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Electric-field-induced layer reorientation in ferroelectric liquid crystals: An x-ray study

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We use x-ray diffraction on aligned samples of the smectic-A and -C^* phases to confirm the existence of a chevron-layer structure even within the smectic-A phase. Furthermore, we demonstrate that an ac electric field can be used to eliminate the chevron structure and produce uniform orientation of the smectic-C^* layers perpendicular to the glass plates. The results of the x-ray study are in agreement with earlier optical observations. The practical implication of the chevron removal is the significant enhancement of the optical contrast of the cell.

Since the discovery of the ferroelectric smectic-C^* (Sm-C^*) liquid-crystal phase,[1] a lot of effort has been devoted to utilizing this phase for high-resolution large-area display devices. The Sm-C^* phase is a layered phase in which the long-molecular axis, the "director," is tilted by an angle θ from the layer normal where θ is typically 25°. In addition, on passing from layer to layer the tilt direction rotates through a small angle about the layer normal, thus forming a macroscopic helical structure. In most display devices, the liquid crystal is contained in what is referred to as a surface-stabilized ferroelectric liquid-crystal (SSFLC) cell.[2] The glass surfaces of these cells are treated with a rubbed polymer coating to promote parallel alignment of the molecules. Moreover, the cell thickness is less than the pitch of the Sm-C^* helix suppressing its formation and, hence, yielding a spontaneous polarization perpendicular to the molecular director and parallel to the layer planes.

When a homogeneously aligned smectic-A (Sm-A) sample is cooled into the Sm-C^* phase in a SSFLC cell, the molecules remain aligned along the rub direction, while the smectic layers rotate away from the cell normal by an angle of magnitude β_0, forming a characteristic chevron-layer structure[3] (Fig. 1). There are two possible chevron orientations with the boundaries between these orientations optically characterized by the appearance of zigzag defect walls.[4]

Although the surface treatment promotes unidirectional orientation of the molecules through the entire thickness of the cell (for example, along $\hat{\mathbf{n}}_-$ in Fig. 1), the direction of the spontaneous polarization, being parallel to the layer planes, changes direction when the chevron midpoint is crossed. Nonetheless, there is a net "up" polarization for one state ($\hat{\mathbf{n}}_+$) and "down" polarization for the other ($\hat{\mathbf{n}}_-$) so that an external electric field can switch molecules between these states (for details see Ref. 4). As the molecules are switched between states $\hat{\mathbf{n}}_-$ and $\hat{\mathbf{n}}_+$, the projection of the molecular tilt angle onto the plane parallel to the cell surface is changed by $2\theta'$ (Fig. 1). We refer to θ' as the *apparent* optical tilt angle. Since θ' and the molecular tilt angle θ are related via $\cos\theta' = \cos\theta/\cos\beta_0$, the presence of the ubiquitous chevron structure reduces the *apparent* optical tilt angle and, hence, cell contrast. Previous investigations[5] showed that an ac electric field partially removed the chevrons; however, the first electric-field treatment which claimed successful elimination of the entire chevron structure was reported by Patel, Lee, and Goodby[6] (PLG).

In this paper, we present x-ray diffraction studies on well-oriented Sm-C^* samples which were electric-field treated as described by PLG. We show that the field treatment irreversibly removes the chevrons. Furthermore, to illustrate that x-ray measurements are necessary to unambiguously determine the layer arrangement, we present x-ray measurements on our sample in the Sm-A phase which clearly indicated the presence of chevrons, although, optically, the sample appeared chevron free. Finally, since the electric-field treatment introduced an asymmetry in the electro-optical switching behavior, we propose a simple method to recover symmetric switching behavior.

