

Observation of a chevron hybrid structure in the smectic A phase of a liquid crystal device

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Small angle X-ray diffraction experiments show the emergence of a chevron structure on cooling from the nematic phase into the smectic A phase of the commercial mixture S3 (Merck Ltd, UK), in a display device. The chevron angle increases from 0° at the nematic-smectic transition temperature, T_{NS} , to a maximum value of 8.5° , which is reached when the sample is 15°C below T_{NS} . Between 5°C and 15°C below the transition temperature a quasi-bookshelf structure emerges, in addition to the prevailing chevron structure; such a structure has not been hitherto reported. There is no further resolvable change in the device structure on cooling lower than $T_{NS} - 15^\circ\text{C}$. The chevron structure is due to the combination of layer thinning and fixed surface layers, as confirmed by a comparison of layer spacing calculated from the Bragg angle equation and from the layer thinning equation ($d = d_{\text{nematic}} \cos \delta$, where δ is the chevron angle).

1. Introduction

X-ray diffraction has been used extensively to show the arrangement of smectic layers in liquid crystal display devices. The chevron structure adopted by the layers within ferroelectric liquid crystal (FLC) devices was first elucidated by X-ray measurements [1], and there has since been an abundance of research into FLC device configurations. The chevron structure forms in these systems as a consequence of layer thinning due to an increasing tilt cone angle on cooling [2]. Besides studies of the unperturbed FLC structure there have also been X-ray studies of the static layer arrangement after high electric field application [3, 4] and time-resolved observations of the layer behaviour during low electric field director reorientation [5]. There has been relatively little research however into the structure of the smectic A phase device. The most obvious reason for this is the lack of commercial interest in these systems. Another reason is that in the absence of director tilt variation there is no clear mechanism for chevron formation; smectic A devices have thus often been assumed to have bookshelf geometry.

Recent investigations have illustrated that the chevron structure is not a peculiarity of the smectic C phase but may also appear on cooling into the smectic A phase from a homogeneously aligned nematic phase. In fact a chevron structure was first observed in the smectic A phase as long ago as 1980 by Stamatoff

et al. [6], even before it had been reported in the smectic C phase. However the authors focused on an analysis of order parameters, the smectic A phase X-ray rocking curve being presented only in a discussion of experimental resolution. Although the chevron structure is evident from the rocking curve, the authors did not comment on it. More recently, Takanishi *et al.* [7] and Ouchi *et al.* [8] experimented with the materials 4-*n*-butyloxybenzylidene-4-*n*-octylaniline (40-8) and 4-*n*-octyl-4'-cyanobiphenyl (8CB). A bookshelf layer structure formed at the nematic to smectic A transition temperature, in a $25\text{ }\mu\text{m}$ cell. This changed to a symmetrical chevron structure on further cooling, the layer tilt angle increasing continuously from 0° to $\sim 7.5^\circ$ over a 10°C temperature range. In addition to the chevron structure, a quasi-bookshelf arrangement was shown to coexist, although it became less and less sharp on cooling, eventually disappearing. The quasi-bookshelf structure did not reappear on heating. It was proposed that the chevron structure formed due to layer thinning, a proposition which was supported by measurements of layer spacing in the case of 8CB [7, 8].

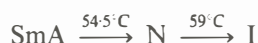
Chevron formation in the smectic A phase was also shown to depend on the cell thickness [8], no chevrons being observed at thicknesses less than $9\text{ }\mu\text{m}$ in cells filled with 40-8 and 8CB. A model for the cell thickness and temperature behaviour has been proposed by Limat and Prost [9] and confirmed by Kralj and Slukin [10]. Other reports of chevron structures in the smectic A phase have been made by Srajer *et al.* [11], who

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observed a 6.5° layer tilt at 9°C below the nematic to smectic A transition temperature in $5\text{--}20\text{ }\mu\text{m}$ cells filled with ZLI3654 (Merck Ltd, UK), and by Taylor *et al.* [12], who observed a layer tilt increasing to $\sim 2^\circ$ at 25°C below the nematic to smectic A transition temperature, in a $2\text{ }\mu\text{m}$ cell. Neither Taylor *et al.* nor Srajer *et al.* reported the presence of coexisting bookshelf and chevron structures. In this work we present X-ray diffraction studies of the layer arrangement in a device filled with the low molar mass mixture S3 (Merck Ltd, UK), performed as a function of temperature.

