2π and π walls in antiferroelectric smectic-C_A^* and smectic-C free-standing films

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We observed, in free-standing films of antiferroelectric liquid crystal, dependence of the wall structure on orientation of walls with respect to the external field direction and on parity of number of smectic layer in the film. These observations are explained by anisotropy of two-dimensional elastic constants and by dependence of polarization direction on parity of the film. Investigations in electric and magnetic field allow us to determine the values of elastic constants and longitudinal polarization of the films. Different mechanisms of ***c***-director reorientation were observed when the electric-field direction was reversed or magnetic field orientation was changed with respect to the film plane.

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I. INTRODUCTION

Domain walls exist in many ordered systems with discrete and broken continuous symmetry [1]. They determine many structural properties of real materials and play an important role in switching between different states of a system in an external field. In the case of two-dimensional (2D) freely suspended films of tilted smectic liquid crystals [2,3], walls are formed by spatial modulation of the molecular ordering. These films can have thicknesses from two to thousands of molecular layers with layers parallel to the free surfaces. In SmC-like liquid crystals the long axes of the molecules are tilted by an angle θ with respect to the layer plane normal $\boldsymbol{z}$ (Fig. 1). In the layer plane $\boldsymbol{x}$-$\boldsymbol{y}$ the 2D vector field ($\boldsymbol{c}$ director) is defined as the projection of the nematic $\boldsymbol{n}$ director onto the $\boldsymbol{x}$-$\boldsymbol{y}$ plane [2]. Walls can be observed directly by optical methods [4]. In the wall region, the azimuthal orientation of the $\boldsymbol{c}$ director φ rotates by an angle 2π and π across 2π and π walls, respectively. Depending on type of tilted smectic (synclinic SmC, SmC^* [5]; anticlinic SmC_A^* [6,7]), in external field (electric E, magnetic H) measurements (static or dynamic) both 2π and π walls may be observed in free-standing films. In ferroelectric SmC^* and antiferroelectric SmC_A^* phases only 2π walls are formed in an applied electric field. The wall structure is formed by competition between elastic and external field energy, and the wall mobility depends on 2D elastic constant K and orientational viscosity η (more exactly on ratio K/η). The study of 2π walls appears to be a powerful method for the determination of macroscopic properties of 2D layer ordering. Pindak *et al.* [4] determined K/P (P is the layer polarization) from measured wall widths in ferroelectric free-standing films. A similar method was used by Link *et al.* [8] for measurement of transverse layer polarization in antiferroelectric SmC_A^* films. The ratio K/η was measured from the collapse rate of circular walls in the SmC^* and SmC_A^* free-standing films [4,8] and from linear wall mobility in SmC films [9].

Up to now, investigations of films with polar ordering of layers were restricted to using an electric field. Moreover, one elastic constant approximation was used in order to keep the number of material parameters low and obtain an analytical solution for the 2π-wall structure. Meanwhile, it is well known that in the SmC^* films the values of bend K_b and splay K_s elastic constants differ significantly [10,11]. Although 2D elastic moduli were not measured in the SmC_A^* thin films, one would expect differences in such anticlinic structures. The $\boldsymbol{c}$ director in antiferroelectric SmC_A^* thin films can be oriented by the electric field, due to the existence of the in-plane net transverse polarization in films with an odd number of smectic layers and longitudinal nonzero polarization in the tilt plane for films with an even number of layers [12,13]. The origin of the net tilt plane polarization has received a great deal of attention in the literature [13–16], however, up to now its value was not determined in chiral SmC_A^* films.

In the present paper we report the (i) dependence of wall structure in antiferroelectric films on its orientation with respect to the electric-field direction and parity of the layer

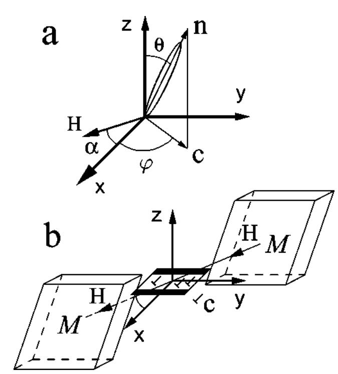

FIG. 1. (a) Molecules in SmC-like structures are tilted by an angle θ with respect to the normal $\boldsymbol{z}$ to the smectic layer. The azimuthal orientation of the molecules is described by a two-dimensional vector $\boldsymbol{c}$ or by an angle φ. The magnetic field $\boldsymbol{H}$ makes an angle α with respect to the $\boldsymbol{x}$ axis. (b) Schematic representation of the experimental geometry. The orientation of the magnetic field $\boldsymbol{H}$ can be varied in the $\boldsymbol{x}$-$\boldsymbol{z}$ plane by rotation of magnets M. The electric field can be applied to the film in the direction of the $\boldsymbol{x}$ axis by two electrodes.