In order to transmit x rays, the sample cells were fabri-

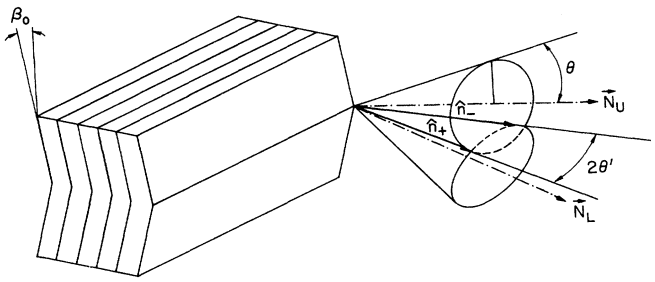

FIG. 1. Director geometry at a chevron interface in the SSFLC cell. An external switching field couples to the spontaneous polarization and causes the director to reorient on a cone defined by an axis which is the local layer normal $\mathbf{N}_U$ (or $\mathbf{N}_L$) and a molecular tilt angle θ. In the SSFLC cell, the director lies in the plane parallel to the glass plates. The external field switches the director between $\hat{\mathbf{n}}_+$ and $\hat{\mathbf{n}}_-$. The angle between these two states is $2\theta'$, which is twice the value of the *apparent* optical tilt angle θ'. Subscripts U and L refer, respectively, to quantities in the upper or lower part of the chevron. β_0 is the layer tilt angle.

cated from thin (~ 150 μm), flat pieces of glass with evaporated (~ 50 Å) transparent chrome-gold electrodes. To obtain an aligned sample, the internal surfaces were polymer coated and unidirectionally buffed.[7] This procedure promotes an alignment of the molecular director parallel to the glass plates which, in turn, means that the Sm-A layers are oriented perpendicular to the boundaries. Several sample cells with thicknesses from 5 to 20 μm were assembled. Excellent alignment was achieved in all samples. The liquid-crystal compound studied was the commercially available ferroelectric-smectic mixture ZLI-3654 (Merck) with the following phase sequence:

$$\text{crystalline} \overset{20\,^\circ\text{C}}{\leftrightarrow} \text{Sm-}C^* \overset{62\,^\circ\text{C}}{\leftrightarrow} \text{Sm-}A \overset{76\,^\circ\text{C}}{\leftrightarrow} \text{cholesteric} \overset{86\,^\circ\text{C}}{\leftrightarrow} \text{isotropic}.$$

The experiment was performed utilizing Cu $K\alpha$ radiation from an 18-kW rotating anode x-ray generator. A vertically bent pyrolytic graphite (002) crystal focused the x rays to a 0.5×2-mm^2 spot on the sample and the scattered radiation was analyzed by slits. The resultant instrumental resolution was 0.2° full width at half maximum in the scan direction and 2° transverse to the scattering plane. The sample cell was placed in a two-stage oven which provided $\pm$ 10-mK temperature stability and optical access. The alignment procedure involved, first, heating the sample to the high-temperature end of the Sm-A range, $T=72\,^\circ$C, where the layers are known to be aligned perpendicularly to the glass plates. Then, the magnitude of the momentum-transfer vector $\mathbf{Q}_s$ was set to a fixed value $|\mathbf{Q}_s|=2\pi/d(T)$, where $d(T)$ is the smectic-layer spacing at temperature T. Subsequently, the sample was rotated about the y axis (β scan in Fig. 2) and about the x axis (χ scan in Fig. 2) to maximize the scattered intensity. We defined the resultant values of χ and β as their zero values. At this orientation, $\mathbf{Q}_s$ was perpendicular to the layer planes (along the z direction in Fig. 2) and, hence, coincident with the first layer-diffraction peak. In Figs. 3(a) and 3(b), χ and β scans through this peak are shown. With the sample so oriented, β scans then probe deviations of the layer planes from being oriented perpendicular to the glass plates and χ scans probe deviations of the layer planes from the normal to the rub direction $\hat{\mathbf{z}}$. As the sample was cooled towards the Sm-C^* phase, a β-scan was done at $T=67\,^\circ$C [Fig. 3(c)] which is 5 °C above the transition temperature. Two symmetrically displaced peaks of comparable intensity [Fig. 3(c)] indicated the presence of a symmetrical split of the layers away from their perpendicular orientation. This is the signature of a chevron structure. Thus, the chevron-layer structure in ZLI-3654 appeared while the sample was still in the Sm-A phase. The difference between our observations of this effect and those previously reported[8] is that in our sample zigzag defects were not observed optically. The texture, as seen by a polarizing microscope, consisted of parabolic focal-conic lines which are usually taken as the optical signature of smectic layers aligned perpendicularly to the boundaries. Thus, it is apparent from our x-ray measurements that such optical observations can lead to erroneous conclusions concerning the layer orientation.

