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Biaxiality and temperature dependence of 3- and 4-layer intermediate smectic-phase structures as revealed by resonant X-ray scattering

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Abstract. – High-resolution resonant X-ray diffraction experiments have been performed on free-standing films of two selenium-containing antiferroelectric liquid-crystal mixtures. Optical studies had indicated that both mixtures exhibit exceptionally wide intermediate phases, over a total range of > 9 K. Through the structural information obtained from the resonant scattering data, we confirm that the intermediate phases of these mixtures show both 3-layer and 4-layer structural periodicities. Moreover, due to the stability of these phases, we report for the first time the temperature dependence of both the helicoidal pitch and distortion angle in the 3-layer phases deduced using the resonant X-ray technique. Analysis using an extension of the theory set out by Levelut and Pansu (Levelut A-M. and Pansu B., *Phys. Rev. E*, **60** (1999) 6803) shows that over the temperature ranges measured, the pitch changes linearly as a function of temperature whilst the distortion angle remains constant.

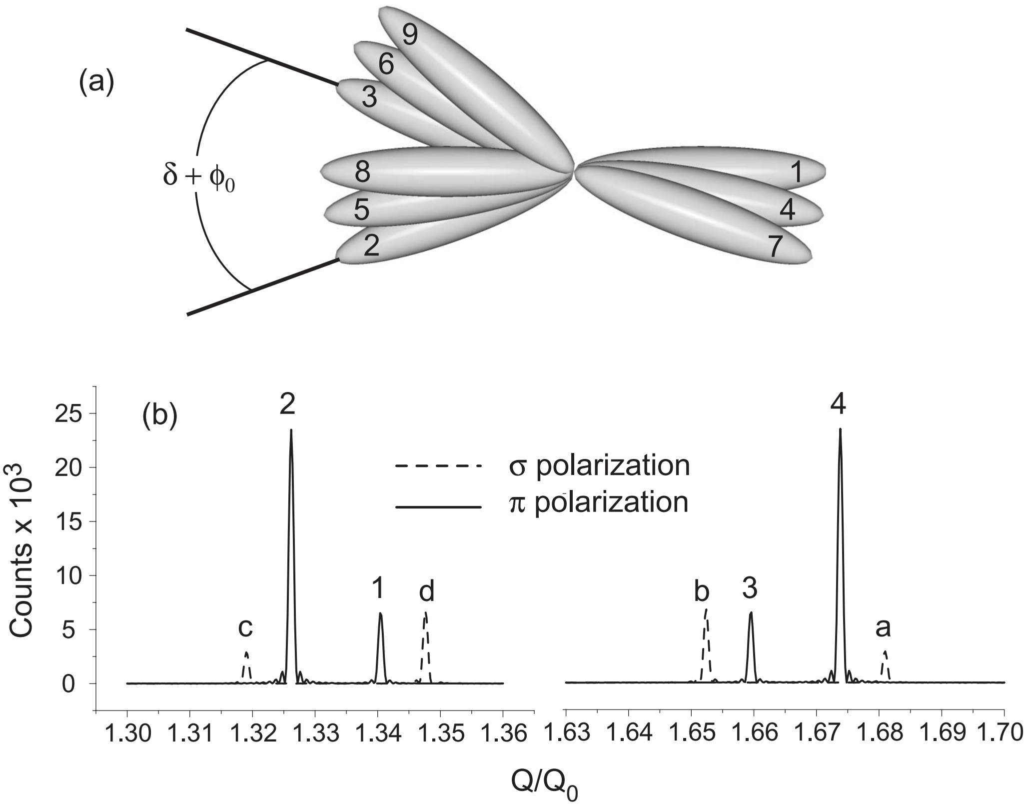
Introduction. – For many years antiferroelectric liquid crystals have been seen as having the potential for significantly improving some current display technologies. As a consequence, a considerable amount of research has been directed towards understanding the variety of liquid-crystal phases which form in these materials. In general, each of the smectic phases exhibited by antiferroelectric liquid crystals can be characterized by their different layer periodicities. The ferroelectric phase (SmC*) is synclinic [1], with the chiral nature of the constituent molecules prescribing a macroscopic helix through the layers. Typically, the helix has a pitch of the order of several hundred nm. The lower-temperature antiferroelectric phase (SmC^*_A) is anticlinic, with the tilt orientation alternating between successive layers within a similar helicoidal structure [2]. Between these two phases there exists at least two other intermediate phases, denoted SmC^*_{FI1} and SmC^*_{FI2}. Each of these shows a more complicated structure, with a 3- and 4-interlayer periodicity existing in the SmC^*_{FI1} and SmC^*_{FI2} phases, respectively [3, 4]. It is worth noting that the SmC^*_{FI1} and SmC^*_{FI2} phases are also referred to as the SmC^*_γ and SmC^*_β phases by others [5, for example].