number, (ii) determination of the K_b and K_s elastic constants in SmC_A^* films with an even number of layers, (iii) determination of longitudinal polarization in SmC_A^* films, and (iv) observation of different mechanisms of tilt plane switching in electric and magnetic fields.

II. EXPERIMENT

The experiments were carried out on the antiferroelectric liquid-crystal compound 4-(1-trifluoromethylheptyloxycarbonyl)phenyl 4'-octylbiphenyl-4-carboxylate (TFMHPBC) [7]. Some investigations of ***c***-director reorientation in an external field were made on the nonchiral Sm*C* liquid crystal 4-hexyl-4'-hexyloxy-2'-hydroxybenzalaniline (HHHOBA). Two types of cells were used for the preparation of thin smectic films. First, freely suspended liquid-crystal films were drawn over a conical hole in a glass coverslip. Second, films were prepared in a frame consisting of two movable brass blades. The film thickness (number of smectic layers *N*) was determined from the optical reflectivity in the reflection geometry [17]. To the film one can apply both an in-plane electric field using two parallel electrodes and a magnetic field. The electric field is applied in the direction of the ***x*** axis, the magnetic field in the ***xz*** plane at an angle α with respect to the film plane (Fig. 1). Our setup allows the possibility of magnetic-field rotation with respect to the film plane. For a positive magnetic anisotropy χ_a [2], the external magnetic field forces the tilt plane to orient along the direction in which the field is applied (projection of $\boldsymbol{H}$ on the film plane H_x is responsible for this orientation). The field component normal to the film plane H_z favors orientation of the ***c***-director vector ($\varphi=0$ or $\varphi=\pi$) in the plane of the film.

To examine the in-plane azimuthal distribution $\varphi(x,y)$ of the ***c*** director, the films were imaged using a reflected-light microscope. The images were recorded by means of a charge-coupled device (CCD) camera and then processed to amplify the small contrast of intensity. The investigations were made in two geometries. In the measurements when the walls were stationary (at a constant external field), the images were obtained by polarized reflected-light microscopy (PRLM) with crossed polarizers. When we studied an optical response to the change of the field direction, depolarized reflected-light microscopy (DRLM) [18] was used to decrease the exposure time. We can neglect the SmC_A^* helical structure in both measurements, because the film thickness is much less than the helical pitch. When PRLM is used, the regions where the ***c*** director is parallel or perpendicular to the polarizer, look darkest. On the other hand, the regions look brightest where the ***c*** director makes an angle of $\pm\pi/4$ with respect to the polarizer direction. When the polarizer is so adjusted that the regions far separated from the walls become darkest, then, the $n\pi$ wall consists of $2n$ bright bands corresponding to the $\pi/4, 3\pi/4, 5\pi/4$, and $7\pi/4$ rotation of the ***c*** director. When DRLM is used, the sample is aligned so that the external electric field (E_x or H_x) makes an angle $\pi/4$ with respect to the polarizer. The region free from any walls looks either dark or bright, depending on the direction of the small rotation of the analyzer with respect to its crossed position. The best contrast in DRLM images is achieved for a rotation angle from one to several degrees depending on the anisotropy of the film. At a fixed rotation of the analyzer, the regions of opposite brightness have the ***c***-director orientations perpendicular to each other. This implies that the $n\pi$ wall is imaged as *n* bright (dark) bands.

