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In situ observation of smectic layer reorientation during the switching of a ferroelectric liquid crystal

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A thin plastic cell containing the ferroelectric liquid crystal ZLI3654 (4 μm) was placed edge-on to a pin-hole collimated horizontal X-ray beam. In this way, the smectic layers were brought into register. Subsequently, triangular voltage waves with various peak (V_p) values were applied across the cell and diffraction photos were obtained during the application of the alternating voltage. Up to $V_p = \pm 30$ V, no significant movements in the initial tilted orientation of the smectic layers with respect to the surfaces (chevrons) could be observed. During the application of $V_p = \pm 32$ V an increasing fraction of the smectic layers changed their initial tilt angle with respect to the cell surfaces to make larger tilt angles. At a slightly higher voltage, the layers became upright (bookshelf structure). Upon removing the voltage and short circuiting the cell, the quasi-bookshelf structure was sustained. The new method described here can be used in combination with a fast detector for time resolved experiments.

In the ferroelectric liquid crystal (FLC) phase the director is oriented at an angle θ with respect to the smectic layers. In the bulk, the director rotates about a helix with the axis perpendicular to the smectic layers. In surface stabilized ferroelectric liquid crystal (SSFLC) [1] cells, the helix is suppressed in very thin cells. For this purpose FLC materials showing the nematic—smectic A—ferroelectric phase sequence are frequently used. In the chiral nematic phase, the pitch is suppressed in thin cells (few μm thick) where the thickness is much less than the pitch of the helix. Upon cooling the sample into the smectic A phase, smectic layers oriented perpendicular to the director are formed. When the system is further cooled into the ferroelectric phase, the smectic layers become tilted with respect to the cell surfaces (so called chevrons [2] form). This occurs as the smectic layers become thinner due to the tilted orientation of the molecules with respect to the layers. The orientation of the FLC molecules and the chevron structure have been carefully studied using X-ray diffraction and optical means, since they are very important in determining the quality of the optical devices produced. Using X-ray diffraction, the origin of various defects and the effect of the pre-tilt angle of the molecules have been investigated. It was also shown that changes in the chevron orientation occurred with increasing temperature and under various electric fields [3, 4]. Optical measurements [5] indicated that at high electric fields, irreversible changes in chevron structure occur. Using static electric fields and X-ray diffraction [6–8], these changes could be observed directly. However, other processes can take place during the application of alternating electric fields. For example, frequency dependent dielectric torque and movement of ions can result in a different behaviour from that obtained under static fields. For example, low frequency high fields in order to induce the bookshelf structure [5] and high frequency fields during passive addressing are used in order to stabilize the molecular orientation (a.c. stabilization) [9]. Furthermore the crystal rotation method used in previous work meant that dynamic changes in the smectic layer orientation could not be observed simultaneously during the application of electric fields. Here we describe a new method which can enable the *in situ* observation of the changes occurring in the smectic layers during the application of alternating electric fields. In this short report, time-average measurements made during the switching are also described.

In the experiments, the commercially available FLC mixture ZLI3654 was used. The transition temperatures of ZLI3654 as determined by optical microscopy are

$$\mathrm{Cr} - 30^\circ\mathrm{C}\ \mathrm{S}_\mathrm{C}^*\ 62^\circ\mathrm{C}\ \mathrm{S}_\mathrm{A}\ 76^\circ\mathrm{C}\ \mathrm{N}\ 86^\circ\mathrm{C}\ \mathrm{I}$$

In order to form a 5 mm long 2 mm wide cell, polyester films provided with transparent electrodes were used as substrates. The ITO surfaces were covered by nylon orientation layers which were subsequently uniaxially rubbed. Spacers of 4 μm were used to form a cell where the rubbing directions of the surfaces were antiparallel. The cell was glued together only at two ends as shown in figure 1 (*a*). The FLC was introduced into the cells in the isotropic phase. Subsequently the system was cooled down slowly to room temperature through the nematic and smectic A phases into the ferroelectric phase.

