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X-RAY DIFFRACTION STUDIES OF THE SMECTIC A TO SMECTIC C* TRANSITION WITHIN A SURFACE STABILISED LIQUID CRYSTAL CELL.

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Abstract The smectic A to smectic C* transition of a commercial ferroelectric mixture (SCE13 and its racemic mixture) has been studied within a surface stabilised cell using X-ray 'rocking curve' techniques. An unusual distribution of the layer orientation in the smectic A phase implies the existence of a tilted structure. This phenomenon in the smectic A phase is believed to be a result of an unusual temperature dependence of the layer thickness and a comparison with a typical material is reported.

INTRODUCTION

Ferroelectric liquid crystals have been studied extensively since the discovery of the surface stabilised ferroelectric liquid crystal (SSFLC) effect by Clark and Lagerwall[1]. SSFLC devices offer the possibility of switching at greater speed than is currently available with the extensively used twisted nematic display cells. The technology required to manufacture large area displays is only now beginning to emerge. One of the major problems in the design of such displays is a lack of information on how to influence the detailed structure of these devices. It is necessary to know the distribution of the smectic layers within the device in order to understand the alignment and switching process.

Initially it was thought the smectic C* phase would form

a bookshelf arrangement, similar to that of the smectic A phase as illustrated in figure 1(a), when in the surface stabilised cell. However, X-ray studies[2,3] have shown a chevron geometry of the layers, illustrated in figure 1(b), frequently occurs for the smectic C* phase.

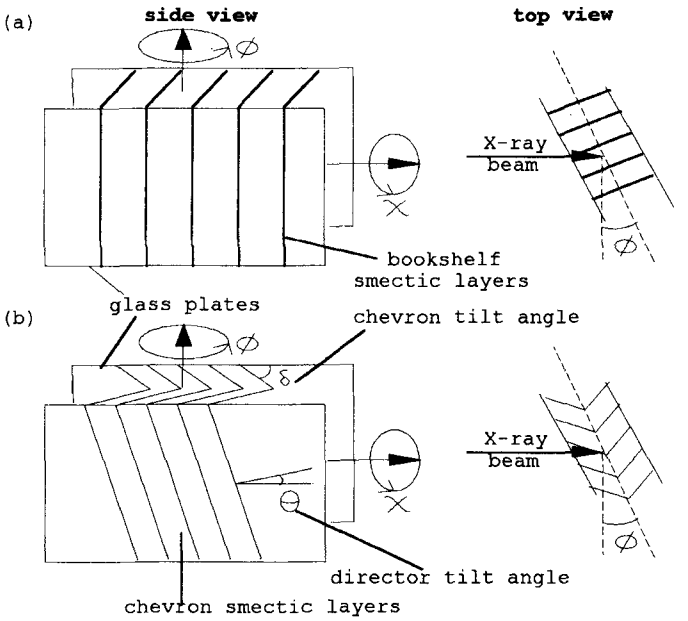


FIGURE 1 (a) The bookshelf structure of the smectic A phase, (b) The chevron structure of the smectic C phase.

Further studies[4-7] have suggested that the formation of the chevron structure was due to the layer thinning which was caused primarily by the director tilting away from the layer normal below the smectic A to C* transition.

Recent investigations[8-10] have illustrated that the chevron structure was not a peculiarity of the smectic C* phase, but may also be obtained by cooling the smectic A phase. Takanishi *et al.*[8] and Ouchi *et al.*[9] both performed studies on 4-n-butyloxy benzylidene-4n-octylaniline (4O.8) and 4-n-octyl-4'-cyanobyphenyl (8CB). Cooling from a planar

homogeneously aligned nematic into the smectic A phase a bookshelf structure was formed initially. On further decrease of temperature a chevron structure emerged where the layer tilt angle increased continuously from zero to a few degrees (7-8°) over a temperature range in the order of 10°C. Both of the liquid crystals studied gave optical textures with zigzag like defects similar to those observed for smectic C* cells with chevron layer structures.

Takanishi *et al.*[8] and Ouchi *et al.*[9] suggested that the formation of chevrons within the smectic A phase could be due to a layer thinning effect. Indeed, the temperature dependence of the layer thickness for 8CB was investigated and a thinning of the smectic layers was found on cooling the smectic A.

