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Synchrotron x-ray study of the smectic layer directional instability

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We have investigated the phenomenon of field-induced smectic layer instability, as monitored by synchrotron x-ray scattering. This instability means that, upon application of time-asymmetric electric fields to chiral smectics, the layer direction seems to ''rotate'' locally around an axis given by the direction of the applied field. For moderate values of field amplitude and asymmetry, domains with a favored layer inclination grow at the expense of unfavored ones, while larger fields and asymmetries generally lead to a chaotic flow behavior. At moderate amplitudes, we have followed the process of the horizontal layer folding (or horizontal chevron domain formation) and the smectic C^* layer reorientation of ferroelectric liquid crystals by applying symmetric and asymmetric wave forms, respectively, and performing time resolved x-ray measurements. The studies unambiguously show the formation of a horizontal (in-plane, i.e., in a plane parallel to the cell substrates) chevron domain structure from a nonoriented sample by application of a symmetric electric field of sufficient amplitude. It is then demonstrated that a transition from the horizontal chevron domain structure to an in-plane uniform smectic layer direction takes place on application of asymmetric electric wave forms. Reversal of the field asymmetry reverses the inclination direction and selects the other layer normal direction as the uniform end state. The in-plane smectic layer reorientation process is followed here as it evolves, and analyzed directly by means of x-ray scattering.

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I. INTRODUCTION

Smectic C^* (SmC^*) liquid crystals possess a one-dimensional positional order in addition to the orientational order of the long molecular axis of calamitic molecules. The SmC^* phase thus exhibits a layered structure with the centers of mass of the molecules randomly positioned within an individual smectic layer. The director $\mathbf{n}$ is inclined with respect to the layer normal $\mathbf{k}$ by an angle called the director tilt angle θ. Lowering the temperature from a well-oriented cholesteric or smectic A^* into the smectic C^* phase, there are several possibilities for a geometry combining layer and director order. The structure generally desirable from an applicational point of view is the bookshelf geometry [1], with smectic layers perpendicular to the substrate and the layer normal parallel to the rubbing direction, leaving a conical freedom to the director. This structure is generally not observed, but instead the so called (vertical) chevron geometry is formed [2,3]. Here the smectic layers are inclined with respect to the substrate normal, by an angle which is smaller than the director tilt angle, but which may sometimes approach it. In this latter case the long molecular axis is allowed to be oriented within the substrate plane along the rubbing direction. This, or a similar structure, is generally observed for parallel rubbed substrates, and invasive zigzag defects [4,5] are formed where regions of opposite layer inclination meet. Substrates rubbed in the antiparallel direction usually give rise to simply tilted layer structures with the layer normal being oriented at an angle to the substrate plane. It has been shown by x-ray investigations [6–8] that application of a sufficiently large electric field may cause a smectic layer straightening. It has also been demonstrated that this process may involve slight reorientation components in the plane of the substrate [9]. In 1986 Patel and Goodby [10] demonstrated that cooling a cholesteric phase across the transition into SmC^* under an applied electric field can produce well aligned samples with two kinds of domains, having the smectic layer normal inclined with respect to the rubbing direction. These structures involve what are now called *horizontal chevrons*, or in-plane chevrons, as the layers are broken to change direction in an alternating fashion in the plane of the cell. They can also be induced in materials with a SmA^* phase mediating the cholesteric and the SmC^* phase. The angle of layer inclination with respect to the rubbing direction is in all cases approximately equal to the director tilt angle [11]. The dynamics of this horizontal chevron formation process with respect to external parameters was investigated optically in Ref. [12]. In this paper, we present x-ray diffraction images verifying the actual smectic layer structure of horizontal chevrons and reflecting the dynamics of its formation process.

