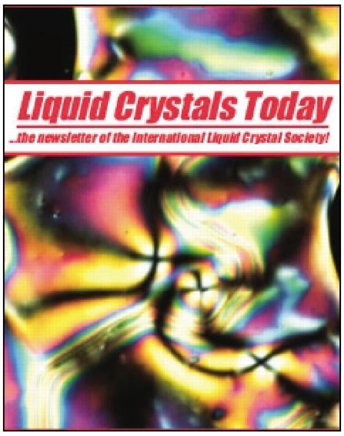

Liquid Crystals Today
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713681230

Devil' Staircase and Frustoelectricity in Chiral Smectic-C like Liquid Crystals

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To cite this Article Matsumoto, Takahiro and Fukuda, Atsuo(1998) 'Devil' Staircase and Frustoelectricity in Chiral Smectic-C like Liquid Crystals', Liquid Crystals Today, 8: 4, 6 — 8
To link to this Article: DOI: 10.1080/13583149808047718
URL: http://dx.doi.org/10.1080/13583149808047718

Without going into further details we remark that in the case of an isotropic structureless film, reflection also occurs at the second interface. Interference between the two reflected signals–that have acquired a phase difference proportional to the film thickness–leads to interferences (Kiessig fringes) on top of the Fresnel reflectivity (see figure A2(*b*)). Finally in the case of a freely suspended smectic film the periodic layer structure gives rise to finite size broadened Bragg-like peaks, that in turn are superimposed on this structure (see figure A2(*c*)). Hence specular X-ray reflectivity measurements can be interpreted as the result of these various effects, with the average electron density profile along the film normal as an important parameter. In addition roughness or fluctuation effects have to be taken into account.

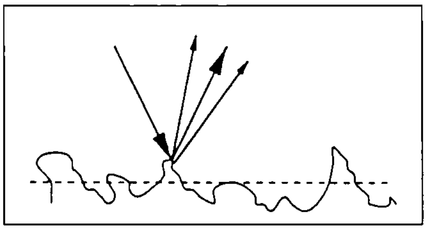

Figure A3. Microscopic roughness or fluctuations leading to a diffuse component of the reflectivity.

Figure A3 shows roughness c.q. fluctuations on a microscopic scale which causes scattering away from the specular condition. The resulting diffuse reflectivity can be measured by rocking the film so that $\alpha+\beta=$ constant with $\alpha \neq \beta$ at $\psi=0$ (q_x scan, see figure A1). As smectic A systems are uniaxial alternatively the detector can be moved out of the scattering plane over an angle ψ (q_y scan, see figure 5(*b*)). In figure 5(*a*) the wavelength dependence of the fluctuations is probed by making q_z scans ($\alpha = \beta$, parallel to the specular direction) at various offsets of ψ setting q_y.

References

1. See, for example, CHAIN, P. M., and LUBENSKY, T. C., 1995, *Principles of Condensed Matter Physics* (New York: Cambridge University Press).
2. CAILLÉ, A., 1972, C. R. Acad. Sci. Paris **B 274**, 891.
3. ALS-NIELSEN, J., LISTER, J.D., BIRGENEAU, R.J., KAPLAN, M, SAFINYA, C.R., LINDEGAARD-ANDERSEN, A., and MATHIESEN, S., 1980, *Phys. Rev.* B, **22**, 312.
4. NACHALIEL, E., KELLER, E. N., DAVIDOV, D., and BOEFFEL, C., 1991, Phys. Rev. A, 43, 2897.
5. SAFINYA, C. R., ROUX, D., SMITH, G. S., SINHA, S. K., DIMON, P., CLARK, N. A., and BELLOCQ, A. M., 1986, *Phys. Rev.* Lett., **57**, 2718.
6. HOLYST, R., 1991, *Phys. Rev.* A, **44**, 3692; SHALAGINOV, A. N., and ROMANOV, V. P., 1993, *Phys.Rev.* E, **48**, 1073.
7. MOL, E. A. L., SHINDLER, J. D., SHALAGINOV, A. N., and DE JEU, W. H., 1996, *Phys. Rev.* E, **54**, 536.
8. GRAMSBERGEN, E. F. and DE JEU, W. H., 1988, *J. chem. Soc. Faraday Trans.* 2, **84**, 1015.
9. SINHA, S. K., 1991, *Physica* B, **173**, 25.
10. MOL, E. A. L., WONG, G. C. L., PETIT, J.-M., RIEUTORD, F., and DE JEU, W. H., 1997, *Phys. Rev. Lett.*,**79**, 3439.
11. TERENTJEV, E. M., WARNER, M., and LUBENSKY, T. C., 1995, *Europhys. Lett.*, **30**, 343.
12. ZENTEL, R., and BENALIA, M., 1987, *Makromol. Chem.*, **188**, 665.
13. WONG, G. C. L., DE JEU, W. H., SHAO, H., LIANG, K. S., and ZENTEL, R., 1997, *Nature*, **389**, 576.
14. KAGANER, V. M., OSTROVSKII, B. I., and DE JEU, W. H., 1991, *Phys. Rev.* A, **44**, 8158.