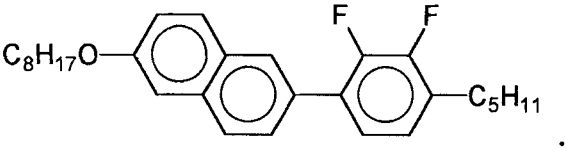
The phenomenon of the chevron formation in the smectic A phase was also found to depend on the thickness of the cell, as no chevrons were formed for cells below 9μm. Recently Limat *et al.*[10] have proposed a model suggesting a critical point exists between a bookshelf structure and the appearance of a chevron. This point was shown to be dependent on the cell thickness and layer thickness variation with temperature.

X-ray studies by Srajer *et al.*[11] indicated a chevron structure formed within the smectic A phase of ZLI3654(Merck). Unlike Takanishi *et al.*[8] and Ouchi *et al.*[9] no optical zigzag defects were observed to indicate the presence of a chevron layer geometry.

In this work we present X-ray diffraction studies performed as a function of temperature with the objective of understanding how the chevron geometry of the smectic C* phase forms from the smectic A phase. We have studied the layer orientation distribution of the commercial mixture SCE13* in a thin cell and as the bulk material in order to elucidate how this tilted structure forms in the smectic A phase.

EXPERIMENTAL

Two ferroelectric liquid crystal materials were studied: The commercially available SCE13* (available from Merck Ltd.) and the naphthalene derivative, MH236[12].



A mixture of 10% of the chiral material SCE13* with 90% of its racemate was used (10%SCE13*). The phase sequences are;

SCE13		S_C*	60.8	S_A	86.3	N	100.8	I	/°C
MH236	Cry. 59.0(36.0)	S_C*	45.0	S_A	75.0	N	83.0	I	/°C

For the X-ray rocking curve experiment the surface stabilised cells were fabricated from two cover glass plates about 110μm thick in order to reduce X-ray absorption. Both plates were coated with i.t.o. and an aligning polymer which was unidirectionally buffed. This technique promotes an alignment of the molecular director roughly parallel to the glass plates which, in turn, leads to alignment of the smectic A layers roughly perpendicular to the cell glass. The cell spacing was measured to be about 2μm with a pretilt angle of approximately 2-3°. All the rocking curve studies were collected at the Daresbury Laboratories using station 8.2 which had beam dimensions of 2mm by 0.8mm. The wavelength of radiation used was 1.5Å with an intensity approximately 100 times greater than that achieved with a sealed tube source.

The cell was placed in a purpose built heating block controlled by a Eurotherm 815 to within $\pm$0.1°C. The heating block was mounted on a computer controlled stepping motor enabling the rotation of the cell about the ϕ axis, as shown in figure 2. Positioning of the cell was obtained

using an optical telescope cross wire, thus a chosen area free from defects such as zigzags remained on the axis of rotation at all times.