The reorientation of horizontal chevrons is linked to the more general phenomenon of smectic layer instability under applied *asymmetric* electric fields, which was first demonstrated for the SmA^* [13] and SmC^* phases [14], and later verified to occur also in the antiferroelectric SmC_a^* modification [15–17]. The dynamics of this layer reorientation (macroscopically speaking) has recently been further investigated by optical means with respect to external parameters [18], such as field asymmetry, amplitude, frequency, or width of the cell gap. For well-defined samples in commercially available liquid crystal test cells, the reorientation pro-

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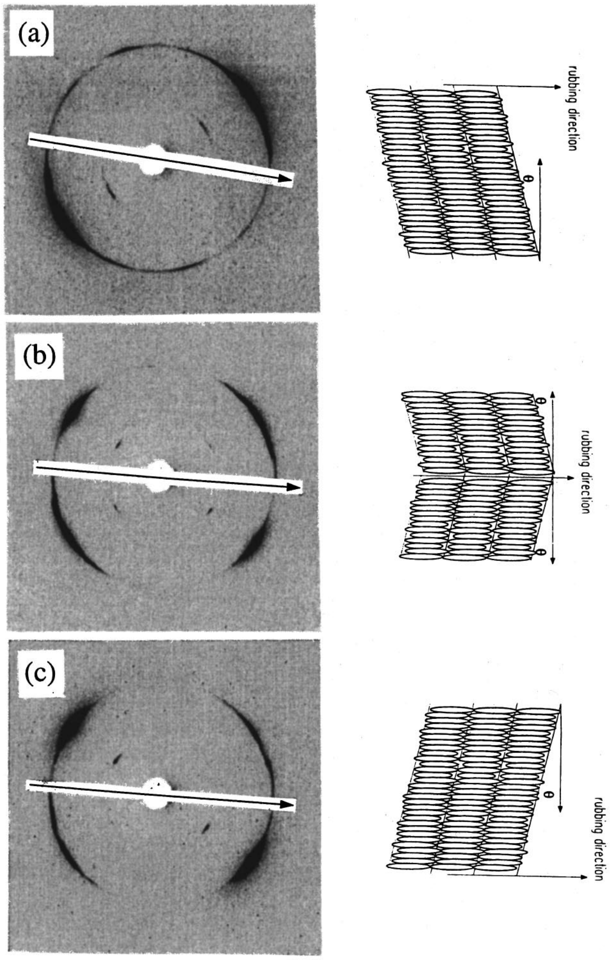

FIG. 1. X-ray diffraction diagrams at different sample areas, demonstrating the horizontal chevron structure. (a) Domain with smectic layer normal inclined counterclockwise, (b) sample area with both inclination directions, and (c) domain with smectic layer normal inclined clockwise with respect to the rubbing direction (indicated by an arrow in the diffraction image). The right part of the figure shows a schematic picture of the corresponding smectic layer arrangement.

cess does not consist of a rotation of whole domains into the other orientation, but is rather a domain growth process, where (depending on electric field asymmetry and sign of the spontaneous polarization) favored domains grow at the expense of unfavored ones, until layers within the whole electrode area are uniformly inclined with respect to the rubbing direction. It was also pointed out that the dynamics of this domain growth process is very sensitive to enantiomeric excess [19], ionic contamination [20], smectic polymorphism [21], and surface treatment [22]. In contrast to the SmA^* phase, where the layer reorientation can only be induced by time-asymmetric sawtooth fields, the SmC^* reorientation is observed for all kinds of asymmetric electric fields [23], like amplitude and time-asymmetric square wave fields (both with a dc component) as well as dc free time-asymmetric sawtooth fields. It has been shown [24] that the SmC^* layer reorientation may be angle limited to twice the tilt angle for samples with monostable boundary conditions, but unlimited for substrates with degenerate planar alignment. In this investigation we have used substrates with strong monostable anchoring and present time resolved synchrotron x-ray diffraction measurements of the angle limited in-plane smectic layer reorientation.