Over the last 5 years, resonant X-ray scattering techniques have proved the most successful tool in directly measuring the director orientations between successive smectic layers and thus establishing the unit cell structure of these intermediate phases [3, 4, 6, 7]. Generally, these works have aimed to distinguish between different models of the intermediate phases. However, a significant outcome from one high-resolution study [3] was the determination of the temperature dependences of some of the physical parameters, such as the helicoidal pitch and the differences in the azimuthal orientation direction of successive layers, in the SmC^*_{FI2} 4-layer structure. Similar measurements have not yet been made in the SmC^*_{FI1} phase, primarily due to the narrow (≈ 1 K) temperature range which the SmC^*_{FI1} phase is normally stable over. Furthermore, the predicted resonant scattering peaks with specific polarization states have yet to be observed experimentally in the SmC^*_{FI1} phase [4].

This paper presents a study of two new antiferroelectric liquid-crystal mixtures in which optical studies indicate exceptionally wide intermediate-phases (from 4–11 K for the individual phases and a total intermediate-phase range of > 9 K). We identify the characteristic resonant scattering features and use these to determine for the first time details of the structure of the three-layer phase, including the temperature dependence of the helicoidal pitch and the distortion angle, δ (defined in fig. 1a).

Resonant X-ray scattering. – Whilst for many years conventional X-ray scattering has provided considerable information relating to the layer structure and device geometries of numerous smectic liquid-crystal phases, the technique is intrinsically insensitive to inter-layer variations in molecular orientation. By contrast, resonant X-ray scattering probes the relationship between the orientation of the molecules in each layer. Consequently, extra resonant satellites of the principal peaks ($l = 1, 2 \ldots$) can be detected at positions which are unique representations of the unit periodicity in the different smectic phases. By extending the crystallographic resonant scattering theory of Dmitrienko [8], Levelut and Pansu [9] calculated several specific cases of resonant scattering from different smectic liquid-crystal phases. They showed for example that for a three-layer distorted (biaxial) phase, with incident σ polarized radiation, first-order resonant satellite peaks would appear at positions $Q_z/Q_0 = l + m(\frac{1}{3} \pm \epsilon)$ and be π polarized. Here, $\epsilon = \frac{d}{P}$, is the ratio of the smectic-layer spacing, d, to the optical pitch, P and l and m are both integers with m taking a value of ± 1. Further information can be obtained from the satellite peaks regarding the degree of biaxiality in the unit structure since the distortion angle (defined in fig. 1a) may be calculated from the intensity ratio of the two peaks. Figure 1b illustrates the calculated first and second resonant satellite peaks and their respective polarizations expected for a 3-layer structure with a distortion angle, δ of 40° and pitch of 170 layers.

The experiments were performed on two binary mixtures comprising different concentrations of a chiral dopant mixed with an antiferroelectric liquid crystal, a material which has previously been described elsewhere [4]. The molecular structures of the two components of the mixtures are shown in fig. 2 together with the phase sequences of the two mixtures studied. Both phase sequences were determined by a combination of optical microscopy and layer spacing data from small-angle X-ray scattering measurements [10].