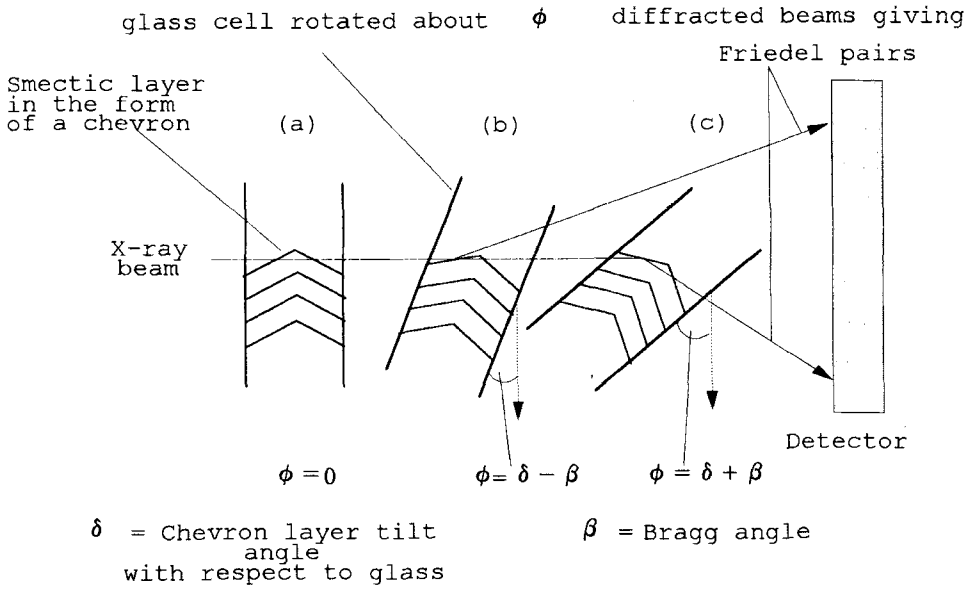


FIGURE 2 Experimental geometry used for collecting rocking curves. Three sample orientations are illustrated: (a) where there is no Bragg reflections from the smectic layers and (b) and (c) which show the Bragg reflections from either side of the smectic layers in one arm of the chevron. The reflected beams fall either side of the main X-ray beam and are known as a Friedel pair.

The absolute zero of the sample angle, that is when the cell is perpendicular to the X-ray beam direction, was calculated using the X-ray intensity monitors of the incident and transmitted beams. The transmission of the sample was at a maximum when the glass plates were perpendicular to the beam direction. A precision of $\pm 0.01°$ was obtained by fitting a theoretical line shape to the transmission verses sample angle data.

The intensity of the Bragg reflection from the layers was monitored as a function of the sample angle, ϕ, with respect to the incident beam by a two dimensional position sensitive detector. This results in a Friedel pair of reflections which are from Bragg reflections from either side of the same smectic layer as the sample is rotated, as shown in figure 2. For each sample angle, ϕ, the intensity of the Bragg reflections either side of the detector was determined by summing over the peaks and subtracting a flat background. The plots of Bragg intensity against ϕ are known as 'rocking curves' and correspond to the distribution of the layer normals shifted by $\pm\beta$, the Bragg angle. The cell was rotated about the ϕ axis from -30° to 30° in 0.25° steps and the rocking curves were obtained at regular intervals of temperature on cooling. The sample was initially heated to the nematic phase then cooled to the first rocking curve temperature in the smectic A phase.

Bulk sample studies were also conducted using samples placed in a 1mm Lindemann capillary. The samples were heated to the isotropic phase in a purpose built oven and then cooled in the presence of a magnetic field, approximately 0.25T, through the various phases. The temperature was controlled using a Eurotherm 815 controller to within ±0.1°C. The X-ray diffraction patterns were recorded at Bristol University at several different temperatures using a two dimensional position sensitive detector[13]. Graphite monochromated CuK_α radiation of wavelength 1.54Å from a 1.5kW sealed tube was used. Layer spacings, d, were determined from plots of the scattered intensity as a function of the scattering vector, $\mathbf{Q}$, for the layer reflections.

RESULTS AND DISCUSSION

Figure 3 illustrates the rocking curves obtained whilst

cooling the 10%SCE13* sample through the smectic A to C* transition. For clarity only one of each Friedel pair has been plotted.

The figure shows a split peak centred at $\phi = \beta(\sim 1.6°)$ within the smectic A phase. In the smectic C* phase a further two peaks emerge, the positions of which change to larger values of phi with decreasing temperature.
The two peaks within the smectic A phase are a direct indication of a tilted structure contrary to the widely accepted uniform bookshelf model, illustrated in figure 1(a). The peaks observed for the smectic A phase do not change continuously into the more widely split pairs from the chevron geometry in the smectic C* phase.