2. Experimental

The devices were constructed using $50\text{ }\mu\text{m}$ thick spacers and $100\text{ }\mu\text{m}$ thick glass, and filled with S3, which possesses the following phase sequence:



The liquid crystal was aligned homogeneously by anti-parallel rubbing of the substrates with a 1% w/w solution of polyvinyl alcohol in water and slow cooling (1° min^{-1}) through the high temperature nematic phase and the smectic A phase. The X-ray experiments were carried out at the Synchrotron Radiation Source, Daresbury, UK [13]. The apparatus used is similar to that described previously [14] and the experimental arrangement is shown schematically in figure 1(a). The device is held in a heating stage (Linkam THMS 600) with a stability of $\pm 0.1^\circ\text{C}$. The stage has been modified for X-ray diffraction work and is operated by a Linkam TMS91 temperature control unit. A $1 \times 1\text{ mm}^2$ beam is incident on the sample. The device is rotated about the z -axis, a procedure known as 'rocking'. Peaks in the rocking curve occur when the layers are oriented to the Bragg condition [figure 1(b)]. The precision in angular measurement of the cell orientation is 0.072° , although for logistical reasons the rocking angle step size was 1° in the experiment described here. The sample was cooled from the nematic-smectic A transition temperature, T_{NS} , to

$T_{\text{NS}} - 5^\circ\text{C}$, in intervals of 1°C . The sample was cooled further from $T_{\text{NS}} - 5^\circ\text{C}$ to $T_{\text{NS}} - 25^\circ\text{C}$ in intervals of 5°C . A rocking curve was determined at each temperature, using only one of the Friedel pair spots on the detector. The use of an area detector allowed measurement of the Bragg angle at each temperature.

3. Results and discussion

Figure 2 shows the rocking curves obtained at each reduced temperature. The reader should note the change in temperature step below $T_{\text{NS}} - 5^\circ\text{C}$. The intensity has been normalized to account for changes in apparent substrate thickness with angle, and background counts have been removed. The integrated diffraction intensity is the total intensity within the area of an imaginary box around the Bragg spot. The box dimensions are chosen such that the Bragg spot is always 'captured', but are kept as small as possible so that the signal to noise ratio is optimized. The error in the peak heights comes from the intrinsic counting error in the raw count (equal to the square root of the number of counts in a given time). The propagated relative error accordingly varies from 0.2% for the strongest peak, to 1% for the weakest diffraction. The curves drawn in figure 2 are simply interpolations between data points. The curves and the shaded areas beneath them are intended as a guide to the eye; the small number of data points rendered meaningful curve fits impossible.

The chevron peak heights show a general increase on cooling, due to the increase in the smectic order parameter, which defines the layer sharpness. There are also small changes from one temperature to the next, and quite marked differences from one arm of the chevron to the other. The reason for this is that the integrated diffraction spot intensity (the peak height) is very sensitive to rocking angle and the (large) 1° rocking steps are insufficient to resolve the fine structure. It is not possible, for example, to rule out the presence of an asymmetric chevron structure.

The conventional bookshelf structure begins to emerge

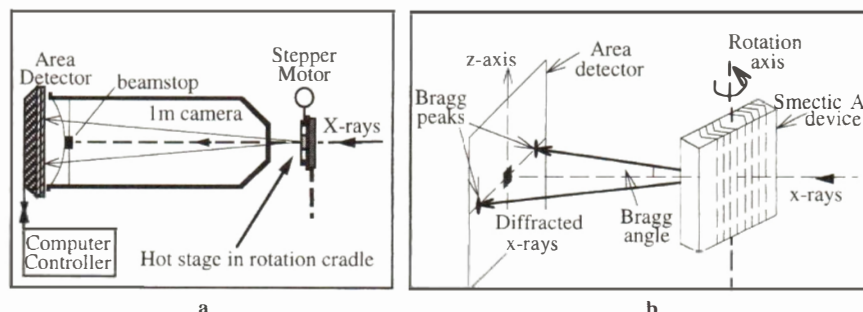


Figure 1. (a) The experimental set-up; (b) the experimental geometry. The device rotates about the z -direction to give Bragg diffraction off the chevron structure.