Devil's Staircase and Frustoelectricity in Chiral Smectic-C like Liquid Crystals

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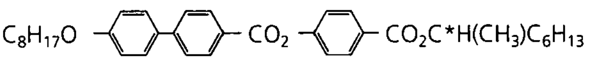
In 1989, Chandani et al. showed that the tristable switching, already observed by themselves and by others in 4-(1-methylheptyloxycarbonyl) phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC), is the electric-field-induced transition between antiferroelectric and ferroelectric phases [1, 2]. Thus they disclosed antiferroelectricity in liquid crystals, clarifying an antiferroelectric smectic C*-like phase, designated as Sm C_A^*, where the tilting occurs in the same direction but in the opposite senses in adjacent layers as also reported in the smectic O* phase [3].Three other smectic C*-like phases were observed in MHPOBC at that time [4]; Chandani *et al.* designated these phases as Sm C_α^*, Sm C_β^*, and Sm C_γ^* in the order of decreasing temperature, identifying Sm C_β^* as ordinary ferroelectric C* [5–7]. Gorecka *et al.* soon proved that Sm C_γ^* is a ferrielectric phase [8]. Since then, more than 1000 related compounds have been synthesized because of a potential application to liquid crystal displays, and several additional Sm C*-like phases have been found. A possible, most general phase sequence experimentally revealed is [9]:



$$I^*-I_A^*-\boxed{\begin{array}{c}C_A^*\\ q=\frac{1}{2}\end{array}}-\begin{array}{c}\text{spr3}\\(\text{FI}_L)\end{array}-\begin{array}{c}C_\gamma^*\\ \frac{1}{3}\end{array}-\begin{array}{c}\text{spr2}\\(\text{FI}_H)\end{array}-\begin{array}{c}\text{AF}\\ \frac{1}{4}\end{array}-\begin{array}{c}\text{spr1}\\(\text{FI})\end{array}-\boxed{\begin{array}{c}C^*\\ 0\end{array}}-C_\alpha^*-A$$

When the tristable switching is typically observed, it appears as follows: Sm C_A* and Sm C* are the fundamental phases and the others between them, together with Sm C_α*, are the subphases; ferrielectric Sm C_γ* and antiferroelectric AF phases seem to be secondarily fundamental. A few subphases may emerge in the temperature regions, spr1, spr2, and spr3, where spr refers to subphase region. At least one ferrielectric phase (FI_L, FI_H, or FI, where the suffixes L and H indicate the low and high temperature sides of Sm C_γ*, respectively) was confirmed to exist in each subphase region. When V-shaped switching, i.e. the disappearance of threshold and hysteresis of the tristable switching, is observed in homogeneous cells as illustrated in figure 1 [10–12], an apparently single ferrielectric phase alone, different from Sm C_γ*, may frequently emerge in a temperature range as wide as 100°C or more in free-standing films; hence this ferrielectric phase appears to be fundamental [13]. Thus, it is not easy to say what phases are fundamental and what others are subphases. We need some model that can appropriately describe the successive phase transitions and the V-shaped switching.