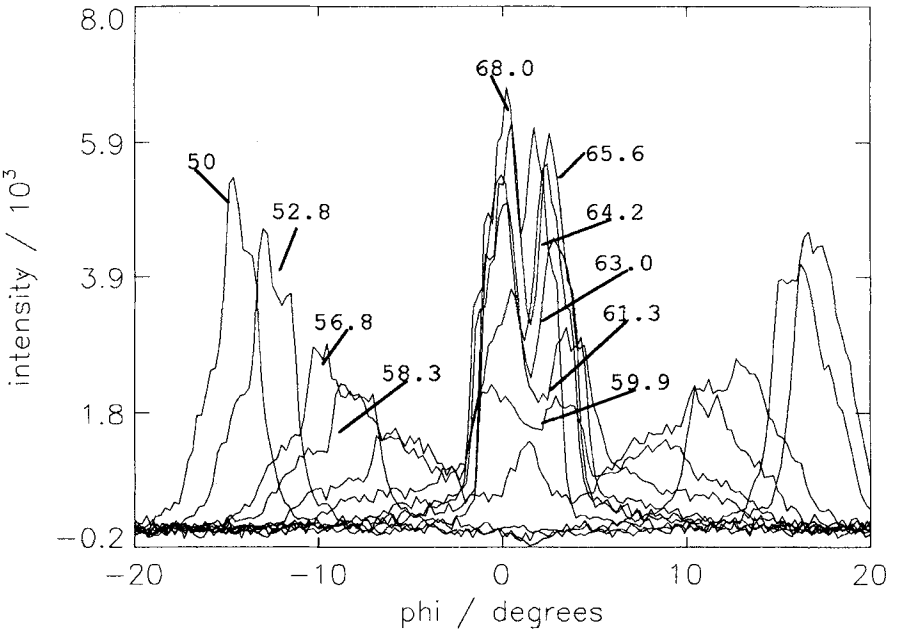


FIGURE 3 Rocking curves of 10%SCE13* whilst cooling through the smectic A to C* transition, all figures quoted in °C.

At the transition, 59.9°C, there are four peaks in the rocking curve as shown more clearly in figure 4. There are two pairs of peaks, each centred at $\phi=\beta$. One pair is split

by $\pm 1.9°$ about β and arises from the layer distribution in the smectic A phase and the other two, split by $\pm 7.18°$, arise from the chevron structure in the smectic C* phase. This clearly shows the two peaks split by $\pm 1.9°$ in the smectic A phase are not derived from the same chevron structure as in the smectic C* phase.

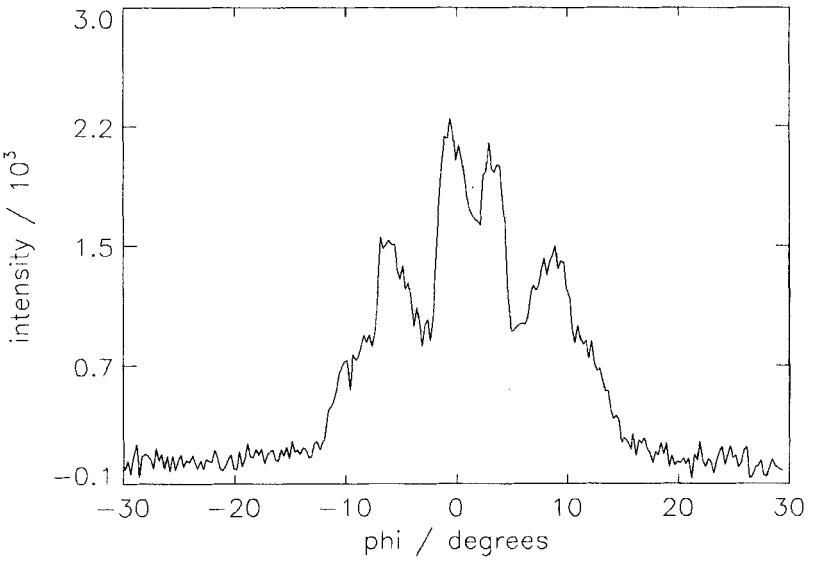


FIGURE 4 The rocking curve of 10%SCE13* at 59.9°C

Figure 5 illustrates the layer tilt angle, δ, as a function of temperature. The layer tilt angle was calculated from the Friedel pair peak position. This would be at $\delta+\beta$ and $\delta-\beta$, as shown in figure 2. Within the smectic A phase δ increases slightly over the temperature range to a value of 2°. At the transition the tilt angle jumps to 7.18° then continues to increase with decreasing temperature. Figure 5 clearly shows the coexistence of the tilted structure in the smectic A phase and the chevron within the smectic C* phase at the transition. The smectic A to C* phase transition in the bulk material is believed to be second order. This is strongly supported by the fact that the smectic layer

spacing changes continuously at the A to C* transition. It seems that the transition in this cell has become slightly first order.