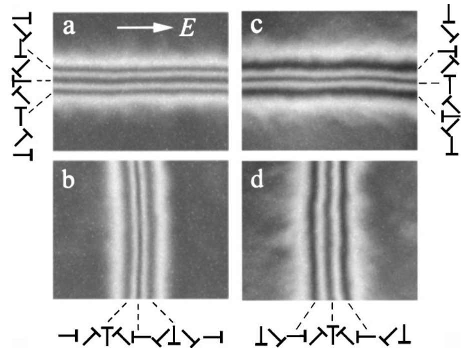

FIG. 2. The 2π walls in the SmC_A^* films with longitudinal [$N=10$ (a, b)] and transverse [$N=11$ (c, d)] polarization. The images reveal orientation and *N*-odd - *N*-even dependence of the 2π-wall structure. The electric field is parallel to the horizontal direction, as shown by the white arrow. Black nails schematically show the ***c***-director rotation in 2π walls. The horizontal and vertical orientation of the ***c*** director correspond to dark bands. Polarizers are oriented parallel to the sides of the pictures. The horizontal dimension of the images is about 175 μm, TFMHPBC, $E=6$ V/cm (a, b), $E=2.5$ V/cm (c, d), $T=60$ °C.

III. RESULTS AND DISCUSSION

A. Determination of splay and bend elastic constants and polarization

Figures 2(a)–2(d) show 2π walls parallel and perpendicular to the applied electric field in *N*-odd and *N*-even films observed in PRLM. The ***c*** director is parallel to the electric field in *N*-even films, while it is perpendicular in *N*-odd films [12]. The ***c***-director orientation changes when crossing the 2π wall, as illustrated schematically by dark nails. The horizontal and vertical orientation of the nails corresponds to dark bands in the walls. In the 2π wall parallel to the ***c***-director orientation far from the defect [Figs. 2(a) and 2(d)], the ***c*** director is splayed in the central dark band, while it is bent in the two side dark bands. In the 2π wall perpendicular to the ***c*** director [Figs. 2(b) and 2(c)], on the other hand, the situation is just the opposite; the bend and splay deformations occur in the central dark band and in the two side dark bands, respectively. Within a single elastic constant approximation [1,4], the distance between two central bright bands w_1 should be independent of wall orientation in films of the same thickness. As is clearly seen in Fig. 2, this is not the case. The width w_1 in Fig. 2(a) is larger than in Fig. 2(b), (see also Table I). In *N*-odd films the situation is the opposite: width w_1 in Fig. 2(c) is less than in Fig. 2(d). These differences in the wall width result from the anisotropy of the 2D elasticity.

Taking into account the difference of 2D bend and splay elastic constants enables one to describe the observed struc-

TABLE I. Experimental and calculated distances between bright-bright (w_1, w_3) and dark-dark (w_2) bands in walls. w_1, w_2, w_3 correspond to relative rotation of the $\boldsymbol{c}$ director by angles $\pi/2, \pi$, and $3\pi/2$, respectively. Type of walls, number of smectic layers N, and orientation of walls with respect to electric and magnetic field are listed in the first three columns. $E=6$ V/cm($N=10$), $H=2$ kG($N=10$), $E=2.5$ V/cm($N=11$), $T=60$ °C. The last column shows the values of K and P obtained from wall structure in N-even film with longitudinal polarization. The accuracy of determination of the distances in 2π walls is ±0.6 μm for w_1, ±1 μm for w_2, ±2 μm for w_3, and ±2 μm for π walls in N-even films. In N-odd films the accuracy is ±0.6 μm for w_1, ±2 μm for w_2, and ±3 μm for w_3. The latter bands have a larger uncertainty in width than the other ones.

Wall type	N	Orientation	Experimental (μm)			Calculated (μm)			K, P
			w_1	w_2	w_3	w_1	w_2	w_3	
2π wall	10	$\parallel\mathbf{E}$	12.0	22.6	37.3	12.1	22.4	38.6	$K_s=1.1\times10^{-11}$ N
2π wall	10	$\perp\mathbf{E}$	9.2	23.2	43.8	8.8	23.2	45.1	$K_b=3.7\times10^{-12}$ N
π wall	10	$\parallel\mathbf{H}$	37			36.3			$P_l=6.9\times10^{-5}$ C/m^2
π wall	10	$\perp\mathbf{H}$	48			48.7			
2π wall	11	$\parallel\mathbf{E}$	10.5	26	52				
2π wall	11	$\perp\mathbf{E}$	14.8	30	51				

ture of the defects quantitatively. In the following, the angle φ will be measured from the $\boldsymbol{x}$ axis. Considering 2D $\boldsymbol{c}$-director distortions with two elastic constants, the free energy of a polar film is given by