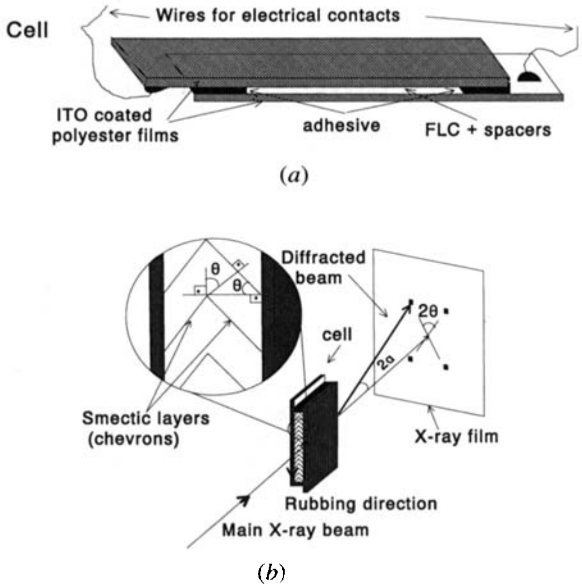

Figure 1. (*a*) The construction of the cell. (*b*) Schematic representation of the geometry used in the X-ray measurements.

For the X-ray diffraction measurements, a Statton camera and pin-hole collimated Ni filtered CuK$_\alpha$ radiation were used. The pin-holes of the camera were 0·325 mm in diameter and 17 cm apart. Using this set-up, an X-ray beam with a diameter of about 0·25 mm and a divergence of about $\pm 0{\cdot}1°$ was obtained. The cell was placed on a sample holder which was directly attached to the pin-hole collimator. In this way the rubbing direction was chosen to be perpendicular to the horizontal X-ray beam and the surfaces of the cells parallel to the X-ray beam. The set-up used in the measurements is schematically shown in figure 1 (*b*). The polyester substrates used in the cells are quite transparent to X-rays, showing no diffraction in the small angle region; therefore diffraction from the ferroelectric layers could be easily registered on the X-ray film. Electrical contacts with the electrodes were made using thin copper wires. An alternating voltage could be applied across the cell using a Philips PM5167 function generator. In the experiments, a sample-to-film distance of 19 cm was used. Using a shutter, the film was exposed to X-rays for 30 min. After each set of experiments (first exposure during the application of the electric field and the second after removing the electric field and short circuiting the cell), before increasing the voltage, the cell which was attached to the pin-hole collimator was taken out of the camera and heated in an oven above the clearing temperature. It was then slowly cooled down to room temperature, restoring the initial chevron orientation, before it was put back into the camera. This procedure ensured that the alignment of the cell with respect to the X-ray beam stayed the same in all experiments.

In the geometry described in figure 1 the Bragg condition

$$2d\sin(\alpha) = n\lambda \qquad (1)$$

was satisfied and any change in the orientation (change in θ in figure 1) during the application of the electric field could be registered by the X-rays. Triangular wave voltages with various peak values (V_p) were applied across the cell at 0·1 Hz. In figure 2 examples of diffraction patterns obtained during the application of various voltages are shown. In figure 3 optical density scans of the diffraction peaks of such photographs are plotted. The X and Y axes in this figure correspond to the horizontal and vertical directions in figure 2, respectively. Here it is important to point out that the intensities of the peaks are not the same. In the photographs, the diffraction spots on the left side are significantly weaker. This effect is probably caused by the cell not being exactly perpendicular to the X-ray beam and making a slight angle with respect to the beam normal. Further in the text we shall mainly consider these strong diffraction peaks as the changes observed during the experiments are most evident in these peaks. At $V = 0$, the peaks correspond to θ about $\pm 21°$ and d was calculated to be 2·76 nm.