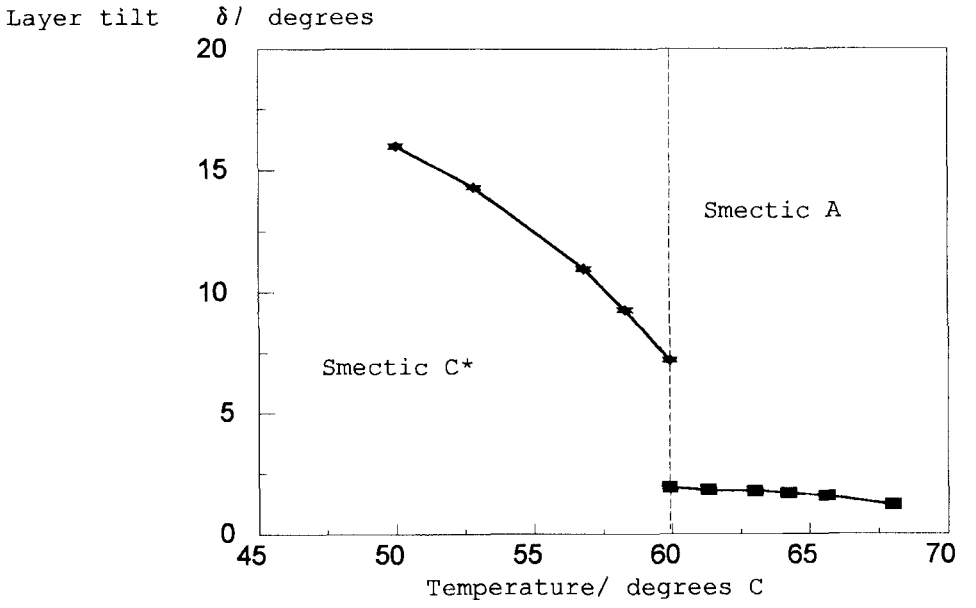


FIGURE 5 Layer tilt angle, δ, as calculated from the rocking curves for 10%SCE13* against temperature.

Figure 6 shows that the total integrated intensity of the rocking curve. In the smectic A phase, the intensity decreases as the transition is approached. This is indicative of some loss of order. This may be a reduction of the smectic order within the layers or alternatively a breaking up and reformation of layers as the layer distribution changes.

The tilt within the smectic A phase is generally associated with thinning of the layer spacing. We therefore measured the smectic layer spacing in bulk samples of SCE13*. Figure 7 illustrates the layer spacing variation with temperature for a SCE13* mixture. As shown the smectic A phase layer spacing slightly decreases with decreasing temperature, the rate of change, that is d(d)/dt, is 0.015±0.002Å/°C.

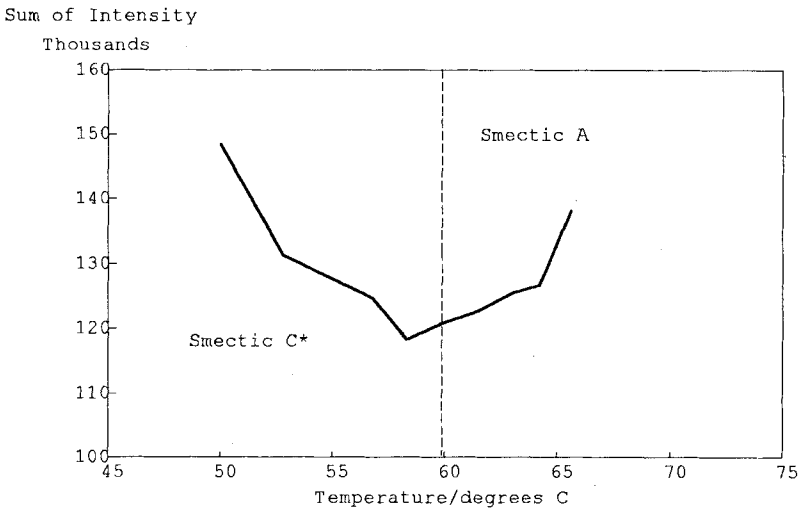


FIGURE 6 The integrated intensity of the whole rocking curve as a function of temperature.