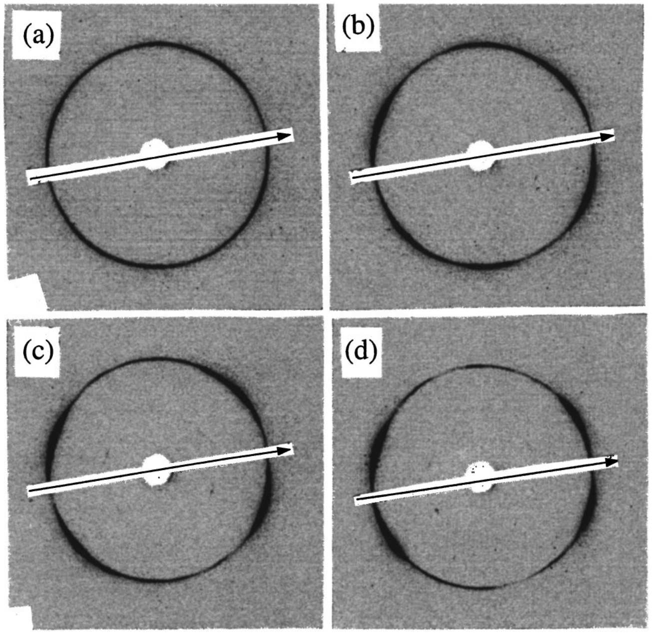

FIG. 2. Series of x-ray diffraction diagrams, demonstrating the dynamic process of the horizontal chevron domain formation from a nonoriented SmC^* sample; (a) $t=0$ s, (b) $t=2$ s, (c) $t=6$ s, and (d) $t=20$ s. The horizontal chevron domain structure is evidenced by the four diffraction spots inclined by an angle with respect to the rubbing direction, indicated by an arrow. The electric field amplitude during the formation process was $E=2\ \mathrm{MV\,m^{-1}}$, and frequency $f=200$ Hz.

II. EXPERIMENT

Adequate cells for x-ray investigations need to have very thin glass plates to reduce background scattering, and thus cannot be commercially available. We used standard borosilicate microscope cover slips of thickness 150 μm, which were coated with a thin film of ITO (as electrodes) of approximately 100 Ω per square (Central Research Laboratories, CRL, England). The glass plates were carefully cut in half ($18\times 9\ \mathrm{mm}^2$) and spin coated at 3500 rpm for 30 s with a solution of polyimide. The polyimide film was then tempered for 2 h at 180 °C and subsequently rubbed unidirectionally with a velvet cloth to produce monostable planar anchoring conditions. Three 10-μm-thick spacer foils were glued to the bottom substrate, and the cell was assembled such that parallel rubbing was obtained. The glue was UV cured, putting the cells under slight pressure to assure a constant cell gap.

The cells so prepared were filled with an epoxyde liquid crystal (commercially available from Aldrich), 4-[(S,S)-2,3-epoxyhexyloxy]-phenyl-4-(decyloxy)-benzoate [25] by capillary action. The optical characterization of the cells with respect to horizontal chevron formation and in-plane smectic layer reorientation was carried out using a polarizing microscope (Nikon OPTIPHOT-POL2) equipped with a hot stage (Mettler FP82 HT) and a temperature controller (Mettler Toledo FP90). Electric wave forms were applied by a function