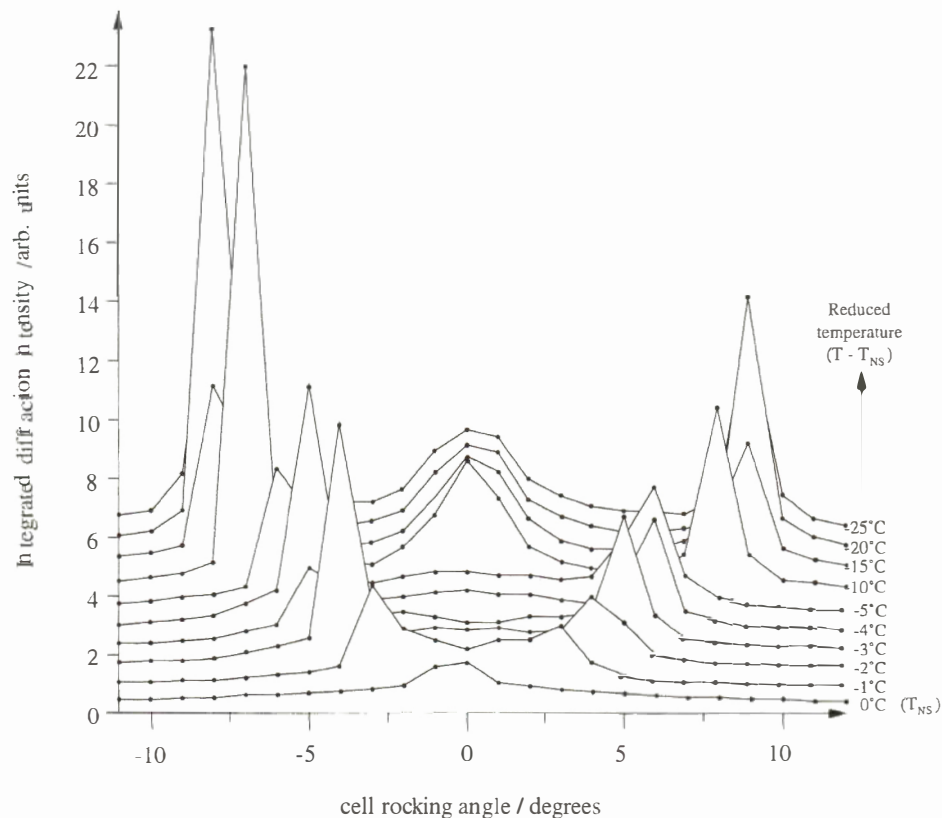


Figure 2. Normalized X-ray rocking curves as a function of reduced temperature ($T - T_{NS}$), for the smectic A cell. Lines connecting data points are included solely as a visual aid and do not represent a fit of any kind.

at the point of transition from the nematic phase to the smectic A phase (reduced temperature 0°C). On cooling, the rocking curve peak splits into two clearly resolvable peaks, indicating the formation of a chevron structure. The presence of a chevron structure was confirmed by observation of tell-tale parabolic defects using a polarizing microscope. These defects form in order to overcome the strain caused by increased director splay at the chevron apex [7]. The splay energy is much larger in smectic A chevron structures than in ferroelectric structures, because the molecules in smectic A cells cannot tilt as they approach the chevron apex. The rocking curve peaks move apart on further cooling, as the chevron angle increases. A central, broad peak emerges at some stage between the reduced temperatures $T_{NS} - 5^\circ\text{C}$ and $T_{NS} - 10^\circ\text{C}$. This central peak coexists with the chevron peaks, indicating the formation of a chevron/bookshelf hybrid structure. The hybrid structure forms when the chevron angle is between 6° and 7.5° . The experiment does not distinguish between a cell with separate chevron and bookshelf areas and a cell with layers that are chevron near the cell edges and bookshelf in the cell centre. In the case of the latter, the large energy associated with layer space changes would necessitate layer breaking. Indeed the quasi-bookshelf struc-

ture may be due to the layer arrangement within the parabolic defects themselves. Further evidence for this hypothesis is provided by an analysis of the Bragg spot structure at the 0° cell orientation. The area detector allowed us to monitor qualitative layer distortions in the plane of the cell, without the need for rocking about a second axis. The Bragg spot was seen to spread on cooling, indicating some bending of layers in the plane of the device, as would also be expected from the appearance of parabolic focal conic defects. As the sample is cooled between the reduced temperatures $T_{NS} - 10^\circ\text{C}$ and $T_{NS} - 15^\circ\text{C}$, the proportion of the sample adopting the quasi-bookshelf structure appears to increase, since the relative intensity of the central broad peak (with respect to the chevron peaks) increases. In addition the chevron angle increases to $\sim 8.5^\circ$. No structural changes were seen on further cooling, i.e. the chevron angle remained constant at $\sim 8.5^\circ$. It is interesting to note that the emergence of a quasi-bookshelf structure on cooling is contrary to the observations of Takanishi *et al.* and Ouchi *et al.*, who, as previously mentioned, reported the presence of a quasi-bookshelf structure which disappeared slowly on cooling.