$$F = F_0 + (L/2)\int [K_s(\nabla\cdot\boldsymbol{c})^2 + K_b(\nabla\times\boldsymbol{c})^2 - PE\cos\psi]dxdy, \tag{1}$$

where L is the thickness of the film. The first two terms constitute the elastic free energy [19]. As the polarization is parallel to the $\boldsymbol{c}$ director in N-even films and perpendicular to it in N-odd films, the angle ψ between the polarization and the electric field equals φ in N-even film and $\varphi-\pi/2$ in N-odd film. F_0 is the φ-independent free energy. For a description of the wall structure, the free-energy expansion may be limited to the terms present in Eq. (1). Galerne and Najjar [20] introduced a term linear in $\boldsymbol{c}$ gradient for the description of spontaneous $\boldsymbol{c}$ distortions in smectic layers wetting the isotropic interface. This linear elasticity is localized at the smectic-isotropic interface [20]. In the case of SmC_A^* free-standing films we neglected the elastic energy that is linear in $\boldsymbol{c}$ gradient. The first reason is that in the absence of the field, we did not observe any instability in the form of a regular array of distortions that appear in samples with a large value of linear elastic constant [20]. The second reason is that there is no asymmetry of 2π walls (Fig. 2) for positive and negative splay or bend zones, which means that linear elasticity is negligible. The electric effects due to space-charge density - $\nabla\cdot\boldsymbol{P}$ [21] are also negligible if the electric charge interaction energy $P^2q/8\epsilon$ is smaller than the elastic energy of the film Kq^2 [20]. For our values of P and K in films with longitudinal polarization (see later), the electric charge effect may not be taken into account for wavelengths of the distortion smaller than 200 μm. Galerne and Najjar [20] obtained an approximate analytical solution for the periodic spontaneous distortions keeping Fourier terms up to the second order. However, this solution is not valid for a 2π wall and a π wall as a greater number of Fourier terms is necessary to describe an individual wall. We consider, as was the case in our experimental study, 2π walls along and perpendicular to the external electric field. The first derivatives φ'_x, φ'_y were found from the Euler equation obtained by minimizing the free-energy functional (1),

$$\varphi'_{x,y} = (PE)^{1/2}\left[\frac{1-\cos\varphi}{K_\varphi}\right]^{1/2}, \tag{2}$$

where $K_\varphi=K_s\sin^2\varphi+K_b\cos^2\varphi$ for walls parallel (perpendicular) to $\boldsymbol{y}$ in N-even (N-odd) films and $K_\varphi=K_s\cos^2\varphi+K_b\sin^2\varphi$ for walls which are parallel (perpendicular) to $\boldsymbol{x}$ in N-even (N-odd) films. Rotation of $\varphi(x)$ or $\varphi(y)$ across the walls can be found by numerical integration of Eq. (2). In our geometry of observation, rotation of the $\boldsymbol{c}$ director by $\pi/4, 7\pi/4$ and $3\pi/4, 5\pi/4$ corresponds to two pairs of bright bands, while rotation by $\pi/2, 3\pi/2$ corresponds to dark bands. Experimentally measured and calculated distances between these bands were used to estimate the elastic anisotropy. The ratios K_s/P and K_b/P served as fitting parameters. The resulting values for N-even films with longitudinal polarization P_l are $K_s/P_l=(1.6\pm0.1)\times10^{-7}$ V·m, $K_b/P_l=(5.3\pm0.3)\times10^{-8}$ V·m, with elastic anisotropy $K_s/K_b\approx3$. The agreement between experimental and calculated distances between bands in N-even films is good (Table I). In N-odd films the structure of walls parallel and perpendicular to the field is different, which indicates the anisotropy of elastic constants. However, the outer bright bands have nonuniform halfwidth and a larger dispersion in their location with respect to N-even films. N-odd films also behave unusually in magnetic field. These observations will be discussed later.