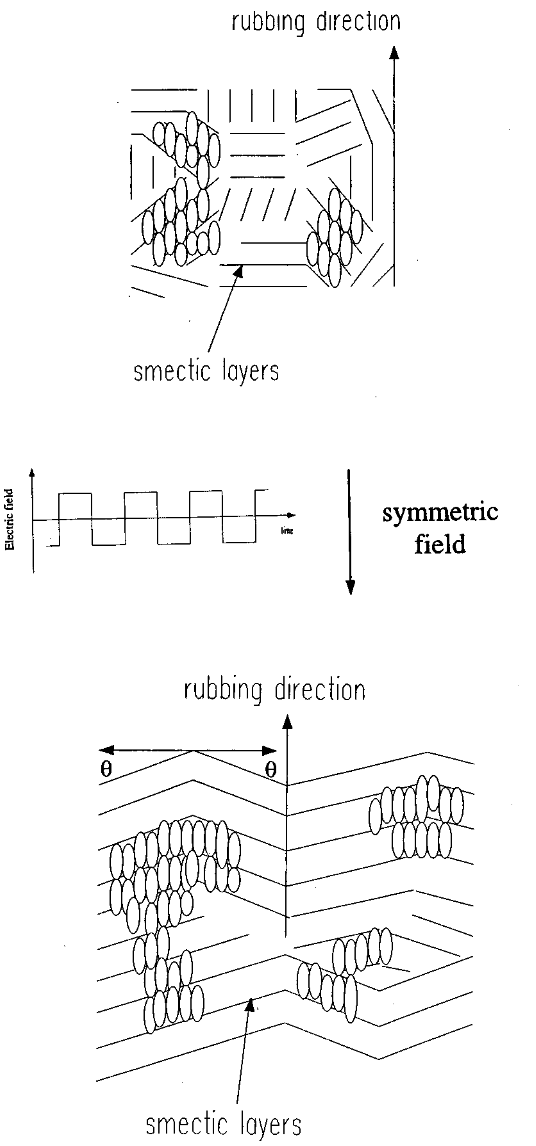

FIG. 3. Schematic illustration of the horizontal chevron formation process from a nonoriented smectic layer arrangement as demonstrated in the diffraction images of Figs. 2(a) and 2(d), respectively.

generator (HP8116A) in conjunction with a voltage amplifier (Trek Model 10-10) and monitored by a Tektronix 465B oscilloscope.

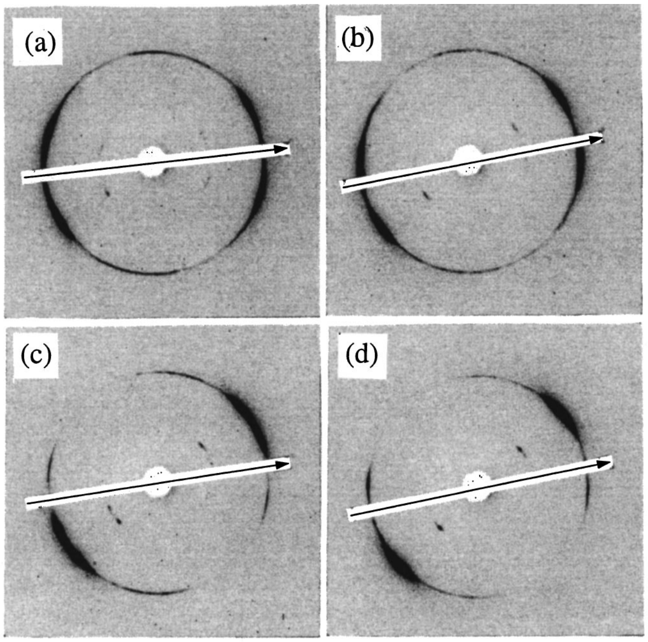

FIG. 4. Series of x-ray diffraction diagrams, demonstrating the dynamics of the smectic layer reorientation from a horizontal chevron sample [(a) $t=0$ s] to an inclined smectic layer configuration [(d) $t=90$ s]. The favored domain type (here the smectic layer normal inclined counterclockwise to the rubbing direction) grows at the expense of the unfavored one (here the layer normal inclined clockwise with respect to the rubbing direction) [(b) $t=30$ s, and (c) $t=60$ s].