First order satellite peaks

	peak index l,m	position Q/Q$_0$	pol
1	1,1	$1^1/3+\varepsilon$	π
2	1,1	$1^1/3-\varepsilon$	π
3	2,-1	$1^2/3-\varepsilon$	π
4	2,-1	$1^2/3+\varepsilon$	π

Second order satellite peaks

	peak index l,m	position Q/Q$_0$	pol
a	1,2	$1^2/3+2\varepsilon$	σ
b	1,2	$1^2/3-2\varepsilon$	σ
c	2,-2	$1^1/3-2\varepsilon$	σ
d	2,-2	$1^1/3+2\varepsilon$	σ

Fig. 1 – (a) A schematic diagram of the projection of the tilt directions onto the layer plane in the distorted 3-layer SmC*$_{FI1}$ structure. The tilt direction of the molecules in each layer is numbered sequentially. The distortion angle, δ, is defined in the figure as the smallest azimuthal angle adopted between two successive layers in the 3-layer structure minus the additional constant interlayer rotation of $\phi_0 = \frac{2\pi d}{P}$ due to the helicoidal pitch. d is the smectic-layer spacing and P is the pitch. (b) Diffraction peaks calculated for a SmC*$_{FI1}$ biaxial 3-layer unit structure with σ polarized incident radiation. The solid lines indicate the first order π-polarized peaks, separated about the $\frac{Q_z}{Q_0} = 1\frac{1}{3}$ and $1\frac{2}{3}$ positions by a value of ϵ, where $\epsilon = \frac{d}{P}$. The dashed lines indicate the second order σ-polarized peaks, separated about the $\frac{Q_z}{Q_0} = 1\frac{1}{3}$ and $1\frac{2}{3}$ positions by a value of 2ϵ. Parameters used in this calculation were $P = 170$ layers and distortion angle $\delta = 40°$.

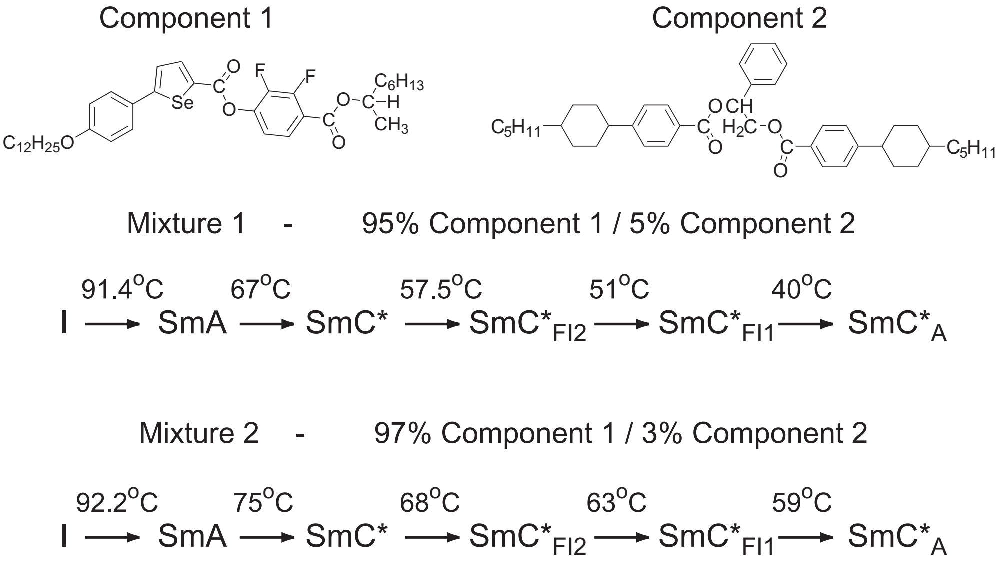


Fig. 2 – The molecular structures of the two components used to create the antiferroelectric liquid-crystal mixtures. The phase sequences of the mixtures studied in this work are shown below their percentage component concentrations (w/w). All transition temperatures are in degrees centigrade and were determined by microscopy and small-angle X-ray scattering measurements.

