Resonant x-ray scattering at the Se edge in ferroelectric liquid crystal materials

L.S. Matkin and H.F. Gleeson
University of Manchester, Dept. of Physics and Astronomy, Manchester, M13 9PL, UK
R. Pindak
Lucent Technologies, Bell Laboratories, Murray Hill, NJ 07974 USA
P. Mach and C.C. Huang
School of Physics and Astronomy, University of Minnesota, Duluth, MN 55812 USA
G. Srajer and J. Pollmann
Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439 USA

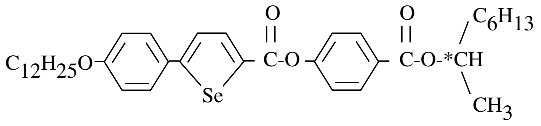
Introduction

The rapid, tristable switching of antiferroelectric liquid crystals [1] has been responsible for the recent interest in their application to display devices [2] and optical elements, such as spatial light modulators. The electro-optic properties of the more complex ferrielectric [3] phases are also of interest, although these phases are far less understood. The ferrielectric structure has been the subject of considerable controversy and several models have been proposed [4, 5]. In general, the liquid crystal ferroelectric (FE), ferrielectric (FI), and antiferroelectric (AFE) phases (smectic C* subphases) are formed from rod-like molecules arranged in a layered structure. The molecules have an average molecular direction (the director) tilted with respect to the layer normal. The director orientation with respect to adjacent layers defines the specific subphase. Recently, the clock model [5] has been shown to agree with the structure of the FI phases in certain sulfur-containing compounds using x-ray resonant scattering combined with polarization analysis [6, 7].

The structures of the smectic C* (SmC*) subphases have been previously investigated using indirect techniques (e.g., electro-optic measurements and conventional x-ray scattering). Resonant scattering allows direct investigation of the director orientation within smectic layers [6]. Understanding the details of the SmC* structures is an important step towards optimizing their potential for device applications. The first application of resonant scattering to a selenium-containing liquid crystal is reported here, studying the detailed structure of the SmC* subphases. Scattering is carried out on thick free-standing films and, for the first time, resonant signals are detected in a liquid-crystal device geometry. Scattering from this device has also allowed us to probe electric-field-induced structural changes.

Methods and Materials

The material used in this work was a selenophene heterocyclic ester, exhibiting the AFE, FE, and FI phases (Fig. 1). The physical properties of this material have been published elsewhere [8,9]. The inherent chirality of the molecules results in a macroscopic helicoidal structure in the liquid-crystal phases; this helix has a pitch typically of the order of the wavelength of visible light.



$\mathbf{I}$ 116.7 $\mathbf{SmA}$ 109.5 $\mathbf{SmC^*}$ 98.5 $\mathbf{SmC^*_{FI}}$ 96.9 $\mathbf{SmC^*_{A}}$→
→ (42.5 $\mathbf{SmI^*_{A}}$ 33.3 $\mathbf{SmI^*}$)→$\mathbf{K}$

Figure 1: The molecular structure and phase sequence.

Free-standing films of smectic liquid crystals provide an excellent layer arrangement. The number of layers in a film are quantized, and different thicknesses can be spread easily. For this experiment, 200 layer films were spread in the SmA phase, then cooled into the SmC* subphases. The free-standing film work was carried out in the specular Bragg scattering geometry where conventional x-ray scattering produces peaks at $Q_o = 2\pi d$ and integral multiples of this value (where d is the smectic layer spacing). Conventional x-ray scattering probes only the average electron density of the material and provides no information on the detailed structures of the SmC* subphases. Resonant scattering, however, is sensitive to the relative director orientation [10]. Therefore, additional peaks are seen along Q_z/Q_o, the position and polarization of these peaks being determined by the substructure.