Time resolved x-ray investigations were carried out at the Cornell High Energy Synchrotron Source (CHESS), Ithaca, NY. We used the D1 bend magnet beamline, equipped with a double-bounce synthetic multilayer monochromator. The radiation flux was approximately 10^{12} photons per mm^2 per second at a wavelength of $\lambda=1.546$ Å, corresponding to Cu $K\alpha_1$ radiation. A Gruner 1-K detector was used to record diffraction patterns. This offers 1024×1024 pixels at 16-bit resolution. The effective beam diameter was adjusted to an area of $230\times200\,\mu\text{m}^2$ by a combination of three slits. The beam profile was checked to have the desired plateau shape to assure constant intensity across the beam diameter. Throughout the investigations a constant exposure time of 10 s was used. Quasi-time-resolved x-ray studies were carried out by successive application of electric fields for a certain time period, turning off the field and recording the diffraction image. This was necessary due to the needed time for exposure and data storage. This procedure does not present a problem with respect to the stability of the system, as the reorientation process (domain growth) is halted, when the electric field is turned off, with the smectic layer structure being preserved. No layer relaxation is detected on a time scale of hours or days.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The geometry of the horizontal chevron domain structure can unambiguously be evidenced by translating the sample through the x-ray beam and imaging the corresponding diffraction patterns. These are illustrated in Figs. 1(a)–1(c). Starting with a domain where the smectic layer normal is inclined counterclockwise with respect to the rubbing direction (indicated by an arrow) [Fig. 1(a)], the sample is translated until the beam area covers a region where both layer inclinations are present [Fig. 1(b)]. This can clearly be detected by the occurrence of reflections on either side of the rubbing direction, corresponding to the two domain types. Further translation of the sample results in a diffraction pattern caused by a domain with the smectic layer normal inclined clockwise to the rubbing direction [Fig. 1(c)]. The right part of Fig. 1 schematically shows the corresponding smectic layer arrangement. From the series of diffraction patterns the domain structure of the horizontal chevron geometry is elucidated.

The dynamic process of the horizontal chevron formation by application of *symmetric* electric fields ($E=2\ \text{MV}\,\text{m}^{-1}$, $f=200$ Hz) is followed in Figs. 2(a)–2(d). Starting with a

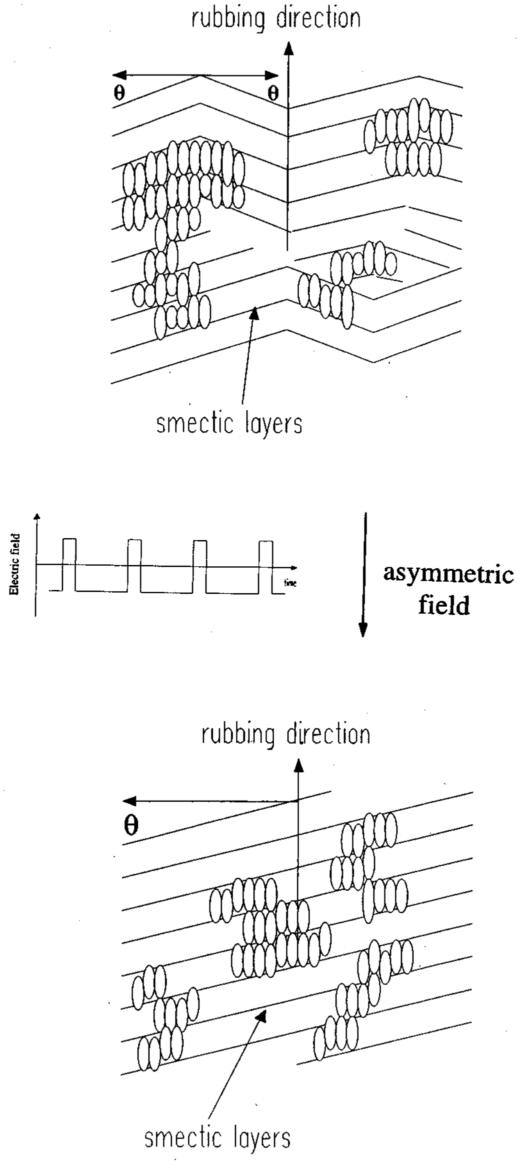

FIG. 5. Schematic illustration of the transformation of a horizontal chevron structure to an inclined layer arrangement before and after asymmetric electric field treatment, as demonstrated in the diffraction images of Figs. 4(a) and 4(d), respectively.