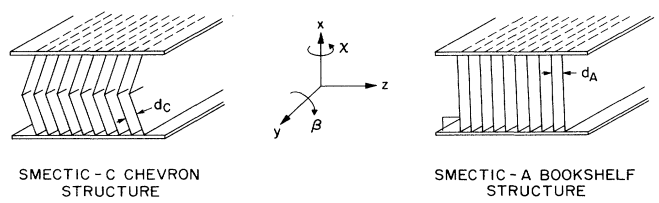

FIG. 2. Schematic illustration of the experimental geometry and of the chevron-layer structure in the Sm-C^* phase (left panel) and the bookshelf layer structure (right panel) in the Sm-A phase. The axes (middle panel) define the x-ray angular scan directions.

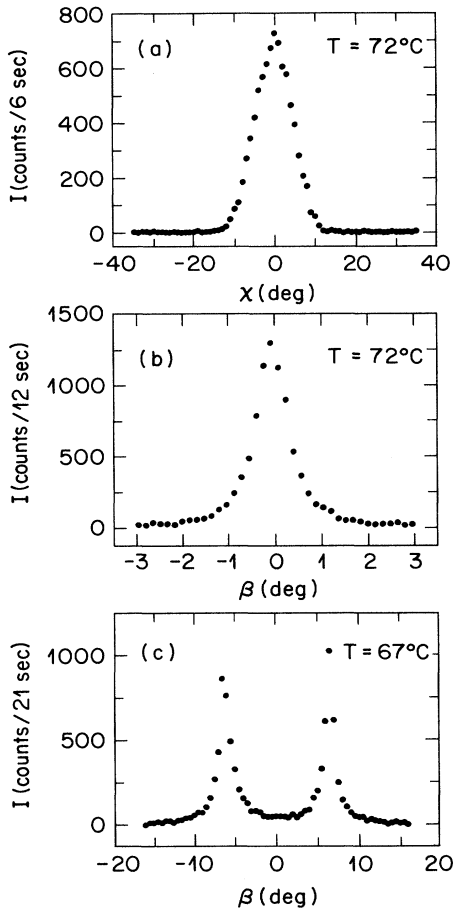

FIG. 3. Scattered intensity I as a function of angle. (a) $T=72\,^\circ$C. At this temperature the sample is in the Sm-A phase. The smectic layers are well aligned, clearly indicated by a single domain in the χ scan. (b) $T=72\,^\circ$C. The smectic layers are oriented normal to the glass plates, as shown by a single, sharp peak centered around $\beta=0$. (c) $T=67\,^\circ$C. Two peaks in the β scan, symmetrical with respect to $\beta=0$, signify the presence of the chevron structure while the sample is still in the Sm-A phase. This temperature is 5 °C above the transition to the Sm-C^* phase.

The sample was then cooled into the Sm-C^* phase. Within the Sm-C^* phase, at $T=23.4\,^\circ$C, a χ scan and a β scan were taken [Figs. 4(a) and 4(b), respectively]. The χ scan was peaked at $\chi=0$, which indicates that the projection of the layer normal onto the plane of the glass plates is parallel to the rub direction. The β scan exhibited two peaks at $\beta=\pm 20^\circ \equiv \pm\beta_0$ which, as previously discussed, is indicative of a chevron structure.

Next, an electric field of 100 V and frequency of 1 kHz was applied for over 2 h. The optimum frequency was comparable to τ^{-1}, where τ is the molecular switching time between states $\hat{\mathbf{n}}_+$ and $\hat{\mathbf{n}}_-$ (Fig. 1). After the electric-field treatment, the single peak in the χ scan split into two symmetrically displaced peaks [Fig. 4(c)]. These peaks, at $\chi=\pm 19^\circ \equiv \pm\chi_0$, indicate that the smectic layers formed two domains in which the layer normals are now $\pm 19^\circ$ with respect to the rub direction. From the sharpness of the peak, we estimate that the spread in the layer alignment is of the order of 3°. When both scans were repeated one month later on the same sample, it was clear that the electric-field-induced layer rearrangement did not deteriorate with time, since the position and widths of the peaks remained unchanged. We were able to obtain larger values of χ_0 ($\chi_0=22^\circ$) after prolonged treatment, but the sample was somewhat damaged in the process due to dielectric breakdown. The layer-reorientation angle of $22\pm 3^\circ$ is comparable with the molecular tilt angle of 25°, as suggested by PLG. Furthermore, a β scan in either of the domains showed a single, sharp peak centered around zero [Fig. 4(d)], hence unambiguously confirming that the layers were aligned normal to the glass plates.