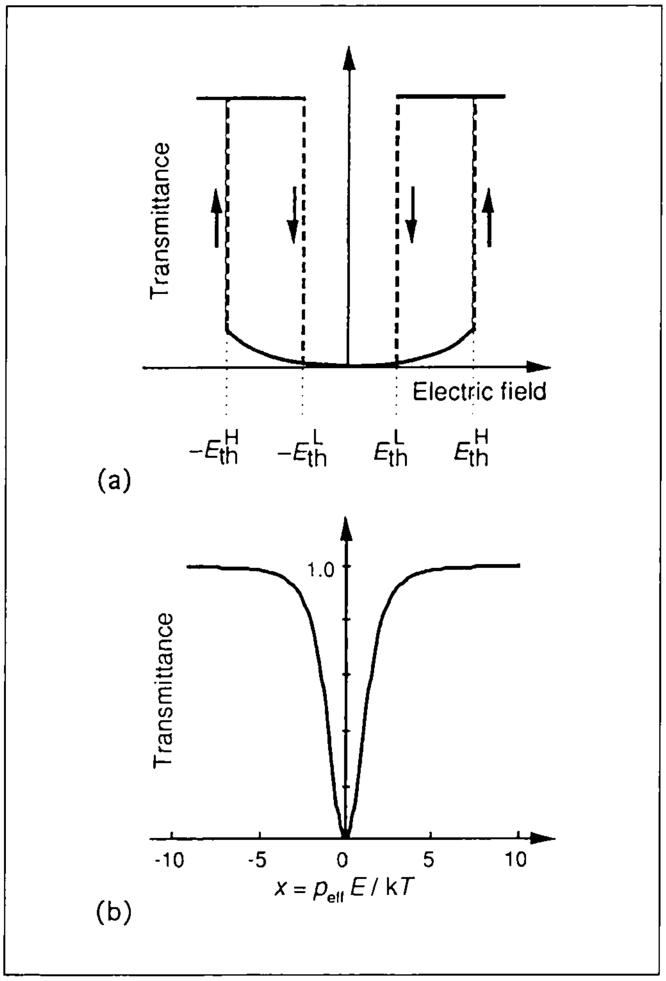


Figure 1. Schematic illustration of (a) tristable switching and (b) V-shaped switching observed in homogeneously aligned cells placed between crossed polarizers, the axes of which are parallel and perpendicular to the smectic layer normal.

If we neglect the slight precession of at most a few degrees per layer caused by chirality, the molecular tilting direction (specified by the azimuthal angle ϕ) is restricted parallel to a plane both in ferroelectric Sm C* (ϕ=0) and antiferroelectric Sm C_A* (ϕ=0 or π). Here the tilt angle (specified by the polar angle θ) is constant not only in a smectic layer but also from layer to layer. Because of the Ising character of the tilting directions in Sm C* and Sm C_A* together with the Devil's staircase feature of the successive phase transition, the observed phase sequence can naturally be treated in terms of the frustration between ferroelectricity and antiferroelectricity based on the Ising model. In fact, Yamashita studied this frustration with the ANNNI+J_3 model by identifying Ising spins to the tilting senses, right and left, and obtained a phase diagram as illustrated in figure 1 of [14]. He found four ground states with the wavenumbers q=1/2, 1/3, 1/4, and 0; the states with q=1/2 and 0 refer to Sm C_A* and Sm C*, respectively. In addition, many subphases emerge just below the critical curve, and above it there exists a disordered phase. Consequently, it is preferable to specify a subphase by its wavenumber q. We have concluded that Sm C_γ* and AF have q=1/3 and 1/4, respectively, with several experimental facts supporting this [9, 15].