In antiferroelectric films, values of the 2D elastic constants and longitudinal polarization are not known. Since from investigations in an electric field only ratios K/P can be determined, it does not allow one to extract the individual value of either of these characteristics (K or P). In order to determine their values, investigations of walls in a magnetic field were made. Figure 3 shows images of defects in N-even films. Linear defects formed in a magnetic field in PRLM

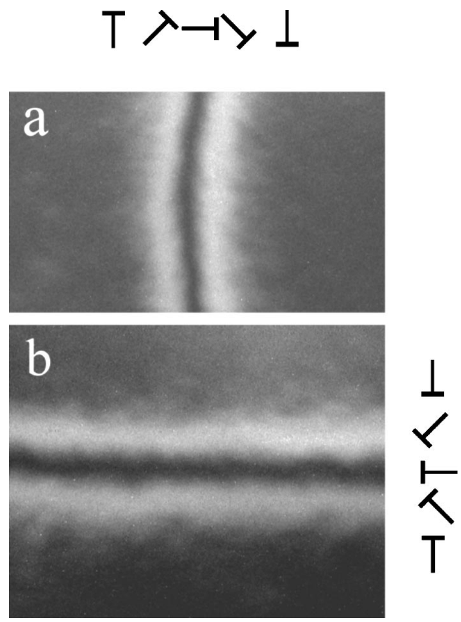

FIG. 3. Photographs of SmC_A^* films (N=10) with π wall oriented (a) parallel and (b) perpendicular to the magnetic field. The separation between bands is smaller for the bend deformation in the center of the wall. Black nails schematically show $\boldsymbol{c}$-director rotation in π walls. Polarizers are oriented parallel to the sides of the pictures. The horizontal dimension of the images is about 285 μm, TFMHPBC, H=2 kG, T=60 °C.

consist of two bands, so they represent π walls. For π walls the $\boldsymbol{c}$-director orientation on two sides of the walls is different. Dark nails in Fig. 3 schematically show the $\boldsymbol{c}$-director rotation in π walls. The distance between bright bands is smaller for the π wall oriented parallel to the $\boldsymbol{c}$ director (vertical direction in Fig. 3). This result is in agreement with the above investigations of 2π walls in an electric field, since in the center of a vertical π wall the deformation type is bend. For the case of an applied magnetic field the free energy of films with an even number of layers has the following form:

$$F = F_0 + (L/2) \int [K_s(\nabla \cdot \boldsymbol{c})^2 + K_b(\nabla \times \boldsymbol{c})^2 - (\chi_a H^2/2)A \cos 2\varphi] dxdy, \quad (3)$$

where $A=\sin^2\theta \cos^2 \alpha$ and α is the angle between the magnetic field and the film plane. Symmetry of the magnetic energy (the π periodicity of the third term) should give rise to the π walls as we observed experimentally. The first derivatives φ_x', φ_y' are given by

$$\varphi_{x,y}' = (\chi_a H^2 A)^{1/2} \left[\frac{\sin^2 \varphi}{K_\varphi} \right]^{1/2}, \quad (4)$$

where $K_\varphi = K_s \sin^2\varphi + K_b \cos^2\varphi$ for the walls which are parallel to $\boldsymbol{y}$, and $K_\varphi = K_s \cos^2\varphi + K_b \sin^2\varphi$ for walls parallel to $\boldsymbol{x}$. The functions $\varphi_{x,y}$ were found by numerical integration of Eq. (4). The magnetic anisotropy was taken to be $\chi_a = 1.2 \times 10^{-7}$ [2]. The calculated π-wall halfwidths, i.e., the separation between the points where the $\boldsymbol{c}$-director orientation changes by $\pi/2$, were compared with experimentally measured distances between bright bands (see Table I). The experimental results can be described with the same elastic anisotropy as in the case of the electric-field measurements ($K_s/K_b=3$) and with $K_s = 1.1 \times 10^{-11}$ N, $K_b = 0.37 \times 10^{-11}$ N. Using these values of elastic constants the longitudinal polarization $P_l = 6.9 \times 10^{-5}$ C/m^2 is determined from the ratio K/P.

Previously, Galerne and Liebert [22] determined the surface longitudinal polarization in the herringbone structure of a nonpolar racemate material MHTAC. Their measurements were made in droplets near the temperature of the SmO-isotropic transition. For layers that wetted the isotropic interface the polarization per surface unit was 3×10^{-7} nC/cm. Since in free-standing films there are contributions to P_l from two surfaces, the polarization per surface unit in SmC_A^* of TFMHPBC is about 10^{-5} nC/cm, which is larger than in the SmO herringbone structure of MHTAC. This difference may occur for two reasons: (i) a different molecular structure and smectic phase of MHTAC [22] from that of TFMHPBC [7,23,24], and (ii) in MHTAC the polarization was determined near the melting temperature in layers that were grown at the isotropic interface.