When the varying voltage is applied across the cell up to $V_p = \pm 30$ V, there is almost no change in the position of the diffraction peaks, although they become slightly broader compared with the virgin sample. This indicates only a slight movement in the orientation of the smectic layers. However, there is no significant change in θ as suggested in some other work [3]. At $V_p \pm 32$ V, it can be seen that the peaks become broadened and cover the angles $5° < \theta \leqslant 21°$, indicating substantial reorientation in the smectic layers. This reorientation occurs mainly by tilting of the layers to smaller angles θ from their tilt angles of $\theta = 21°$. Here it is interesting to note that the major movement in the layer orientation has a very sharp threshold. In the photograph obtained after removing the voltage and short circuiting the cell, it can be seen that the peaks remain broadened and the intensity of diffraction in the broadened regions increases at the cost of decreased intensity of the initial diffraction peaks at $\theta = \pm 21°$. The experiments performed here register the events taking place during the exposure time (30 min). By short circuiting, the cell voltage is reduced to 0 and the chevrons were not expected to make any movement to become upright. Therefore the exposures made after short circuiting represent the layer orientation obtained at the end of the application of voltage. The fact that the in the second exposure made after removing the voltage and short circuiting, the cell shows a broader peak indicates that during the application of $V_p = \pm 32$ V an increasingly larger fraction of the smectic layers becomes reoriented to make smaller angles θ. At a slightly higher field of

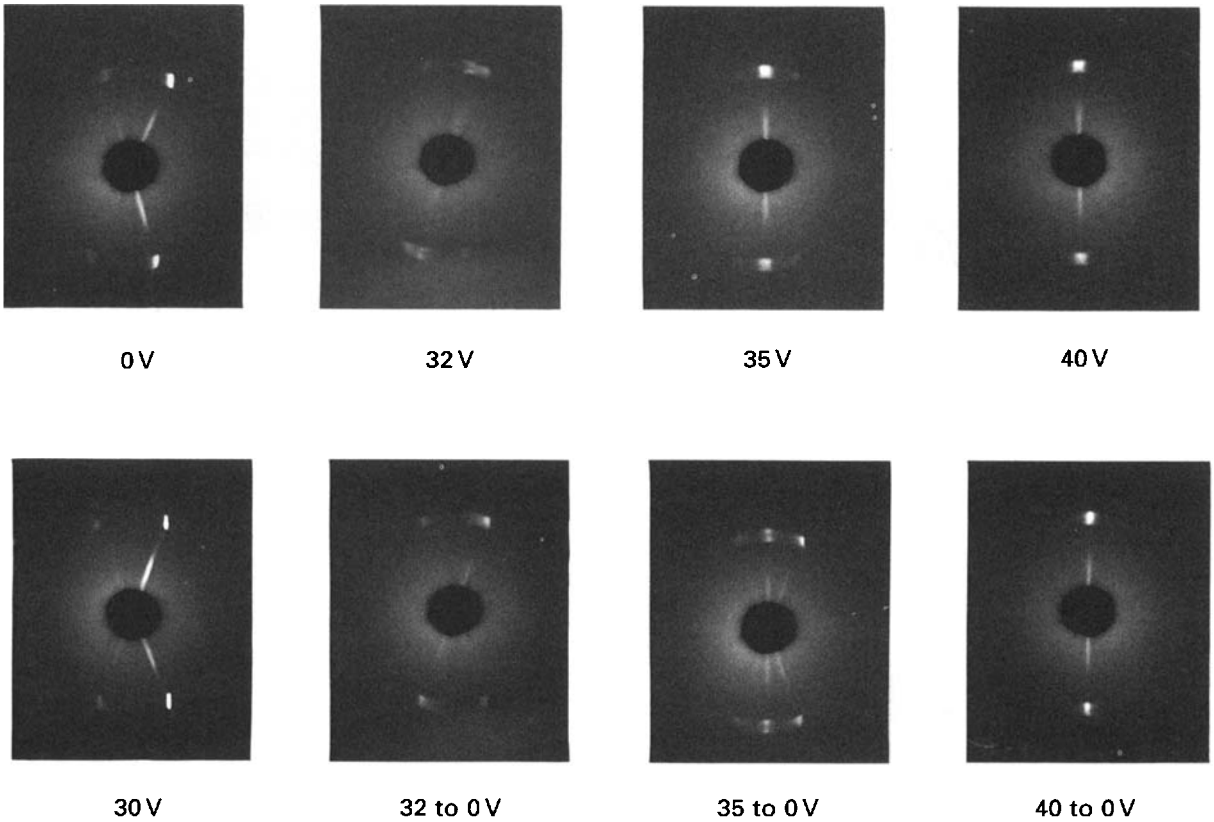

Figure 2. X-ray diffraction photographs obtained during the application of triangular voltages with various peak (V_p) values and also after removing the voltage and short circuiting the cell (V_p to 0 V).