nonoriented smectic layer arrangement [Fig. 2(a), $t=0$ s], corresponding to a ''powder sample,'' which yields a diffraction ring, an electric field is applied. The smectic layers now become ordered, as can be seen by the evolution of diffraction spots to either side of the rubbing direction (again indicated by an arrow) [field applications of $t=2$ and 6 s, from Figs. 2(b) and 2(c), respectively]. After approximately 20 s the horizontal chevron domain structure formation is completed, indicated by the four reflections corresponding to the two layer normal inclination directions. The behavior is schematically illustrated in Fig. 3 as a transformation from a nonoriented sample to the horizontal chevron sample with smectic layers perpendicular to the substrates and the layer normal inclined to the rubbing direction by the amount of the tilt angle. [Figure 3 schematically illustrates the situation before ($t=0$ s) and after ($t=20$ s) the electric field treatment, not the dynamics of the layer rearrangement.] The observed domain formation time is in good agreement with that obtained by optical investigations.

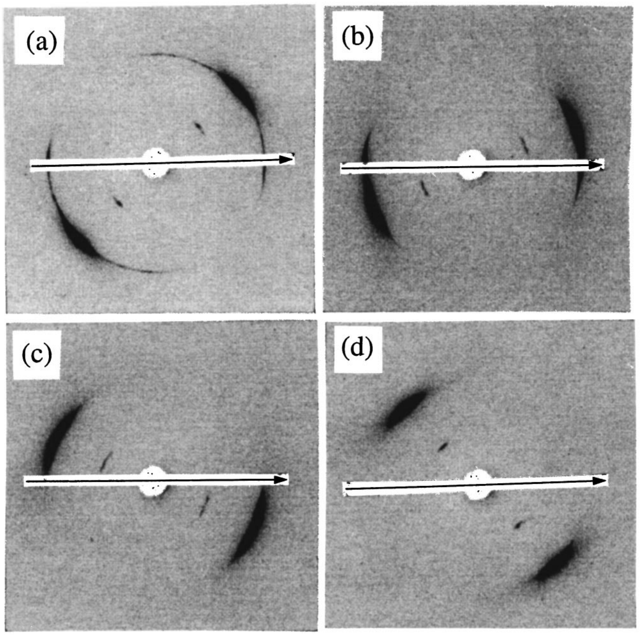

FIG. 6. Series of x-ray diffraction diagrams demonstrating the reorientation of smectic layers after reversal of the time asymmetry of the applied electric field, causing a macroscopic change of the smectic layer normal from a counterclockwise to a clockwise inclination with respect to the rubbing direction. (a) Initial smectic layer arrangement at $t=0$ s (counterclockwise inclination), (b) $t=20$ s, (c) $t=40$ s, and (d) final smectic layer orientation at $t=90$ s (clockwise inclination of the smectic layer normal).

In a similar way, the reorientation of smectic layers in the plane of the substrate by application of *asymmetric* electric wave forms can be monitored. In the case here presented, a time asymmetric square wave field of frequency $f=200$ Hz was used at an amplitude of $E=2$ MV m^{-1}. The sample was heated to the cholesteric phase, subsequently cooled into the SmC^* phase to a reduced temperature of $T-T_C=-2$ K, before a symmetric electric field was applied for 20 s to form the horizontal chevron domains. Here we start with a sample where both domain types are initially present. The diffraction pattern of Fig. 4(a) clearly reveals the existence of the two horizontal chevron domains, as discussed above. Application of a 1:4 time-asymmetric square wave field causes the growth of the favored domain type (depending on field asymmetry, sign of the spontaneous polarization and electroclinic coefficient) at the expense of the unfavored one [$t=30$ s in Fig. 4(b) and $t=60$ s in Fig. 4(c)]. At $t=90$ s the layer reorientation (domain growth) process is completed, and the smectic layer normal is uniformly oriented, inclined counterclockwise to the rubbing direction [Fig. 4(d)]. From polarizing microscopic investigations [20] it is known that during the reorientation process favored domains grow at the expense of unfavored ones, involving permeation flow along the rubbing direction. The layer rearrangement is not accomplished by the rotation of entire domains. This reorientation process, from a horizontal chevron domain structure to an inclined layer structure, is schematically summarized in Fig. 5 before ($t=0$ s) and after ($t=90$ s) the asymmetric field treatment, not referring to the dynamics of the reorientation process. The inclination direction is such that, for positive

