

## Probable Langevin-Like Director Reorientation in an Interface-Induced Disordered $\text{SmC}^*$ -Like State of Liquid Crystals Characterized by Frustration between Ferro- and Antiferroelectricity

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To clarify the thresholdless, hysteresis free V-shaped switching due to frustration between ferro- and antiferroelectricity, we have studied a prototype binary mixture system. The apparent orientational order parameters,  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$ , obtained from polarized Raman scattering in thin homogeneous cells indicate that substrate interfaces induce some randomization of local in-plane directors at the tip of the V. Their correlation lengths,  $\xi_{\parallel} \approx 3.5$  nm and  $\xi_{\perp} \approx 75$  nm, have been estimated by assuming the Langevin-like reorientation. Because of the much shorter  $\xi_{\parallel}$  and  $\xi_{\perp}$  than the visible light wavelength, the switching process looks uniform.

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Until 1989 only one polar structure was known as the chiral smectic-C phase ( $\text{SmC}^*$ ) in liquid crystals [1]. The discovery of several  $\text{SmC}^*$ -like subphases as well as the antiferroelectric  $\text{SmC}_A^*$  phase [2,3] established a variety of structures with different polar orderings of smectic layers, which result from the spatial variation of the in-plane director characterized by the azimuthal angle  $\phi$  with a constant tilt angle  $\theta$ . The fundamental phases,  $\text{SmC}^*$  and  $\text{SmC}_A^*$ , show *indirect* ferro- and antiferroelectricity, respectively. Aside from the macroscopic helical structure, the primary tilt orderings in adjacent layers, synclinic ( $\Delta\phi \approx 0$ ) in  $\text{SmC}^*$  and anticlinic ( $\Delta\phi \approx \pi$ ) in  $\text{SmC}_A^*$ , and hence the *planar* structures are realized locally. The director tilt induces the chirality-dependent in-plane spontaneous polarization in each layer parallel to the tilt plane normal and its sense is uniquely determined by the tilt sign. At the same time, an additional chirality-independent in-plane spontaneous polarization emerges in the tilt plane at each smectic layer boundary of  $\text{SmC}_A^*$  [4,5]. An extremely small difference in free energies between  $\text{SmC}_A^*$  and  $\text{SmC}^*$  together with the azimuthal angle freedom causes frustration between the ferro- and antiferroelectricity in characteristic manners. The frustrated liquid crystal system offers a wide array of scientifically fascinating and technologically useful phenomena. It produces the temperature induced sequence of the phase transitions between  $\text{SmC}_A^*$  and  $\text{SmC}^*$  that resembles the devil's staircase, providing rare examples of *ferrielectricity* [6,7]. Johnson *et al.* [8] recently clarified the 3-layered ferrielectric and 4-layered antiferroelectric structures, showing that they are highly biaxial but *not planar*. The structures of the devil's staircase as a whole and the pertinent intermolecular interactions have not yet been studied in detail. The mysterious phase  $\text{SmC}_\alpha^*$ , which appears just below untilted  $\text{SmA}$ , is also considered to result from the frustration in the small tilt

angle region, waiting unambiguous clarification of its structure [3,9,10].

Of particular interest is the electric field induced phase transition between  $\text{SmC}_A^*$  and  $\text{SmC}^*$ . Usually, the transition is of first order and characterized by dc threshold, hysteresis, and fingerlike boundary propagation; it is designated as the tristable switching [3,11,12]. In some of the compounds and mixtures that exhibit ferro-, ferri-, and/or antiferroelectric phases in thick free-standing films, however, the V-shaped switching is observed in thin homogeneous cells. It shows neither threshold nor hysteresis, occurring uniformly without any boundary movement [13–17]. The V-shaped switching is promising for a new generation of liquid crystal displays [18,19]. The random model was proposed. Because of the frustration and interface effect, the information about the tilt direction is lost when going from one layer to the next, while being maintained over substantially larger length scales in a single layer; an applied electric field tends to cause a Langevin-like alignment of the local in-plane polarizations against thermal fluctuations and constraints imposed by substrate interfaces, inducing the net spontaneous polarization gradually [14–17]. Another explanation has also been made successfully by the effective internal field model on the basis of local planar structures of  $\text{SmC}_A^*$  and  $\text{SmC}^*$  [11]. Moreover, Pocięcha *et al.* [20,21] recognized the importance of the frustration in their mixture and proposed a cluster model. They considered that their observed gradual evolution of polar properties results from the concentration change of ferro- and antiferroelectric clusters of sizes smaller than the visible light wavelength. It also presupposes the local planar structures and may explain the memory effect (hysteresis) that Pocięcha *et al.* mentioned to refute the random model. There exists no big difference between the cluster and random models, if the concept of clusters is replaced by the correlation