Since the evidence was indirect, and since the Sm C*-like phase has two degrees of freedom θ and ϕ, the ANNNI+J_3 model has not been accepted as an established one. Several theoretical treatments based on the X-Y model have also been developed to understand the observed sequence of subphases [16–19]. In fact, freedom in the azimuthal angle must play an important role near the critical curve in the phase diagram. Even in the ANNNI+J_3 model the critical curve is of second order and hence the order grows gradually from zero in the ordered phase. There is no reason to exclude the azimuthal angle fluctuation as a mechanism in reducing the degree of order. A phase with a random azimuthal angle distribution, designated as Sm C_R* (R refers to random), was proposed to explain the V-shaped switching [10–12].The smectic layered structure may cause extremely anisotropic tilting correlation lengths, $\xi\perp \approx$ 100 nm (shorter than a visible light wavelength) and $\xi\parallel <$ 3 nm (layer spacing), producing local in-plane spontaneous polarizations at smectic layer boundaries with random orientations and variable magnitudes. Their Langevin-like alignment results in the V-shaped switching. Since this speculation has been supported experimentally to some extent [20–22], we should combine the ANNNI+J_3 model and the X-Y model to describe successive phase transitions and the V-shaped switching.

So far, however, V-shaped switching has been observed in restricted conditions created by interface effects. Consequently, the azimuthal angle distribution may not be cylindrically symmetric around the smectic layer normal. In an extreme case where the substrate interfaces exert strong anchoring, the in-plane directors distribute very sharply along the rubbing direction [23] and appear to rotate collectively on the cone about the smectic layer normal. Still the reduced tilting correlation makes the system so soft that the V-shaped switching occurs quite uniformly. Clark [24] suggested that the molecular arrangement at the tip of the V is the so-called twisted state stabilized by a large spontaneous polarization. We share the view that the twisted state is easily formed when polar interfaces, such as ITO, are used and an apparently V-shaped switching is observed. However, our accumulated experience clearly indicates that non-polar interfaces are favourable for realizing the V-shaped switching which is attractive for display applications. What we believe is essential in V-shaped switching is the reduced tilting correlation.

It is necessary to understand more details of the phases/states before considering an appropriate nomenclature. It is worthwhile remarking, however, that these phenomena result from the frustration between ferroelectricity and antiferroelectricity in smectic C*-like liquid crystals. Because of the frustration, the tilting correlation between smectic layers is very much reduced. Moreover, the antiferroelectricity results from the characteristic bent shape of constituent molecules of these materials [25]. Overemphasizing the antiferroelectric interaction, all the compounds and mixtures that show any of the subphases including Sm C_A^* and Sm C* are designated as antiferroelectric liquid crystal (AFLC) materials. In some such materials, the V-shaped switching was observed and hence it was thought quite natural to call the materials 'thresholdless AFLCs' from an application point of view. It was inappropriate, however, to designate the dielectric property of Sm C_R^* (Sm C_A^* (disordered)) as 'thresholdless antiferroelectricity', because there exists no antiferroelectric order. Since the frustration causes such an interesting characteristic dielectric response (the V-shaped switching), it would be better called 'frustrated electricity' or 'frustoelectricity (FR)' [26].

In view of the macroscopic symmetry, Sm C_A^* and AF ($q=1/2$ and $q=1/4$) are biaxial smectic A* phases, and Sm C_R^* (Sm C_A^* (disordered)) is a smectic A* phase [26]. However, we do not think it useful to make too much of the similarity to Sm A* and the electro-clinic effect. Molecular tilting is not induced by an applied electric field, but instead, they are tilted by 35 degrees from the smectic layer normal. We would rather emphasize the importance of the frustration as above. Since a crucial role is played by the antiferroelectric interaction in these materials, we would like to call the subphases Sm C_A^* ($q=1/2$), Sm C_A^* ($q=1/3$), Sm C_A^* ($q=1/4$), Sm C_A^* (disordered), etc; the suffix A emphasizes the importance of the antiferroelectric interaction. The dielectric property of Sm C_A^* (disordered) would be better called 'frustrated electricity' or 'frustoelectricity' although it was initially designated as thresholdless antiferroelectricity.