The resonant X-ray studies of the mixtures were carried out on beamline X14a at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratories, NY. The X-ray wavelength was tuned to the K-edge resonant energy of the selenium atom in the core of the principal components of the mixtures by measuring the fluorescence signal. Previous work has shown [4] that it is only necessary for one of the components to contain a resonant atom within its structure. For the mixtures reported here, it was found that the X-ray energy had to be within 4.5 eV of the absorption edge of the system to produce a resonant signal. In the experiment the incident X-ray energy was set to 12.6646 keV for both the 3% and 5% mixtures. Free-standing films a few microns thick were prepared by slowly dragging a small amount of material in the smectic-A phase across a rectangular hole of area $5 \times 25\,\text{mm}^2$. The film was contained within a double oven system (temperature stability 5 mK) and orientated in the beamline at grazing incidence. Windows in the oven allowed *on-line* monitoring of the film texture throughout the experiment with a polarizing microscope.

In the analysis of the experimental results, and in order to determine the physical parameters of pitch and distortion angle in the 3-layer phase, the theory of Levelut and Pansu [9] was fitted to the resonant data with a convolution to the resolution function of the experiment and employing a grid search algorithm. In the determination of the pitch and distortion angle, the resolutions in the grid were 1 nm and 1° for the pitch and distortion angle, respectively.

Results. – Figure 3 illustrates several examples of the experimental data and the corresponding best fits for the two mixtures studied. Figures 3a and b present two data sets for mixture 1 with scattering measurements centered on the reciprocal space positions $Q/Q_0 = 1\frac{1}{3}$ and $1\frac{2}{3}$, measured at temperatures of 48 °C and 42.4 °C, respectively. These data confirm the 3-layer structure of the SmC*$_{FI1}$ phase. Furthermore, the profiles of the two peaks of unequal height confirm the biaxial nature of the phase, something previously only seen in the SmC*$_{FI2}$