B. *c*-director reorientation processes

A difference in the interaction of smectic films with electric and magnetic fields leads to a difference in the field-induced reorientation of the $\boldsymbol{c}$ director. The polarity of films results in $\boldsymbol{c}$-director reorientation after the change of electric-field direction. Due to the quadratic dependence of energy on magnetic field the reversal of magnetic-field direction does not lead to a $\boldsymbol{c}$-director reorientation. In N-even SmC_A^* films a change of magnetic-field orientation with respect to the film plane also does not induce a tilt direction reorientation (the energy is the same for angles $+\alpha$ and $-\alpha$). However, in SmC films, the magnetic energy $F_m = -(\chi_a H^2/2)(A \cos 2\varphi + B \cos \varphi)$, where $B = \sin 2\theta \sin 2\alpha$ [9], depends on orientation of the field with respect to the tilt plane ($+\alpha$ or $-\alpha$). Since the molecules in the SmC structure tilt in the same direction, the film orientations with $+\alpha$ and $-\alpha$ are nonequivalent. Figure 4 illustrates a 180° reorientation of the polarization (and direction of molecular tilt in layers) in a SmC_A^* film (a) and of the $\boldsymbol{c}$ director in a SmC film (b). Change of the electric-field direction to the opposite (a) and orientation of magnetic field (b) from α to $-\alpha$ were made between frames 1 and 2. After the change of the magnetic-field orientation, the SmC film finds itself (at $\alpha < \theta$) in a metastable state [$F_m = -(\chi_a H^2/2)(A \cos 2\varphi - |B| \cos \varphi)$ as a function of φ has a local minimum at $\varphi=0$]. Thus, reorientation of the $\boldsymbol{c}$ director to the stable state should occur, but this reorientation is more favorable through the motion of a switching wave [dark narrow π wall in Fig. 4(b), frame 2]. The π wall is created at the edge of the film and moving through the film reorients the $\boldsymbol{c}$ director by 180°. When the electric-field direction is reversed, the film is in an absolutely unstable state ($F_e = PE \cos \varphi$ now corresponds to the maximum of energy). The formation of a narrow π wall is energetically unfavorable resulting in a collective rotation of the

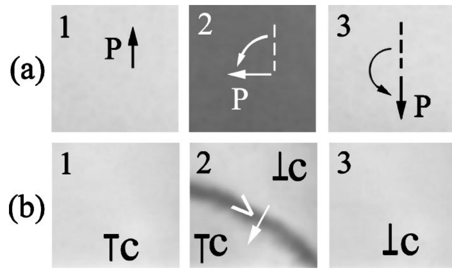

FIG. 4. Response of the films to the change of [(a) upper row of frames] electric- and [(b) lower row] magnetic-field direction: collective molecular reorientation in the (a) SmC_A^* and reorientation through moving π wall in the (b) SmC. The white arrow [frame 2(b)] shows the direction of the wall motion. Electric field was reversed (a) and direction of magnetic field was changed with respect to the film plane (b) between frames 1 and 2. Frames 2 and 3 were made via 1.0 and 3.0 s after changing the field direction. The polarizer and analyzer are slightly decrossed (DRLM). The horizontal dimensions are about (a) 140 and (b) 435 μm. TFMHPBC, $N=12, T=59.9$ °C; HHHOBA, $N=2, T=53.2$ °C. $E=8.5$ V/cm. $H=3.3$ kG, $\alpha=+6.7°(1)$ and $\alpha=-6.7°(2,3)$.

polarization and ***c*** director in a large part of the film [Fig. 4(a), in frame 2, the orientation of molecular ordering in the layers is turned by 90°].