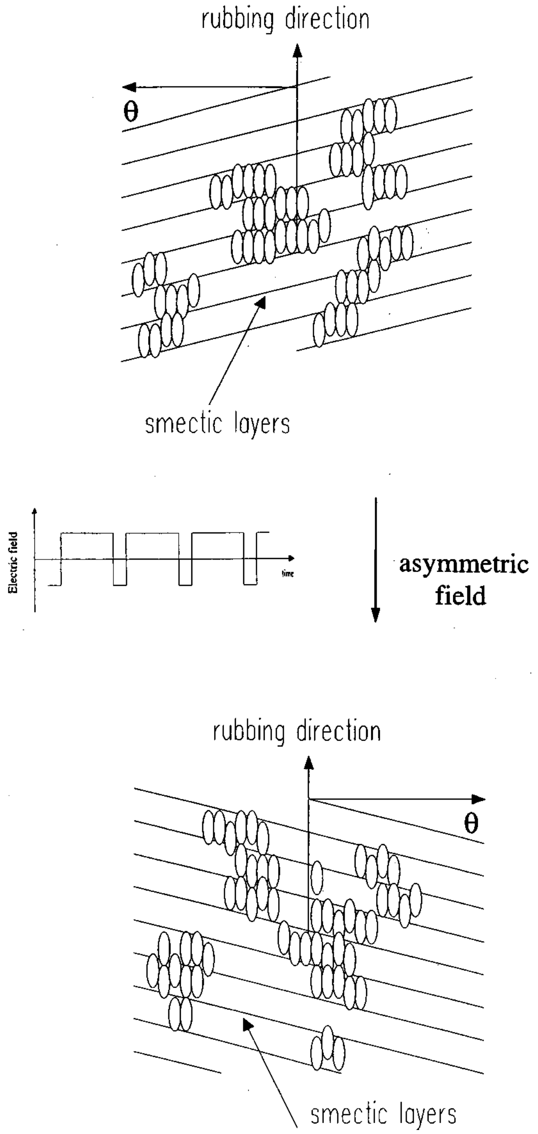

FIG. 7. Schematic illustration of the smectic layer reorientation before and after electric field treatment, as demonstrated in the diffraction images of Figs. 6(a) and 6(d), respectively.

spontaneous polarization and the electric field pointing up, an anticlockwise reorientation is observed.

Reversal of the asymmetry ratio of the time-asymmetric electric field then causes a growth of domains with the other inclination direction via domain nucleation and domain wall motion, as evidenced from polarizing microscopic investigations [20]. In contrast to the data discussed above, we now start with a uniformly layer inclined sample, which is the reason for the nucleation of domains of the opposite inclination after asymmetry reversal. In this process the rate limiting factor is the domain wall motion rather than domain nucleation. The process is followed in the series of diffraction patterns shown in Fig. 6. Starting with a layer structure with layer normal inclined counterclockwise with respect to the rubbing direction [Fig. 6(a), $t=0$ s], the field asymmetry is reversed from 1:4 to 4:1. The smectic layers are observed to rearrange in the plane of the substrate [$t=20$ s in Fig. 6(b), and $t=40$ s in Fig. 6(c)] until the opposite inclination direction is reached, corresponding to a seemingly clockwise ''rotation'' of the smectic layer normal [Fig. 6(d), $t=90$ s]. Figure 7 schematically illustrates this reorientation process of smectic layers in the plane of the substrate, again before ($t=0$ s) and after ($t=90$ s) the electric field treatment. It should be mentioned that the well-defined small q diffraction spots are due to the second harmonic with wavelength $\lambda/2$ of the primary radiation, caused by the monochromatization of the incident synchrotron radiation.