In the clock model, the interlayer change in orientation for the SmC* subphase molecules is a fixed angle with two contributions: a large rotation $2\pi/\nu$ from the ν-layer superlattice, and a much smaller rotation $2\pi\varepsilon$.ε represents the ratio of the smectic layer spacing, d, to the optical pitch (P_o). The different subphases exhibit different superlattice periodicities (values for ν), and a helical clock structure results in resonant scattering peaks located at:

$$Q_z/Q_o = L + m\,[\,(1/\nu) + \varepsilon\,]\,.$$

L and m are integers with $m = 0, \pm1$, and ±2. The clock model may be distinguished from other models by looking at the positions of these peaks and their polarization properties.

Although free-standing films are ideal for determining the subphase structures, it is known that bulk materials confined in a device can behave differently from free-standing films [11] and a device geometry allows the application of large electric fields across the material. The device that we studied consisted of two 150 µm glass plates separated by a ~15 µm spacer. The inner surfaces of the glass were coated with a transparent, conductive layer of ITO (indium-tin oxide) and a rubbed nylon 6/6 layer (0.5 µm). This aligned the molecules parallel to the glass surfaces. The device was mounted so that the beam passed through the sample (Fig. 2). A square wave voltage could be applied to the sample using a trigger pulse to gate the detector. This ensured that data collection occurred only on the application of a positive voltage. The devices were mounted onto a Linkam hot stage, allowing temperature control with a relative accuracy of ± 0.05 K.

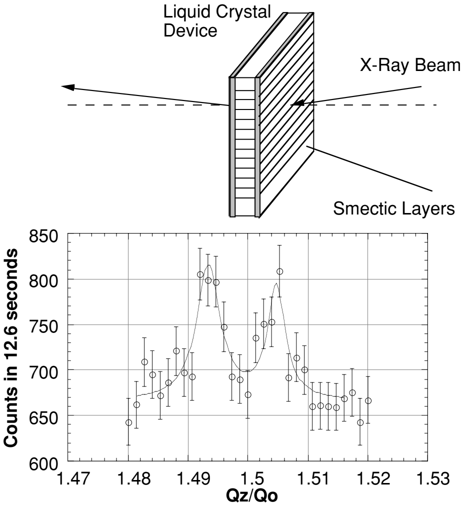


Figure 2: Resonant peaks observed in the antiferroelectric phase in the device scattering geometry.

Results

The FE, FI, and AFE subphases were first studied in free-standing films. In the FE phase, the L = 2 layer peak has first-order (m = ±1) and second-order (m = ±2) resonant satellite peaks spaced apart by ε (Fig. 3a). This scan was taken at T = 104.2 ºC; P_o can then be calculated as 0.39 µm at this temperature. In the next lower temperature FI phase (Fig. 3b), the peaks reveal that this FI phase is composed of a three-layer superlattice, contrasting with the four-layer structure previously observed in the sulfur analogue of this material [7]. In the AFE phase, there is a two-layer superlattice (Fig. 3c), and P_o is determined as 0.58 µm. Cooling into the hexatic phase, AFE peaks remain (Fig. 3d) indicating that this phase also has a two-layer repeat structure.

In the device, a resonant signal was observed in the AFE phase at 90.2 ºC with no applied field (Fig. 2), clearly showing splitting due to the helical pitch in the material. From these data, the pitch of the material inside the device was calculated to be 0.61 µm at 90.2 ºC. On application of 40 V the resonant AFE peaks vanished, confirming that the phase had been forced into an FE structure. The threshold for FE switching was found to be lower than 20 V. No helical unwinding was observed on application of a field in the device geometry. This was evident, as no change in peak positions occurred on application of the voltage.

.