lengths,  $\xi_{\parallel}$  and  $\xi_{\perp}$ , as introduced below in the random model. When  $\xi_{\parallel} \approx$  smectic layer spacing, the memory effect must disappear, otherwise the V-shaped switching could not be used practically in liquid crystal displays. The question concerning the loss of information about the tilt direction is of high physical interest. Studying the same "Inui mixture" previously used to propose the above random model [14–17], however, several publications recently raised objections [22–25]. They emphasized that the frustration does not play any essential role. Instead the charge stabilization and/or the highly collective azimuthal angle rotation of the director on the  $\text{SmC}^*$  tilt cone in a macroscopic scale are indispensable to the V-shaped switching.

This Letter aims at confirming the random switching process due to the frustration, presenting another prototype binary system of compounds 1 and 2 whose chemical structures are given in Fig. 1. A thin homogeneous cell of the "Mitsui mixture" with 1:2 = 63:37 shows V-shaped switching [13]. Seomun *et al.* [17,26] studied the system in detail, obtaining the temperature mixing ratio phase diagram in thick free-standing films and the corresponding diagram in thin homogeneous cells. At the concentration of 63:37, only one liquid crystal phase other than  $\text{SmA}$  is distinguished in the latter, while five tilted phases are observed in the former. Substrate interfaces destroy the phase structures. Readiness of destruction critically depends on the concentration. In a 70:30 mixture, an antiferroelectric phase is stable not only in thick films but also in thin cells; the threshold is clearly seen in the first run of the switching, although some thresholdless switching is achieved dynamically. In the 63:37 mixture, however, no antiferroelectric phase stably exists in thin cells because the threshold does not emerge even in the first run, although it does in thick films. The destruction is also seen as a considerable difference in the temperature dependence of dielectric constants between a 66:34 mixture and the 63:37 mixture. The relative permittivity becomes smaller, the phase transition disappears, and a single phase or state prevails. The state is neither ferroelectric nor antiferroelectric; no helical structure exists, either, in an ordinary sense. Still, it becomes very dark at the tip of the V where the applied electric field is zero. In this way, we concluded that substrate interfaces introduce some randomization of local in-plane directors. In fact, we checked the distribution

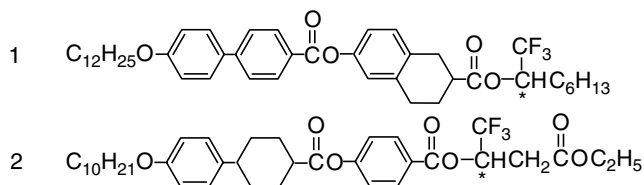


FIG. 1. Chemical formula of compounds used.

at the tip of the V by polarized Raman scattering and confirmed the randomization.

Homogeneous cells were prepared by sandwiching the Mitsui mixture between two quartz glass substrates separated by  $2 \mu\text{m}^{\phi}$  spacer particles. The substrates were coated with ITO ( $\sim 50 \text{ nm}$  thick,  $\sim 100 \Omega/\text{sq.}$ ,  $\sim 80\%$  transmission at  $500 \text{ nm}$ ) and aligning polyimide (Nissan Chemical, RN-1266,  $\sim 200 \text{ nm}$  thick). Only one of the substrates was rubbed along one direction and sense. The cell was mounted in a temperature controlled oven ( $\pm 0.1 \text{ K}$ ). Raman spectra were obtained in the backward scattering geometry along the  $Y$  axis perpendicular to the substrates [27,28]. The  $0.5 \text{ W}$  exciting radiation of  $514.5 \text{ nm}$ , which was polarized along the  $Z$  axis initially parallel to the smectic layer normal, was focused on a well-aligned area of the sample cell. Here the  $X$ ,  $Y$ , and  $Z$  axes constitute the right-handed laboratory frame. The diameter of a focused spot was about  $700 \mu\text{m}$ . The scattered light was collected by a telescope lens ( $f = 130 \text{ mm}$  and  $f/d = 1.3$ ) and focused on an optical fiber, which transmits the light to a monochromator (Spex, 270M,  $200 \mu\text{m}$  slit width) combined with a multichannel detector (Princeton Instruments, IPDA 512). We observed the  $Z$ - and  $X$ -polarized Raman intensities due to the C-C stretching mode of three benzene rings with a frequency of  $1600 \text{ cm}^{-1}$  under applied electric fields by rotating the sample cell about the  $Y$  axis.