The temperature dependence of the layer-reorientation angle χ_0 [inset, Fig. 4(d)] was also measured. We found that in the electric-field-treated sample χ_0 decreased as the temperature was increased and reached a finite value of $\chi_0=10^\circ$ in the Sm-A phase. β scans at each χ_0 had, similar to Fig. 4(d), a sharp peak at $\beta=0$. The sample was then gradually, in 5 °C steps, cooled from 70 °C to room temperature and both scans were repeated at each step. While χ_0 remained constant at 10° through the entire temperature range, β scans showed that, not surprisingly, the chevron structure reemerged. The chevron tilt angle varied from $\beta_0=3^\circ$ at $T=65$°C, to $\beta_0=20^\circ$ at $T=23.4\,^\circ$C. Thus upon cooling, a novel layer structure was observed: chevrons rotated around the x axis by 10°

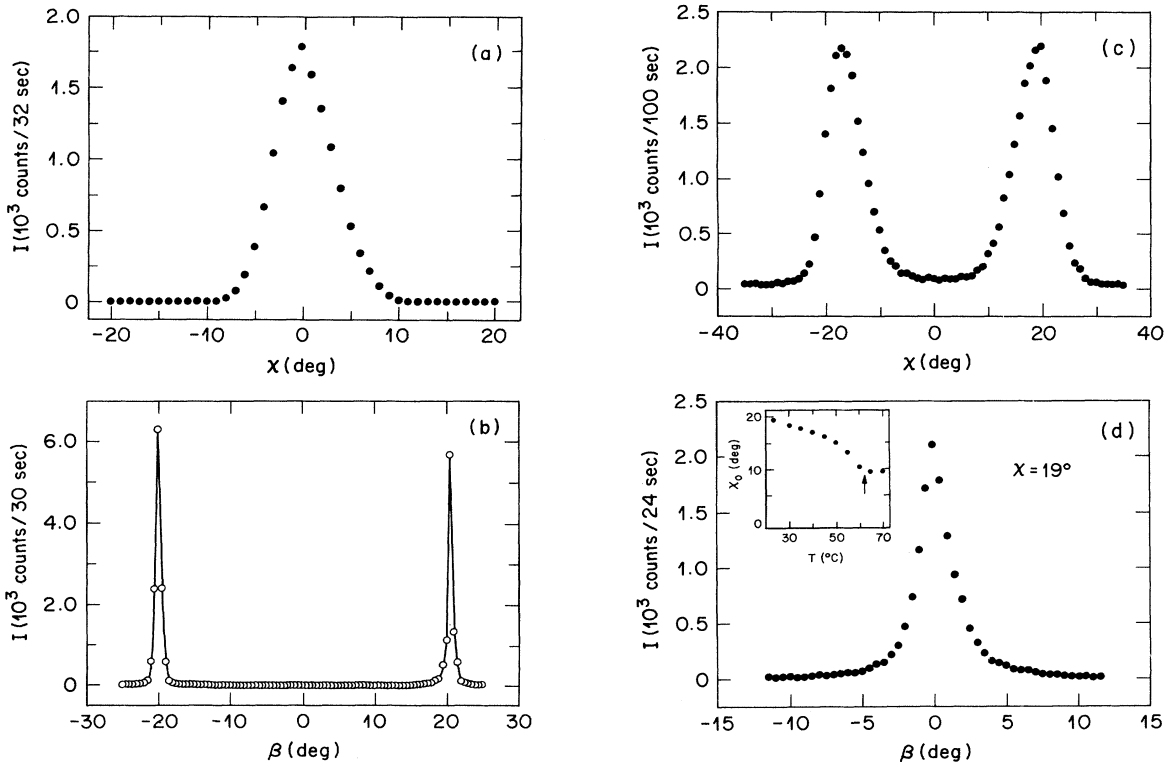

FIG. 4. Scattered intensity I as a function of χ and β angular scans at $T=23.4\,^\circ$C. At this temperature the sample is in the Sm-C^* phase. (a) Without the electric-field treatment, a single domain is found in the χ scan, and (b) two peaks in the β scan symmetrical with respect to zero indicating a well-developed chevron structure. The solid line through the data points is only a guide for the eye. (c) The sample was treated with 100-V, 1-kHz electric field for 2 h. Contrary to (a), two peaks in the χ scan show that the projection of the layer normal is rotated away from the buffing axis. The amount of layer reorientation corresponds to the molecular tilt angle. (d) β scan on the same sample. Compared with the scan in (b), only a single peak was observed, which confirms that the chevron structure has completely vanished in the electric-field treatment. The measurement was taken at $\chi=19^\circ$. The inset shows the temperature dependence of the layer-orientation angle. Note that the layer-orientation angle does not go to zero at the transition to the Sm-A phase (transition point indicated by an arrow), but stays finite at $\chi_0=10^\circ$.

from the rub direction. If the sample was heated to the isotropic phase, the effect of the electric-field treatment diminished and the smectic layers formed in the usual way, with the layer normal along the rub direction. We also note that, by applying a small (± 5 V) dc bias on top of the 100-V, 1-kHz field, it is possible to favor the growth of only one of the domains.