References

1. Chandani, A. D. L., *et al.*, 1989, *Jpn. J. appl. Phys.*, **28**, L1265.
2. Furukawa, K., *et al.*, 1988, *Ferroelectrics*, **85**, 451.
3. Cladis, P. E., 1992, *Liq. Cryst. Today*, **2**(3), 7.
4. Fukui, M., *et al.*, 1989, *Jpn. J. appl. Phys.*, **28**, L849.
5. Chandani, A. D. L., *et al.*, 1989, *Jpn. J. appl. Phys.*, **28**, L1261.
6. When the enantiomeric excess is high, Sm C_β^* is different from Sm C* and may belong to spr1. [See Hatano, J., *et al.*, 1994, *Jpn. J. appl. Phys.*, **33**, 5498; Panarin, Yu. P., *et al.*, 1997, *Phys. Rev.* E, **55**, 4345].
7. Gleeson, H. F., *et al.* [ILCC98 Strasbourg, P2-187] treated Sm C_β^* in a way completely different from ours. Our standpoint is that all the subphases under consideration results from a common cause; on the other hand, they tried to explain C_β^* alone separately.
8. Gorecka, E., *et al.*, 1990, *Jpn. J. appl. Phys.*, **29**, 131.
9. Itoh, K., *et al.*, 1997, J. *Mater. Chem.*, **7**, 407.
10. Fukuda, A., 1995, *Proc. Asia Display'95*, Hamamatsu, p. 61.
11. Fukuda, A., and Matsumoto, T., 1997, *Proceedings IDW'97*, Nagoya, p. 355.
12. Fukuda, A., *et al.*, 1997, *Mol. Cryst. liq. Cryst.*, **303**, 379.
13. Motoyama, H., *et al.*, 1996, Japanese Patent Gazettes, H8(1996)-337555.
14. Yamashita, M., 1997, *Mol. Cryst. liq. Cryst.*, **303**, 153 and references therein.
15. In ILCC98 Strasbourg, Pindak *et al.* [Invited A2-I1; and also see: Mach, P., *et al*, 1998, *Phys. Rev. Lett.*, **81**, 1015] reported the first direct structural observation of distinct superlatice periodicities by resonant X-ray scattering. They confirmed the three-layered ($q=1/3$) and four-layered (q=1/4) periods in ferri I and ferri II phases, respectively; the ferri I phase has been identified as Sm-Cγ* by the miscibility test [Nguyen, H. T., *et al.*, 1994, *Liq. Cryst.*, **17**, 571]. Our various experiences lead us to believe that the ferri II phase must be antiferroelectric and miscible with AF. Without proposing any detailed structural models, they suggested that their experimental results could be explained by the *X-Y* (clock) model. However, we are quite puzzled about their suggestion, because the *X-Y* model could not explain the fact that the helicoidal structure is clearly observed optically in both Sm C_A^*(q=1/3) and Sm C_A^*($q=1/4$) in some compounds.
16. Cepic, M., and Zeks, Z., 1997, *Mol. Cryst. liq. Cryst.*, **301**, 221.
17. Sun, H., *et al.*,1993, *J. Phys. Soc. Jpn.*, **8**, 2706.
18. Gisse, P., *et al.*, 1996, *Ferroelectrics*, **178**, 297.
19. Roy, A., and Madhusudana, N. V., 1998, *Europhys. Lett.*, (in the press).
20. Seomun, S. S., *et al.*, 1997, *Jpn. J. appl. Phys.*, **36**, 3586.
21. Seomun, S. S., *et al.*, 1998, *Jpn. J. appl. Phys.*, **37**, L691.
22. Seomun, S. S., *et al.*, 1998, *Liq. Cryst.*, (in the press).
23. Pauwels, H., *et al.*, 1998, ILCS98, Strasbourg, P4-64.
24. Clark, N. A., 1998, Comment on Plenary B by A. Fukuda at *ILCC98*, Strasbourg.
25. Bo, J., *et al.*, 1996, *Phys. Rev.* E, **53**, R4295.
26. Stebler, B., 1998, *Information Display (Official Monthly Publication of the Society for Information Display)*, **14**(2), 20.