Figures 2(a)–2(d) illustrate observed intensities as a function of the sample rotation angle,  $I_{ZZ}(\Omega)$  and  $I_{ZX}(\Omega)$ , at  $60^\circ\text{C}$ . By applying dc fields above the saturation value,  $E_s = \pm 2 \text{ V } \mu\text{m}^{-1}$ , we obtained  $I_{ZZ}(\Omega)$  and  $I_{ZX}(\Omega)$  in  $\text{SmC}^*$  given in Figs. 2(a) and 2(c). Figure 2(b) shows  $I_{ZZ}(\Omega)$  and  $I_{ZX}(\Omega)$  at  $E = 0$ , which is symmetric about the rubbing direction almost parallel to the smectic layer normal; the interface-induced electroclinic effect is small in the Mitsui mixture. We also measured dynamically  $I_{ZZ}(\Omega)$  and  $I_{ZX}(\Omega)$  at the tip of the V by applying a triangular wave electric field of  $\pm 2.9 \text{ V}_{\text{pp}} \mu\text{m}^{-1}$  and  $1 \text{ Hz}$ . The result is given in Fig. 2(d). The time resolved technique was used and the gate time at the tip of the V is  $4 \text{ ms}$  which corresponds to  $\Delta E = 0.023 \text{ V } \mu\text{m}^{-1}$ , about  $1.2\%$  of  $E_s$ . The signal was accumulated 1200 times. Actual measurements were made at only seven sample rotation angles; still it takes  $140 \text{ min}$ . Without making any detailed analysis, Figs. 2(b) and 2(d) clearly indicate that the substrate interfaces do not induce any ferroelectric  $\text{SmC}^*$  order aligned parallel to a plane perpendicular to the substrate, which was reported to be realized in the Inui mixture [22–25]. By taking into account birefringence effects appropriately, we obtained the apparent orientational order parameters,  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$ , which are summarized in Table I.

We simulated the order parameters by assuming three typical distributions of local in-plane directors with a standard deviation  $\sigma$  on the basis of the bookshelf smectic layer:

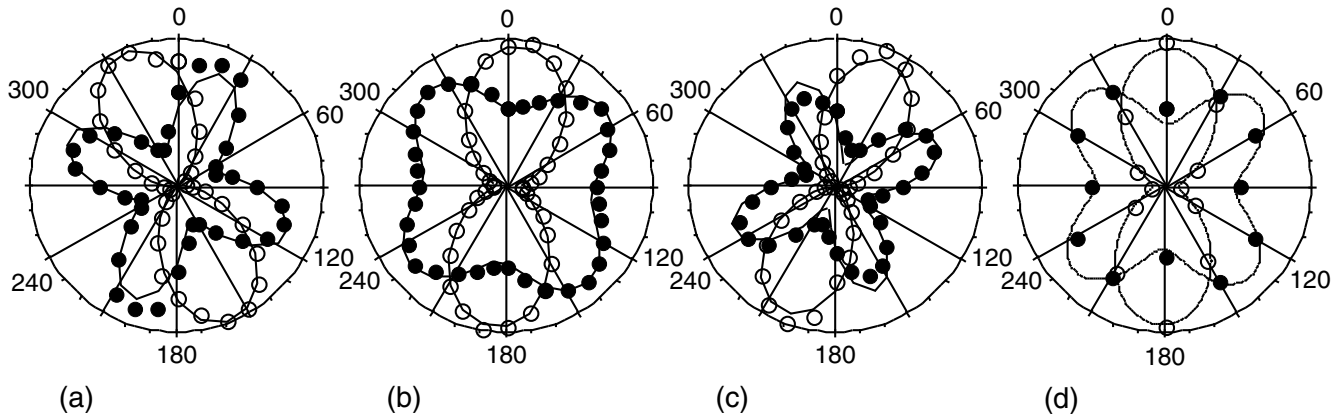


FIG. 2. Raman scattered intensities as a function of the sample rotation angle,  $I_{ZZ}(\Omega)$  ( $\circ$ ) and  $I_{ZX}(\Omega)$  ( $\bullet$ ), at  $60^\circ\text{C}$ . The relative intensity of  $I_{ZX}(\Omega)$  is 3 times as enlarged compared to that of  $I_{ZZ}(\Omega)$ . (a)  $E = -4.8 \text{ V } \mu\text{m}^{-1}$ , (b)  $E = 0 \text{ V } \mu\text{m}^{-1}$ , (c)  $E = 4.8 \text{ V } \mu\text{m}^{-1}$ , and (d) at the tip of the V.

$$f(\phi) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(\phi + \pi/2)^2}{2\sigma^2}\right], \quad (1)$$

$$f(\phi) = \frac{1}{2\sqrt{2\pi}\sigma} \left\{ \exp\left(-\frac{\phi^2}{2\sigma^2}\right) + \exp\left[-\frac{(\phi - \pi)^2}{2\sigma^2}\right] \right\}, \quad (2)$$

and

$$f(\phi) = 1/(2\pi). \quad (3)$$

Here  $\phi = 0$  corresponds to the  $x$  axis in the right-handed liquid crystal frame. The  $z$  axis is along the smectic layer normal and the  $y$  axis is perpendicular to the substrate plates. The  $y$  and  $Y$  axes are taken to coincide with each other. Equation (1) is motivated by  $\text{SmC}^*$  in the Inui mixture [22–25], Eq. (2) by surface stabilized  $\text{SmC}_A^*$  [29], and Eq. (3) by the random model [14–17]. The chevron structure complicates these equations [27] but a chevron angle up to  $12^\circ$  [22,24] does not bring about any essential difference in  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$ . We further presupposed that  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  in  $\text{SmC}^*$  mainly result from molecular level fluctuations and the imperfect alignment of the smectic layers as manifested by textures. Table II indicates that the distributions at  $E = 0$  are well described by Eq. (2). The standard deviation is rather narrow at  $40^\circ\text{C}$  but it is as broad as  $30^\circ$  at  $60^\circ\text{C}$ . One may suspect that the antiferroelectric, anticlinic molecular alignment parallel to the substrate plates is realized at  $40^\circ\text{C}$  [29]. However, the state realized is different from that of bulk  $\text{SmC}_A^*$ . In fact, the V-shaped switching is observed and the threshold does not emerge

TABLE I. Experimentally obtained orientational order parameters at  $40$  and  $60^\circ\text{C}$ .

	$40^\circ\text{C}$		$60^\circ\text{C}$	
	$\langle P_2 \rangle$	$\langle P_4 \rangle$	$\langle P_2 \rangle$	$\langle P_4 \rangle$
No electric field	0.45	-0.11	0.54	0.04
With dc electric field	0.78	0.48	0.77	0.47
At the tip of the V	0.59	0.20	0.60	0.12

even in the first run as emphasized above. The director distributions at the tip of the V almost coincide with the simulated result given by Eq. (3). One may suspect that the uniform distribution is caused by the helical structure, since the pitch is rather short in the bulk phases. However, at  $60^\circ\text{C}$  where the much more ideally uniform distribution is realized than at  $40^\circ\text{C}$  as shown in Table II, the bulk phase is ferroelectric  $\text{SmC}^*$  but the Goldstone mode is completely suppressed. Moreover, the pitch at  $60^\circ\text{C}$  is longer than that at  $40^\circ\text{C}$ . Thus we conclude that substrate interfaces diminish the tilting correlation and induce some randomization of in-plane directors.