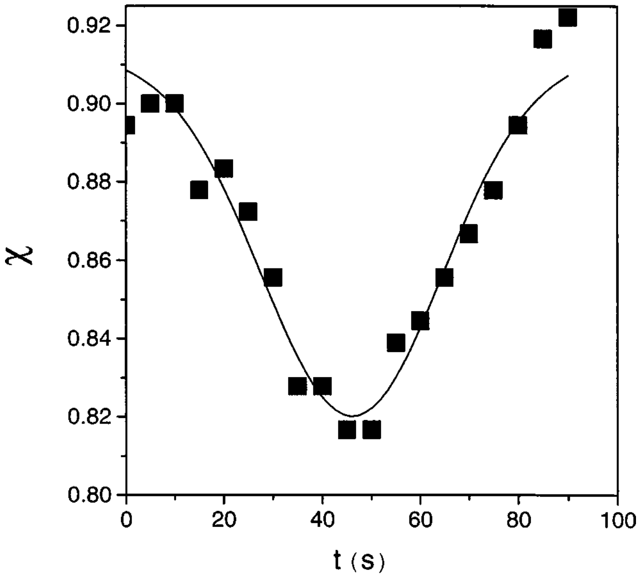

FIG. 8. Directional order parameter of the smectic layer normal, defined as $\chi=(1-\Delta\phi/180)$, as a function of time during the smectic layer reorientation. The layer structure is ordered at the beginning and end of the layer reorientation process. During the smectic layer reorientation, χ decreases, indicating a wider distribution of the angular position of the smectic layer normal.

From the beam diameter of approximately 200 μm and the time needed for domain growth across this width (≈ 80 s), the domain wall velocity can be estimated to $v_{\mathrm{wall}}=2.5\,\mu\mathrm{m\,s}^{-1}$, which is in good agreement with values determined from optical experiments. It should be noted, however, that the domain wall velocity depends on the applied electric field parameters, especially asymmetry ratio, amplitude, and frequency, as well as on temperature.

The angular width of the diffraction spot (difference in azimuthal angle $\Delta\phi$) is a measure for the degree of disorder of the smectic layer normal. For complete disorder the diffraction pattern degenerates to a ring ($\Delta\phi=180°$), while for perfect order a point reflection is expected ($\Delta\phi\to 0°$). Determination of $\Delta\phi$ as a function of time during the smectic layer reorientation, exhibits a clear maximum during the reorientation process. This indicates that the macroscopically averaged distribution of layer normal directions is more narrow at the beginning and end than during the dynamic reorientation process. This observation is in accordance with texture studies and reflects the nature of the angle limited smectic layer reorientation process. We may define an order parameter χ to characterize the degree of directional order of the smectic layer normal as $\chi=(1-\Delta\phi/180)$. If this is plotted as a function of time of electric field application (Fig. 8), we observe a well-ordered sample with quite uniform orientation of the layer normal for $t=0$ s and at the end of the reorientation process ($t=90$ s). During the reorientation process this order always decreases, which illustrates that the layers—naturally—do not rotate as such, but that the field acts on the local director, destroying and recreating the layers in the other orientation during the course of the process. This is in accordance with texture observations.

IV. CONCLUSIONS

From synchrotron x-ray diffraction studies on oriented samples of a ferroelectric liquid crystal, we have verified the structure of the horizontal chevron domain texture, as consisting of regions with the smectic layer normal inclined to opposite directions with respect to the rubbing direction. A macroscopic reorientation of smectic layers by application of asymmetric electric fields has been demonstrated conclusively by x-ray diffraction. The smectic layer inclination direction can be reversed by a reversal of the field asymmetry. For the given experimental conditions, the domain wall velocity during the reorientation process can be estimated to approximately 2.5 $\mu\mathrm{m\,s}^{-1}$. The order parameter of the smectic layer normal decreases in the course of the reorientation process.

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