$V_p = \pm 35$ V, three very well-defined diffraction peaks corresponding to θ values of 0° and ± 21° superimposed on a low level, broad background arc are present. The existence of these discrete peaks indicates that during switching, the smectic layers mainly have these states of orientation. The low intensity of the background arc indicates that the intermediate states of $0° < \theta < 21°$ are short term. Upon removing the electric field and short circuiting the cell, the picture obtained is very similar to that obtained during the application of $V_p = \pm 35$ V. The main difference between these pictures lies in the relative intensities of the peaks corresponding to $\theta = 0°$ and $\theta = 21°$. The intensity of the central peak ($\theta = 0°$) obtained upon removing the voltage is much higher than that of the side peaks. Here again, during the first exposure, events taking place during the application of the electric field are recorded. In the second exposure which was made after short circuiting, the structure which developed at the end of the application of the field is recorded. The fact that the intensity of the peak at $\theta = 21°$, after short circuiting, is much lower than that observed during the application of the field indicates that continuously during the application of $V_p = \pm 35$ V an increasing population of the layers became upright. However, this does not rule out the possibility that in the experiment, during the application of the voltage, the smectic layers may also have been switching between the two states or that they all suddenly became upright, for example, half way through the exposure. During the application of higher alternating fields ($V_p = \pm 40$ V), from the presence of the dominant peak at $\theta = 0°$, it is clear that the layers become totally upright from their initially tilted ($\theta = 21°$) orientation and that no more layer movement is present. When the electric field is removed, it can be seen that the central peak becomes slightly broader, indicating that the layers relax to a slightly tilted state from $\theta = 0°$ (quasi-bookshelf structure).

Before discussing the X-ray results any further, it is appropriate to consider some optical observations. In the measurements, the sample cell was placed between crossed polarizers with the rubbing direction parallel to one of the polarizers. The same voltages were applied across the cell as those used in the X-ray measurements. In figure 4 transmission voltage curves obtained during the application of alternating fields with various peak values are shown. In these figures, we plotted only the changes occurring within the ± 10 V region where most changes occur. In all these figures, it can be seen that the