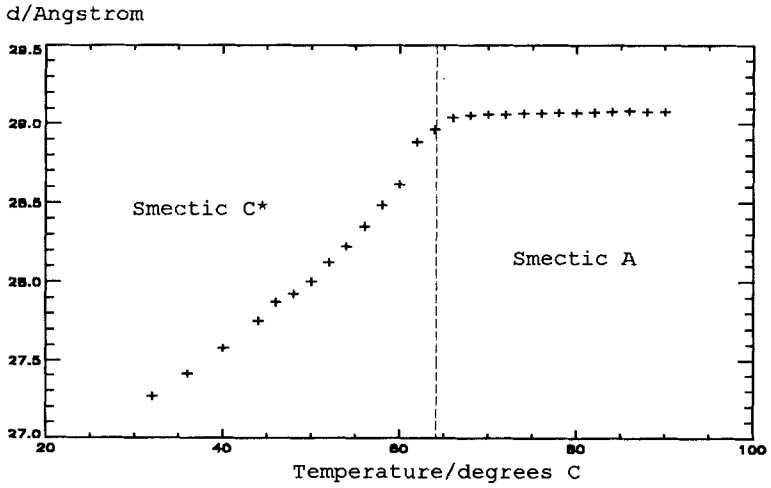


FIGURE 7 The layer spacing variation with temperature for the SCE13* mixture as a bulk sample.

This is an unusual result for the smectic A phase which normally increase layer spacing with decreasing

temperature[14]. The predicted tilt angle for the smectic A phase has been calculated as a function of temperature and is illustrated in figure 8. This calculation uses the following equation

$$\cos\delta_A = d_A/d$$

where δ_A and d_A are the tilt angle and layer spacing within the smectic A phase respectively, and d is the value of the layer spacing at the onset of the phase, 29.1Å. The tilt angle for the smectic A phase increases to a value of 10.5° at the transition. This angle is much larger than the one derived from the rocking curves. This suggests that the thinning of the layers is accommodated in some other way. One possibility would be a movement of the surface molecules to allow the thinned layers to fill space.

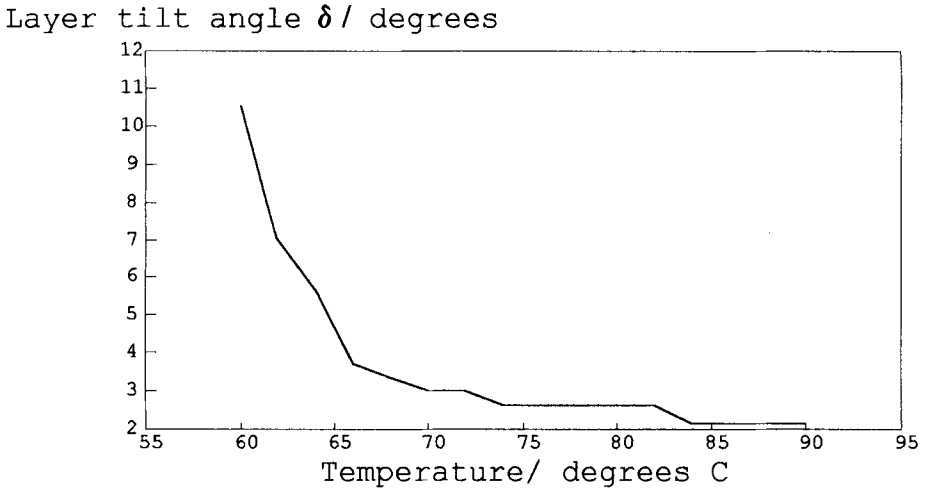


FIGURE 8 Predicted layer tilt angle within the smectic A phase for 10%SCE13*.