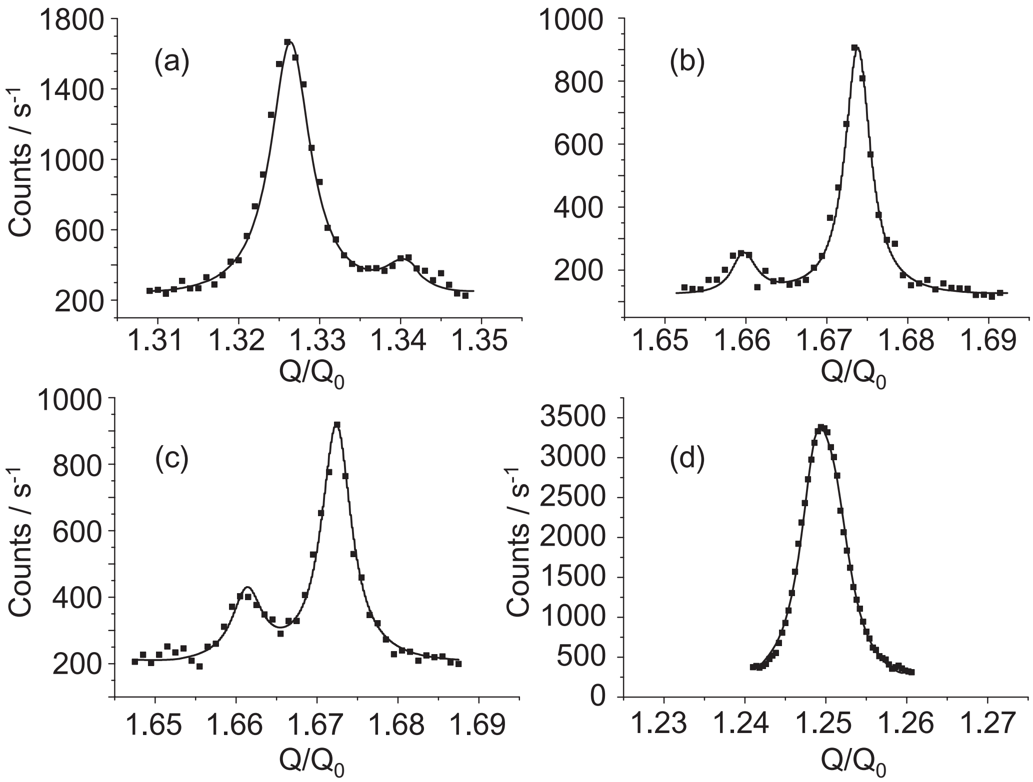


Fig. 3 – Characteristic resonant X-ray scattering data from mixture 1 (a-b) and mixture 2 (c) in the SmC*$_{FI1}$ phase and from mixture 2 (d) in the SmC*$_{FI2}$ phase. The filled squares and the solid line signify the experimental data and the best fits to the data, respectively.

phase [3]. Figure 3c shows a similar data set and best fit obtained in the SmC*$_{FI1}$ phase of mixture 2. These data were measured at a temperature of 62.2 °C. Again the *distorted* biaxial nature of this phase is evident from the unequal heights of the resonant peaks. Finally, an example of the 4-layer data from the SmC*$_{FI2}$ phase of mixture 2 is shown in fig. 3d at a temperature of 64.7 °C. Cady *et al.* [3] noted that in the SmC*$_{FI2}$ phase, the relative positions in the experimental data of the two peaks (*i.e.* whether the smaller of the two peaks is on the higher-Q or lower-Q side) described the similarity in the sense of the unit cell and the optical pitch. The same situation applies to the SmC*$_{FI1}$ phase data from these experiments. All the fits to 3-layer data show the sense of the 3-layer unit cell and the optical helix to be the same.

Surprisingly, only two resonant satellite peaks are evident in the experimental data presented in figs. 3a-c. One would initially expect to have seen both the first-order π-polarized resonant satellite peaks *and* the second-order σ-polarized peaks (those labeled a-d in fig. 1) at positions of $\pm 2\epsilon$ across the $\frac{Q_z}{Q_0} = 1\,\frac{1}{3}$ and $1\,\frac{2}{3}$ positions. However, simulations to the experimental data show that the two measured peaks are the first-order satellites, as calculations using either both the second-order peaks or a combination of first-order and second-order peaks do not at all match the experimental data. Indeed, further simulations indicate that thermal fluctuations could play a significant role in the peak heights of the first- and second-order satellites. By modeling the resonant scattering with the inclusion of a Gaussian distribution