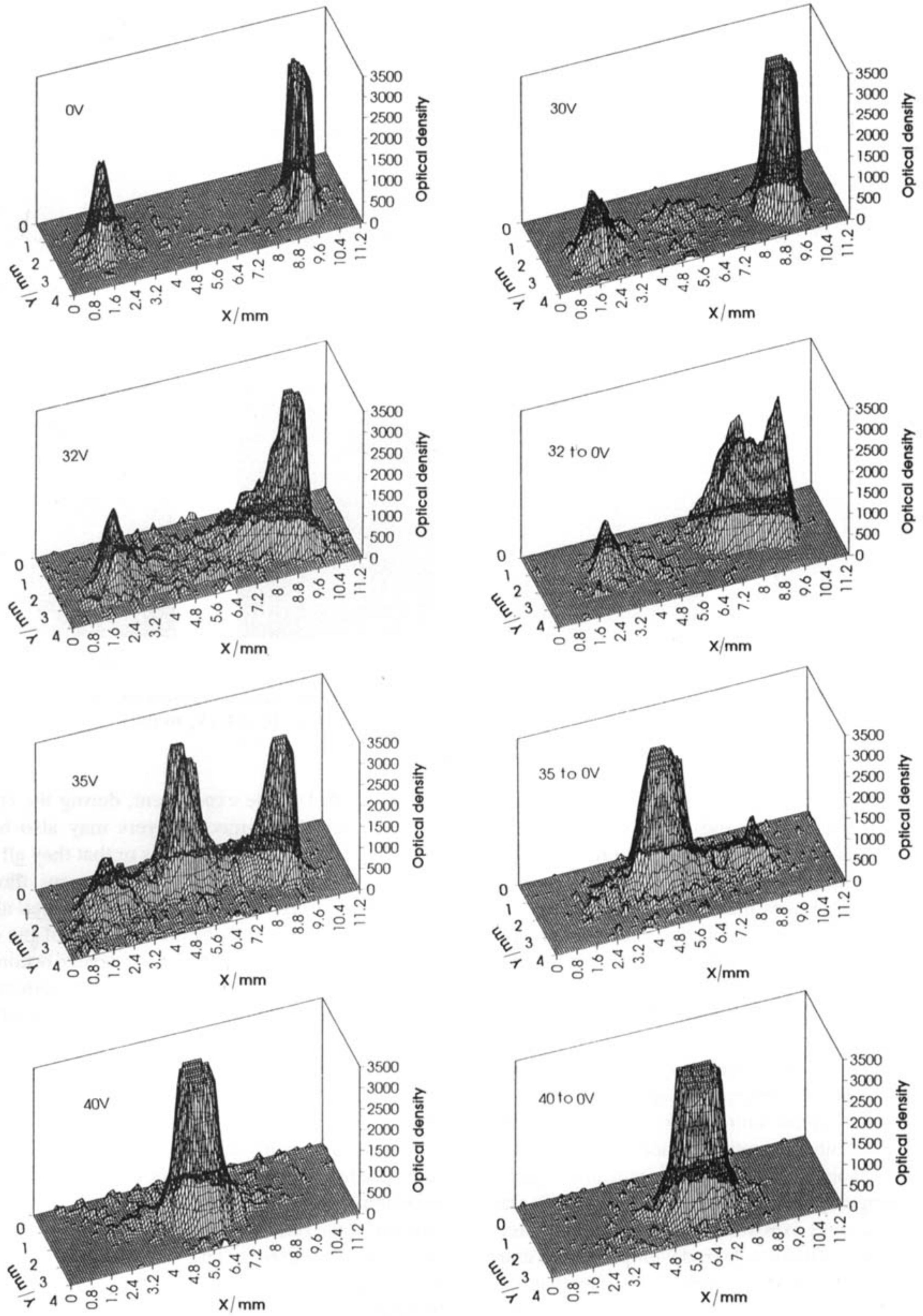

Figure 3. Optical density traces corresponding to the top diffraction spots of the photographs in figure 2, where the *X* and *Y* axes correspond to horizontal and vertical directions, respectively.

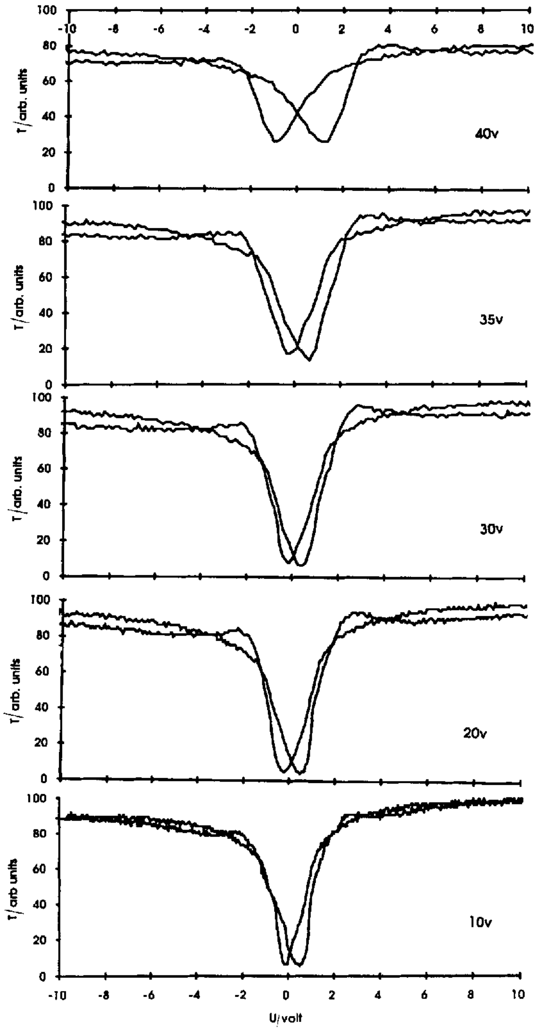

Figure 4. Transmission voltage traces obtained during the application of various fields.

saturation level in the intensity is obtained at relatively small voltages, showing the high degree of director movement during the experiments. When various intensity plots are compared, it can be seen that up to $V_p = \pm 30$ V only slight changes occur. Any significant further deviation from rest is only to be seen at $V_p = \pm 40$ V. These measurements are also in good agreement with the optical observations where up to $V_p = \pm 30$ V, even though changes in the texture occur, irreversible changes only take place above $V_p = \pm 35$ V. At $V_p = \pm 40$ V, a new texture was formed. The optical observations described above are also in a good agreement with earlier reports on the same material [10].