It seems likely that the layer tilting in the smectic A phase of 10%SCE13* is a consequence of the unusual thinning of the layers on cooling. To test this hypothesis further, a

similar control study was made using the same methods on a material with the usual temperature dependence of the layer spacing, MH236. Figure 9 shows the layer spacing variation with temperature for MH236 and as shown the layer spacing within the smectic A phase does slightly increases with decrease of temperature. The rate of change for this increase is -0.014 ± 0.013Å/°C. The relative precision for the layer spacing is worse than for 10%SCE13* because the experiment was carried out with a different sample to detector distance. Despite this, however, the resultant rate of change for MH236 is clearly qualitatively different to that of 10%SCE13* in that the layer spacing increases with decreasing temperature.

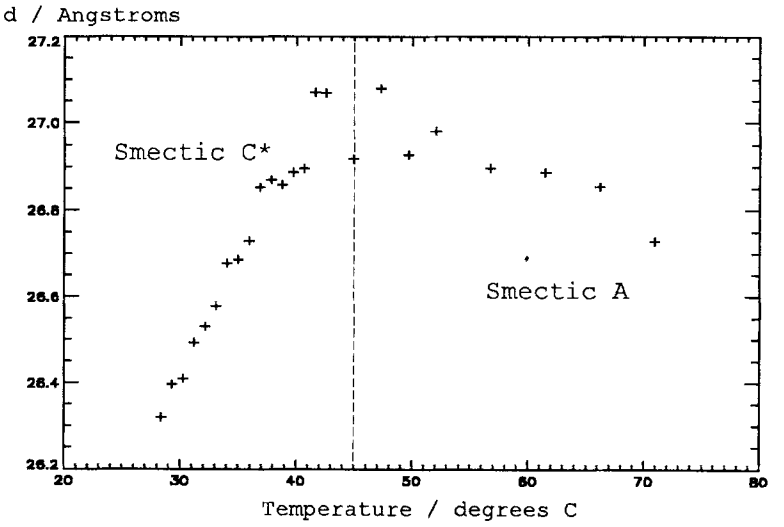


FIGURE 9 The layer spacing variation with temperature for MH236.

The rocking curves of MH236 are shown in figure 10. There is only a single peak throughout the smectic A range indicating the usual bookshelf geometry exists. On cooling into the smectic C* phase this peak splits into two and continues to change in both position and intensity on

further decrease in temperature. The calculated layer tilt angle, δ, from the rocking curve study is shown in figure 11 as a function of temperature.

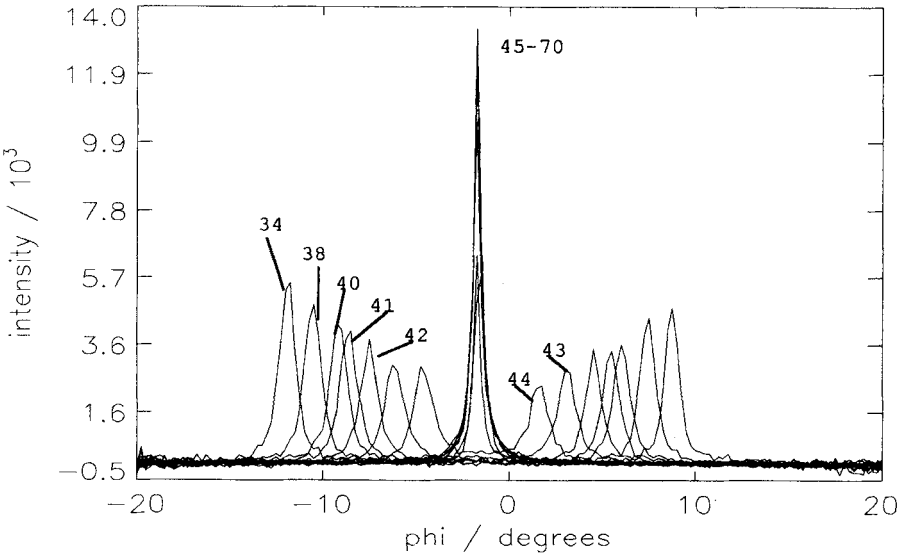


FIGURE 10 Rocking curve studies of MH236 whilst decreasing in temperature through the smectic A to C* transition. All temperatures quoted in °C.