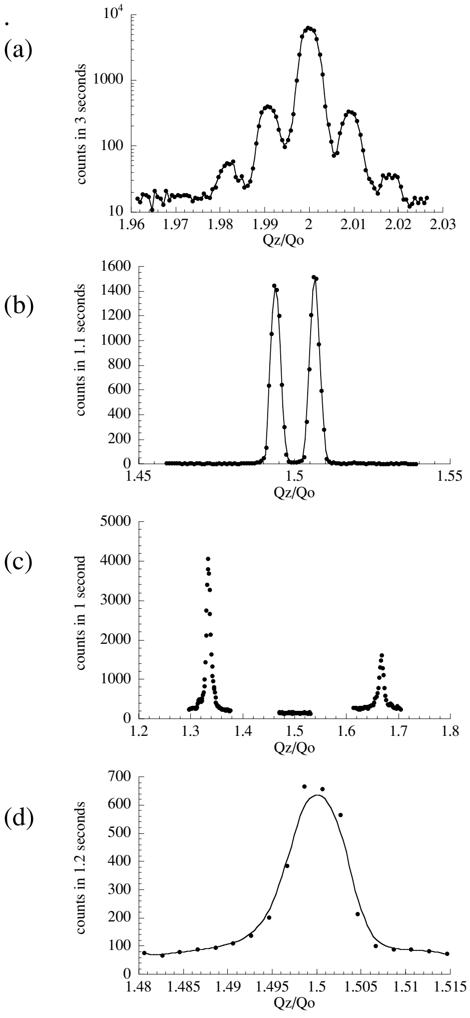


Figure 3: Resonant scattering peaks from free-standing films in the (a) FE, (b) FI, (c) AFE, and (d) hexatic phases.

Discussion

Using the resonant scattering technique at the Se edge together with a polarization analysis, the clock model has been confirmed for this material [12]. The layer structures of the FE and AFE phases have been observed and a three-layer FI phase revealed. In addition, the peak positions in the monotropic hexatic phase confirm the presence of an AFE structure. By studying liquid-crystal samples in a device, structural transitions can be deduced (e.g., helical unwinding and layer motions). The main advantage of studying the device in this geometry is that structural changes that occur as part of the switching process can be directly observed. The switching mechanisms in AFE liquid crystals have been the subject of much discussion. This experiment confirms that the application of an electric field to this material in the AFE phase does not change helical pitch.

Acknowledgments

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. L.S.M. would also like to gratefully acknowledge the EPSRC (98311471).

References

[1] A.D.L. Chandani *et al*., *Jp. J. Phys*. **28**, L1261 (1989).
[2] N. Yamamoto *et al*., *Ferroelectrics* **149**, 29 (1994); E. Tajima *et al*., *Ferroelectrics* **149**, 255 (1994).
[3] A. Fukuda *et al*., *J. Mat. Chem*. **4**, 997 (1994).
[4] K. Hiraoka *et al*., *Jpn. J. Appl. Phys*. **30**, L1819 (1991); T. Isozaki *et al*., *Jpn. J. Appl. Phys*. **31**, 1435 (1992).
[5] M. Cepic and B. Zeks, *Mol. Cryst. Liq. Cryst*. **263**, 61 (1995); V.L. Lorman, *Mol. Cryst. Liq. Cryst*. **262**, 437 (1995); S.A. Piken, *Mol. Cryst. Liq. Cryst*. **262**, 425 (1995); A. Roy *et al*., *Europhys. Lett*. **36**, 221 (1996).
[6] P. Mach *et al*., *Phys. Rev. Lett*. **81**, 1015 (1998).
[7] P. Mach *et al*., *Phys. Rev E* **60**(6), 6793 Part A, (1999).
[8] J. Mills *et al*., *Mol. Cryst. Liq. Cryst*. **303**, 145 (1997).
[9] J. Mills *et al*., *J. Mat. Chem*. **8**(11), 2385 (1998).
[10] V.E. Dmitrienko, *Acta. Cryst. Sect. A* **39**, 29 (1983).
[11] K. Itoh *et al*., *J. Mat. Chem*. **7**, 40 (1997).
[12] A.M. Levelut and B. Pansu, *Phys Rev E* **60**(6), 6803 Part A (1999).