The optical observations described here conform well with the X-ray measurements where at around the same V_p, changes in the layer orientation are observed. In order to explain the way in which the smectic layer movement takes place, we would like to consider two possibilities as shown schematically in figure 5. In case (*a*), gradual bending of the layers as suggested by Hartmann *et al.* [10], is represented. Such a behaviour would give rise to diffraction in a broad range covering the angular region $0° < \theta < 21°$, with a maximum at $\theta = 0$, as the middle part of the chevron would be flat. The fact that in the photographs obtained during the application of $V_p = \pm 32$ V and subsequent removal of the electric field, broad diffraction peaks covering the angular range $5° < \theta < 21°$ are to be seen indicates that the layers tilt towards smaller θ values during the application of the electric field. The absence of diffraction intensity in the centre at $\theta = 0°$ indicates that the layers do not become bent as shown in figure 5 (*a*). In figure 5 (*b*), we represent continuous change in θ with increasing voltage. In experiments such as those performed here, events are recorded over time. Therefore smectic layer movements represented in (*b*) in figure 5, occurring as a result of varying the voltage as a function of time, when recorded over time can give rise to a broadened diffraction peak without a diffraction intensity at $\theta = 0°$ (when the applied voltage is lower than V_4 as indicated in figure 5(*b*)). Furthermore, the fact that after the removal of the electric field, the intensity of the broadened regions increases indicates that the reoriented layers keep their orientation upon removal of the electric field. This can also be seen in the case of $V_p = \pm 35$ V. The three well-defined diffraction peaks corresponding to θ values of 0° and ± 21° and present during the application of the electric field, reduce to almost a single peak at $\theta = 0°$ after removing the field and short circuiting the cell. These results also indicate that up to a certain voltage, the layers remain tilted. Above the threshold voltage, the layers change their tilt angle as they tend to become upright. During the switching, an increasing fraction of the layers becomes upright. The very low level background scattering corresponding to $0 < \theta < 21°$ during the application of

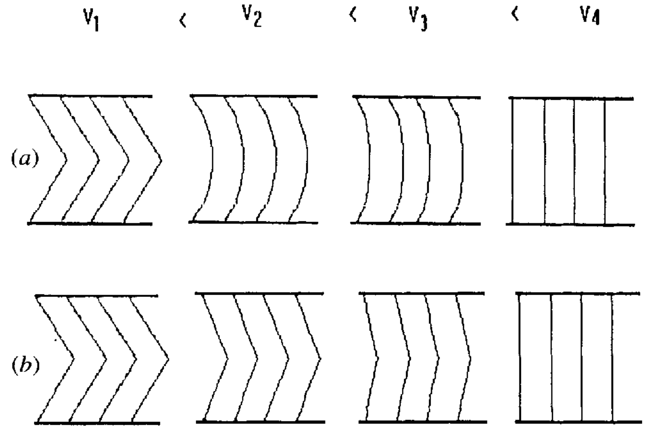

Figure 5. Schematic representation of various possible smectic layer orientations obtained with increasing voltages.

$V_p = \pm 35$ and ± 40 V indicates that the transition from the chevron to the bookshelf structure occurs through short term intermediate states.

Here it is shown that the new method can be used to observe *in situ* changes occurring in the smectic layer orientation during the application of an electric field across a FLC. In the present study, it was shown that layer reorientation starts at a well defined threshold. During the application of voltages with a peak value higher than the threshold, tilting of the smectic layers towards smaller angles occurs. During the application of the voltage, *increasingly more layers* became reoriented. Upon removing the electric field and short circuiting the cell, the reoriented state remains and the layers do not revert to their initial state. Increasing the peak voltage further causes the layers to become quite upright and form a stable bookshelf structure. In the present study events were recorded on X-ray films. Combined with an electronic detector and a stronger source, this method can be used to make time-resolved experiments.

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