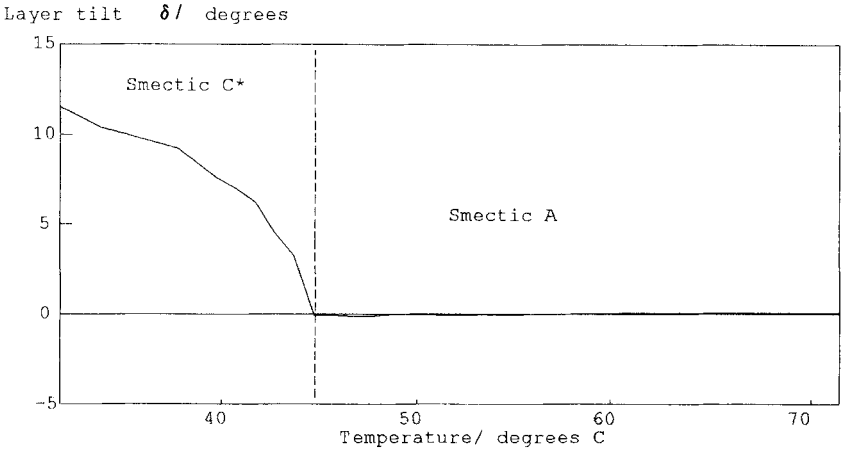


FIGURE 11 Layer tilt angle, δ, calculated from the rocking curves for MH236 against temperature.

This clearly illustrates the usual temperature dependence of the layer tilt angle, in contrast to that of 10%SCE13* shown in figure 5, for both the smectic A and C* phases.
Figure 12 illustrates the integrated intensity of the rocking curve plotted against temperature for the MH236 sample. The intensity in the smectic A phase changes very little on approaching the transition. This also contrasts with the behaviour for 10%SCE13* which is shown in figure 6.

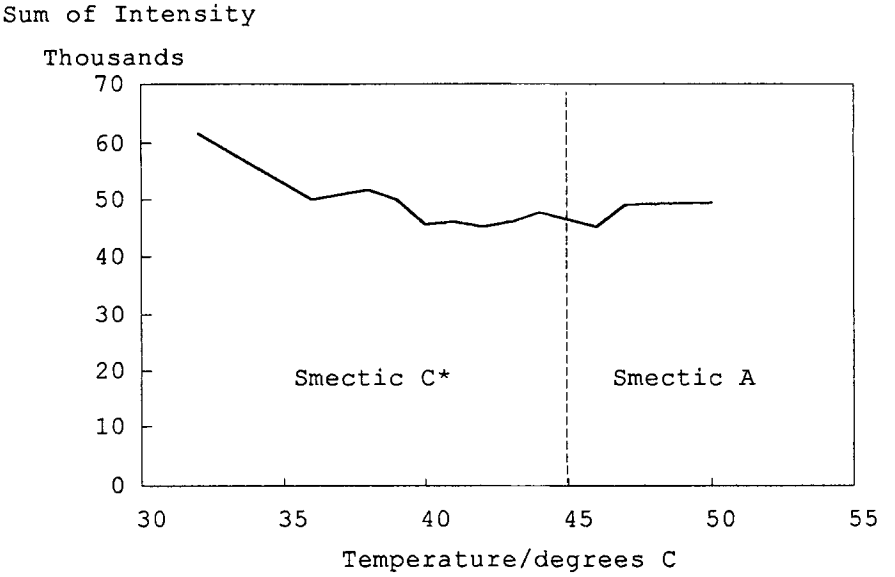


FIGURE 12 The integral intensity against temperature for MH236.

The results of the MH236 study clearly support the idea that the layer thinning within the smectic A phase is responsible for the unusual tilted structure observed within the surface stabilised cells.

CONCLUSION

We have studied the smectic A to C* phase transition of both 10%SCE13* and MH236 within a surface stabilised cell environment. The 10%SCE13* mixture showed an unusual

distribution of layers within the smectic A phase indicating a tilted structure. This phenomenon was not observed for the MH236 sample cell. The layer thinning within the smectic A phase is believed to be the cause of the formation of the tilted structure. It is possible that in the smectic A phase the layers form a tilted bookshelf structure (with 50% tilted each way) or a chevron with a much smaller tilt than in the smectic C* chevron. Further experiments on different materials and different cell thicknesses are required to clarify this point.

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