The next step was to confirm that the reason for smectic A chevron formation was the reduction in layer

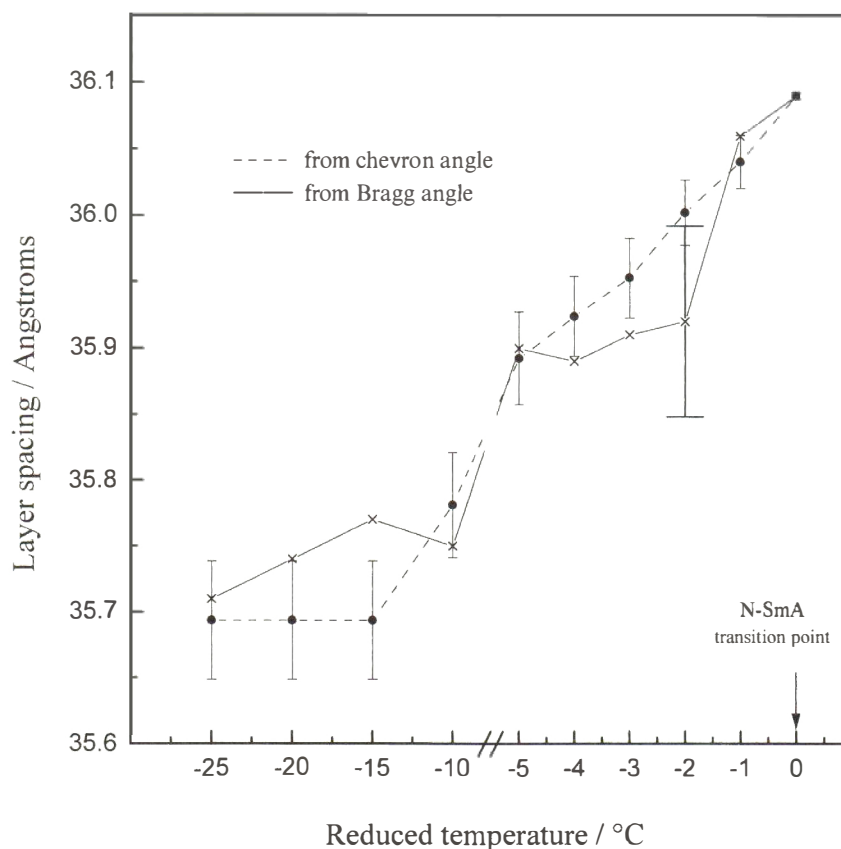


Figure 3. Comparison of chevron equation-derived and Bragg equation-derived layer spacings; the error bars indicate the relative errors. To make the graph more readable the error bar has been plotted for only one of the 'Bragg angle' data points, since this error did not change significantly with temperature. Lines connecting data points are included solely as a visual aid and do not represent a fit of any kind.

thickness. Although driven by changes in conformational length, as opposed to tilt angle changes, the chevrons are ultimately expected to form in the same manner as those routinely observed in ferroelectric cells. This hypothesis was tested using the layer thinning equation: $d(T) = d(S-N) \cos \delta(T)$ [11], where $d(T)$ is the layer thickness below the S_A-N transition temperature, $d(S-N)$ is the layer thickness at the transition temperature, and $\delta(T)$ is the chevron angle. The layer spacings were calculated from the chevron angle at each temperature, using the layer thinning equation and compared with the true layer spacing measurements obtained from the Bragg equation. The chevron equation-based layer spacings are shown in figure 3 alongside those based on the Bragg equation.

At the transition temperature, the spacings are the same by definition. The spacings at temperatures below the transition temperature are self-consistent within experimental error, indicating that layer thinning is likely to be the mechanism for chevron formation in the smectic A phase of S3. This is in contrast to the

observations of Taylor *et al.* [12], where layer thinning is only partially accommodated by chevron formation, the movement of surface layers being postulated as the additional mechanism. The difference in results may be due to a combination of different cell thickness, different elastic constants (S3 versus SCE13) and different pre-tilt ($1/2^\circ$ in our case, $2-3^\circ$ in theirs). Furthermore, in the experiment reported herein, it seems that the emergence of a central parabolic defect structure allows the chevron angle to increase further than it would otherwise be able to do and it can thus compensate for the layer spacing decrease below $T_{NS} - 5^\circ\text{C}$. On cooling below $T_{NS} - 15^\circ\text{C}$, the data seem to indicate that the chevron angle remains constant, although the experimental resolution is not sufficient to make an unequivocal statement or to make a comparison with the Bragg angle.

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