Figure 4(a) shows electric-induced reorientation in films without 2π walls. In a film with 2π walls they play an important role in the reorientation process. Figure 5 shows a series of images after 180° changing (between frames a and b) of the field orientation. The photographs in Fig. 5 were taken using DRLM, so the appearance of 2π walls (two bands) is different from that observed between crossed polarizers (Fig. 2). Orientation of the ***c*** director in different parts of the sample is shown by black nails. In the initial state (frame a) in the center of the 2π walls the polarization is parallel to the "new" (after reversing) direction of electric

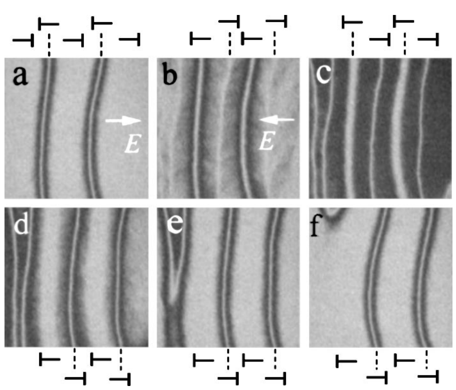

FIG. 5. Response of the SmC_A^* film with 2π walls to 180° change [at $t=0$, between frames (a) and (b)] of electric-field direction: (b) 2.1, (c) 3.1, (d) 6.4, (e) 7.2, and (f) 12 s. Reorientation occurs through transformation of wall structures in the films. White arrows in frames (a) and (f) show the orientation of the electric field. The polarizer and analyzer are slightly decrossed (DRLM). The horizontal dimension of the images is about 300 μm. TFMHPBC, $N=12, T=60$ °C. $E=8.5$ V/cm.

field. After the electric field is reversed, the central bright bands of each wall possess the orientation of the ***c*** director, which is most favorable. So the central parts of the walls start to expand, filling the greater part of the film by corresponding ***c***-director reorientation. It should be pointed out that 2π walls do not break into two narrow π walls, which motion leads to ***c***-director reorientation. Reorientation may occur simultaneously in a large part of the film. In Fig. 5(c) most of the film is dark as the ***c*** director is rotated by 90°. The regions with the "old" orientation of the ***c*** director shrink and between two old 2π walls new 2π walls are formed in the center of which the orientation of polarization remains as before [Figs. 5(e) and 5(f)]. Two linear defects in the left-hand part of Fig. 5(d) disappear with time [Figs. 5(e) and 5(f)]. This is due to the fact that between these defects the ***c*** director rotates in opposite directions, so the defects may coalesce, which decreases the energy of the film.

The SmC_A^* films with N odd have transverse polarization P_t due to the different numbers of layers tilted in opposite directions. The latter allows the existence of 2π walls in a magnetic field tilted with respect to the film plane and π walls in a field parallel to the tilt plane. However, we did not observe perfect orientation of the ***c*** director and stable walls in a magnetic field that was enough for orientation of the ***c*** director and observation of walls in N-even films [25]. The reason for such behavior of N-odd films, as well as a large displacement of outer bands in electric field, is not understood. It should be noted that earlier unusual behavior of N-odd films has been also pointed out, in particular, an intriguing odd-even dependence of the ring-pattern relaxation and the ratio of viscous η and elastic constants η/K on layer numbers was reported [8]. In N-odd films this ratio essentially depends on the transverse polarization. Link *et al.* [8] explained this phenomena by the influence of a large net transverse polarization in N-odd films. Possibly, the unusual behavior of N-odd films in a magnetic field and nonuniform halfwidths of outer bands in an electric field is also connected with their larger polarization than that of N-even films. Possibly, for a description of the structure of walls in N-odd films it is necessary to account for electric charges, however, a quantitative theory of wall structure, taking into account the electric charges, up to now has not been developed.

In SmC_A^* films the longitudinal polarization may be assigned to surface layers. We may evaluate the longitudinal polarization related to a single surface layer $P_i=(N/2)P_l$ [12,13]. Multiplication by $N/2$ results from the fact that in films with anticlinic structure and an even number of layers, the polarization P_l arises from two surfaces [12,13]. Taking our value $P_l=6.9\times10^{-5}$ C/m^2 and $N=10$ the surface longitudinal polarization is about 3.5×10^{-4} C/m^2. In a similar compound, TFMHPOBC, the transverse layer polarization P_s is about 3.6 times larger ($P_s\approx1.25\times10^{-3}$ C/m^2 [26]) at the same relative temperature from the transition point (15 °C).

In summary, we report measurements of the longitudinal polarization and 2d bend and splay elastic constants in SmC_A^* free-standing films with an even number of layers. We observed different mechanisms of ***c***-director reorientation in electric and magnetic fields, which are explained by the absolute instability of ***c***-director orientation, when the electric field was reversed, and by the metastability of ***c***-director orientation when the magnetic-field direction was changed with respect to the film plane.

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