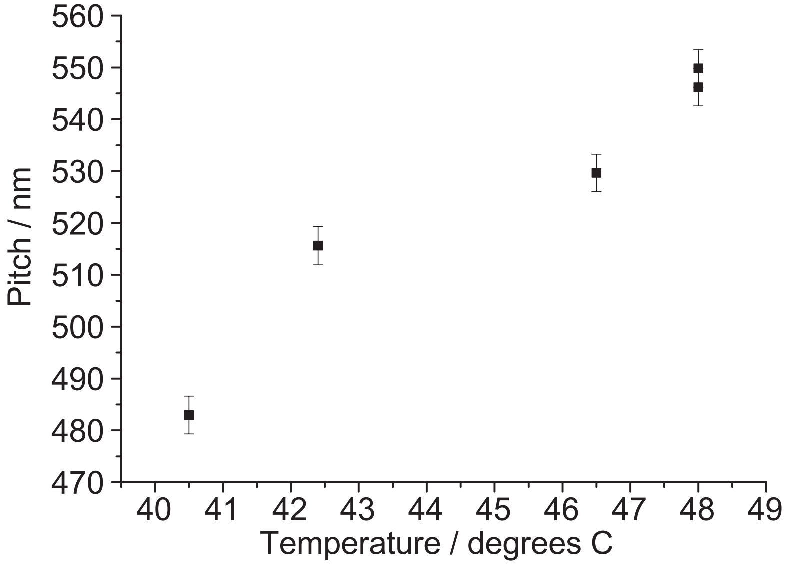


Fig. 4 – Plot showing the dependence of the optical pitch on temperature using values in the SmC*$_{FI1}$ phase of mixture 1 obtained from fitting. Repeated points indicate the reproducibility of the data from independent measurements at different times. Error bars represent the resolution in the best fit for the pitch of ±1 layer.

for the fluctuations of the director local to each layer, intensities of the second-order peaks are seen to drop 2 to 3 times more than those of the first-order peaks. Experimentally, there is no measure of these director fluctuations in this phase, however, these considerations will be addressed in greater detail in a future publication. Further experimental measurements are therefore still needed to confirm details of the resonant second-order peaks scattered from the 3-layer unit cell.

The excellent fits to the data in fig. 3 reveal several of the physical parameters of the system. In mixture 1 (figs. 3a and b), the best fits yielded the pitch, P, to be 546 nm and 516 nm, respectively, whilst the distortion angles of the structure at these two temperatures were calculated to be 55° and 56°, with the resolution in the grid search for the parameters being ±1 nm and ±1°, respectively. Employing null-transmission ellipsometry, Johnson *et al.* [11] obtained a similar value ($\delta = 56°$) for the distortion angle in the SmC*$_{FI1}$ phase of a different liquid-crystal compound. In mixture 2 (figs. 3c and d) the minimized fits to the data give values of the pitch equal to 643 nm and 2980 nm in the SmC*$_{FI1}$ and SmC*$_{FI2}$ phases with the distortion angles 39° and 14°, respectively, again with a resolution of ±1 nm and ±1°. The distortion angle in the SmC*$_{FI2}$ phase is comparable to that reported by Cady *et al.* [3].

To further investigate the temperature dependence of these parameters, a series of Q-scans from mixture 1 were taken at different temperatures. Figure 4 presents the temperature dependence of the pitch in mixture 1 across the SmC*$_{FI1}$ phase. The two repeated points at 48 °C represent repeated first and last measurements checking for and confirming negligible effects of beam damage from the X-rays during our measurements. It is worth noting that from these pitch values one would predict the occurrence selective reflection in this phase. This was confirmed during the measurements with the polarizing microscope mounted on the beamline showing the free-standing film to strongly reflect red wavelengths. The values of the measured distortion angles showed no discernable dependence on temperature, the mean value being $57 \pm 2°$. This is analogous to measurements in the SmC^*_{FI2} phase of a different compound made by Cady *et al.* [3], where the distortion angle also showed no strong dependence on temperature. The data agree well with the theoretical predictions of Emelyaneko and Osipov [12] who suggest that the distortion angle in the SmC^*_{FI2} phase should be neither temperature nor material dependent, though the values reported here and elsewhere are larger than those predicted. The distortion angle in the 3-layer phase is also predicted to be relatively insensitive to temperature [12], but possibly material dependent, again agreeing with the data presented here and elsewhere.

Conclusions. – In summary, the resonant X-ray scattering results reported here unequivocally confirm the biaxial nature of the 3-layer unit cell in the SmC^*_{FI1} phase in both the mixtures studied. The helicoidal pitch of this phase was seen to increase linearly with temperature across the phase range, while the distortion angle exhibited little dependence on temperature. The significantly enhanced phase stability of the SmC_{FI1} phase that results from the addition of a small percentage of high-chirality dopant confirms the importance of chirality in the formation of the phases intermediate between the ferroelectric SmC* and antiferroelectric SmC^*_A phases.

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