Because of the smectic layered structure, the correlation length of local in-plane directors along the layer normal is the order of layer spacing,  $\xi_{\parallel} \approx d$ , and the one in a single layer,  $\xi_{\perp}$ , is very long. Tilting randomization among smectic layers assures the disappearance of net spontaneous polarization, but an applied electric field induces it according to the Langevin-like in-plane director reorientation. The aligning process is described as

$$\langle \cos\phi \rangle = \frac{\int_0^{\pi} \exp(x \cos\phi) \cos\phi d\phi}{\int_0^{\pi} \exp(x \cos\phi) d\phi} \quad (4)$$

TABLE II. Simulated orientational order parameters. The molecular tilt angles used for simulations were  $26.3^\circ$  at  $40^\circ\text{C}$  and  $22.8^\circ$  at  $60^\circ\text{C}$ , which were determined experimentally by applying a dc electric field above the saturation value.

	$\sigma$	$40^\circ\text{C}$		$60^\circ\text{C}$	
		$\langle P_2 \rangle$	$\langle P_4 \rangle$	$\langle P_2 \rangle$	$\langle P_4 \rangle$
By Eq. (1)	0	0.74	0.41	0.74	0.42
	30	0.65	0.25	0.68	0.30
	60	0.57	0.12	0.61	0.19
By Eq. (2)	0	0.43	-0.10	0.50	-0.01
	30	0.48	-0.03	0.54	0.06
By Eq. (3)	...	0.55	0.09	0.60	0.16

by using a ratio of electric aligning energy,  $p_{\text{eff}}E$ , to thermal agitating energy,  $kT_{\text{eff}}$ ,

$$x = p_{\text{eff}}E/(kT_{\text{eff}}). \quad (5)$$

The effective dipole moment  $p_{\text{eff}}$  is given by

$$p_{\text{eff}} = d(\xi_{\perp})^2 P_s, \quad (6)$$

where  $P_s$  is a net spontaneous polarization observed in SmC\*. The thermal agitating energy should also be regarded as an effective one, since constraints imposed by substrate interfaces play an important role. Numerical calculation indicates that the degree of alignment  $\langle \cos\phi \rangle = 0.9$  attains at  $x = 5$ . For the sake of simplicity, let us consider that ferroelectric SmC\* is realized at  $x = 5$ . By inserting the experimentally obtained saturation field  $E = |E_s| = 2 \text{ V } \mu\text{m}^{-1}$  and appropriately presumed  $kT_{\text{eff}} = 1/40 \text{ eV} = 1.6 \times 10^{-19}/40 \text{ C V}$  into Eq. (5), we obtain  $p_{\text{eff}} = 1 \times 10^{-26} \text{ C m}$ . By further inserting measured  $P_s = 0.5 \text{ mC m}^{-2}$  and  $d = 3.5 \times 10^{-9} \text{ m}$  in Eq. (6), we can evaluate  $\xi_{\perp} = 7.5 \times 10^{-8} \text{ m} = 75 \text{ nm}$ . Since the correlation length is much shorter than the visible light wavelength, the switching process looks uniform.

The picture described above, though primitive, may help us understand the first essential to the V-shaped switching; we consider it only one of the many fascinating aspects of the frustration between ferro- and antiferroelectricity that need to be addressed to develop better physical insight into this novel state of nature. The frustration appears to produce complex bulk phases. An interplay between phase and helical structures was observed as the slight jumps of the pitch or the splitting of characteristic reflection bands due to the helical structure [17,26]. These complex structures are closely related with SmC\* variants (subphases). So far at least five subphases other than SmC<sub>A</sub>\* and SmC\* were confirmed to exist [17]. We would like to know what intermolecular interactions are responsible for these subphase emergences. Some explanations were given based on the devil's staircase, but have not been accepted widely [30–33]. Another crucial but still unclear aspect is the detailed mechanism by which substrate interfaces induce an ordered or disordered state different from that in the bulk; it is also crucial to elucidate the detailed structure of the state itself sufficiently stable in practical using as displays. In actual applications, the electrostatic discussions including the insulating and/or aligning films are important [25]. We will have to reconsider these electrostatic effects on the basis of the random switching model.

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