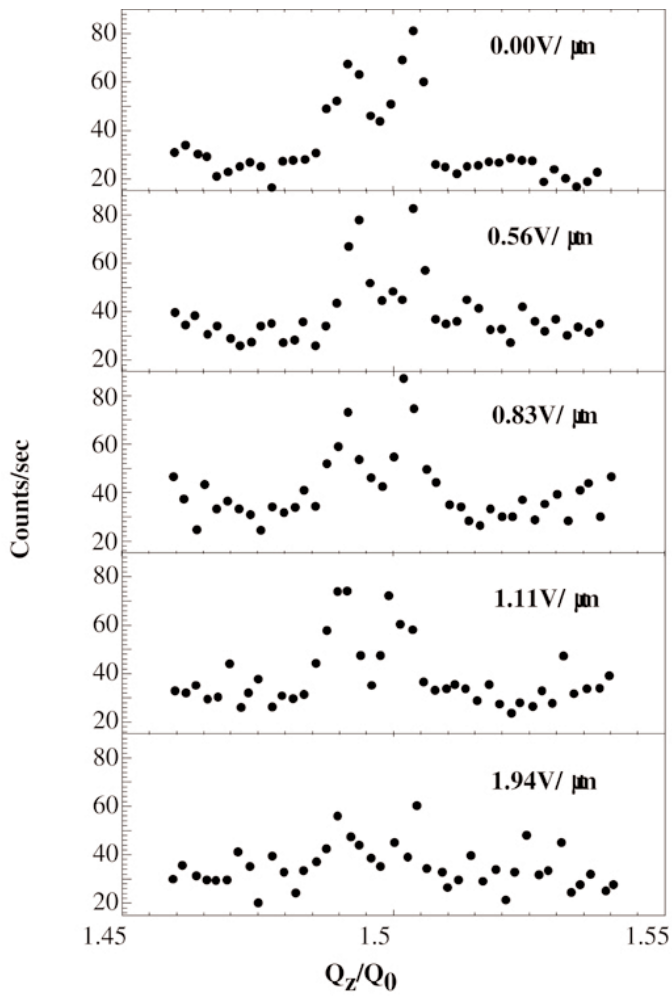

Figure 7. Resonant scattering data for the 4-layer intermediate phase showing the dependence of the resonant peaks on applied field. The resonant peak associated with the 4-layer structure persists for all applied fields, indicating that it is stable with respect to applied field.

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