A plausible mechanism for the layer reorientation in the electric field is that the applied field was sufficiently strong to create substantial molecular motions and, hence, disrupt the molecules adsorbed at the surface with the Sm-A periodicity. Since the surface-treatment biases the molecules to assume a unidirectional orientation, the Sm-C^* molecular layers then reformed, perpendicular to the glass plates, but with the layer normal rotated from the rub direction by the molecular tilt angle θ so that the molecules would be oriented parallel to the rub direction.

Finally, we find that the reoriented smectic-layer structure induced by the electric-field treatment has asymmetric properties in response to external switching fields. This is an expected behavior because, in the field-treated cells, an external ac field switches the director between two possible orientations both parallel to the cell surfaces, but one along the rub direction and the other 2θ away. Clearly, the state in which the molecules coincide with the rub direction has a smaller free energy than the other state. The implication is that, on the one hand, surface anchoring facilitates the return to this state, but, on the other hand, it imposes delays upon the field-polarity reversal. However, symmetrical switching can be restored by buffing both glass plates and assembling them in such a way that the buffing axes differ by an angle equal to twice the molecular tilt angle. Detailed studies of the electro-optical properties have been made in these samples and will be reported elsewhere.[9]

In conclusion, we have performed x-ray experiments on ferroelectric liquid-crystal samples that were treated with a high ac electric field. We have shown that the field irreversibly reoriented the smectic layers and thus eliminated the characteristic chevron-layer structure. Finally, we have confirmed the hypothesis of PLG, that the smectic layers reform at an angle to the buffing axis which is approximately equal to the molecular tilt angle.

[1]R. B. Meyer, L. Liebert, L. Strzelicki, and P. Keller, J. Phys. (Paris) Lett. **36**, L69 (1975).

[2]N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett. **36**, 899 (1980).

[3]T. P. Rieker, N. A. Clark, G. S. Smith, D. S. Parmar, E. B. Sirota, and C. R. Safinya, Phys. Rev. Lett. **59**, 2658 (1987).

[4]N. A. Clark and T. P. Rieker, Phys. Rev. A **37**, 1053 (1988).

[5]Y. Sato, T. Tanaka, H. Kobayashi, K. Aoki, H. Watanabe, H. Takeshita, Y. Ouchi, H. Takazoe, and A. Fukuda, Jpn. J. Appl. Phys. **28**, L483 (1989).

[6]J. S. Patel, S. Lee, and J. W. Goodby, Phys. Rev. A **40**, 2854 (1989).

[7]J. Patel, T. M. Leslie, and J. W. Goodby, Ferroelectrics **57**, 137 (1984).

[8]Y. Takanishi, Y. Ouchi, H. Takazoe, and A. Fukuda, Jpn. J. Appl. Phys. **28**, L487 (1989).

[9]G. Srajer, R. Pindak, and J. Patel (unpublished).