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Methods for Preparing SSFLC Cells and their Electro-Optical Properties

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The methods of preparing monodomain cells of ferroelectric liquid crystals are reviewed. A sophisticated novel method based on the epitaxial growth of the smectic phase from a spacer edge under a temperature gradient is concluded to work quite well in preparing SSFLC (surface stabilized ferroelectric liquid crystal) cells of high quality at least for the three phase sequences: (1) Iso→Sm A→Sm C*, (2) Iso→N*→Sm A→Sm C* and (3) Iso—Sm C*. By using these high quality cells of DOBAMBC, three findings are made: (1) The characteristic "zigzag line" defects are the screw and edge dislocations decorated by the singularities of the director field. (2) A new kind of walls is observed and tentatively assigned, which moves not only in the twisted (splayed) states but also in the uniform state. (3) The bump due to the polarization realignment shows two peaks corresponding to the two kinds of wall movements induced by the applied triangular wave; one is due to the transition from the uniform to the twisted state and the other from the twisted to the opposite uniform state.

1. INTRODUCTION

Ferroelectric liquid crystals present some interesting problems of helix unwinding processes induced by an electric field or by the bounding surfaces; the electric field induced transitions among the several unwound surface stabilized states are particularly important from an applicative point of view.[1–4] Because any defects may disturb the study of the processes and the transitions, it is necessary to prepare liquid crystal cells of high quality. We have been trying to obtain

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them by several methods.[5–8] In this report, we summarize these methods and show that epitaxial growth from a spacer edge under a temperature gradient is most appropriate for preparing surface stabilized ferroelectric liquid crystal (SSFLC) cells. Then we mention three findings, which are brought about because of the high qualtiy of these SSFLC cells.

2. PREPARATION OF MONODOMAIN CELLS

There are two typical alignments of liquid crystal molecules in a cell; one is the homogeneous alignment where the molecules are parallel to the bounding plates, while the other is the homeotropic alignment where they are perpendicular to the plates. In this report, we will restrict our attention to the nearly homogeneous alignment, because the surface stabilized states may appear in this case. Table I lists several methods for homogeneously aligning nematic liquid crystals now widely used in display panels. We can align the molecules by introducing materials into a cell in the nematic state. This is because nematic liquid crystals are fluids anyway, and hence their viscosity is relatively low. In the smectic state, on the other hand, introducing materials into a cell does not result in a monodomain, even when the bounding surfaces of glass plates are treated properly or a field, electric or magnetic, is applied. Only exception is the application of shearing stress in the Sm A phase used by Clark and Lagerwall[1] to obtain monodomain cells. Generally, because of the lack of fluidity, it is necessary to grow the smectic phase in a higher temperature phase, isotropic or nematic, by lowering the temperature slowly.

2.1. Aligning of bâtonnets (aggregates of molecules)

Table II summarizes the phase sequences above the Sm C* phase, where the practically interesting ferroelectricity appears. Type 1 has been studied most in detail, because the first discovered ferroelectric liquid crystal, DOBAMBC, has this phase sequence.[9] Here we mainly treat this type, and unless otherwise stated the sample used is DOBAMBC. Rubbing and oblique evaporation are very effective methods for producing the uniaxial planar boundary, where the molecules align along a particular direction parallel to the bounding surfaces. Lowering the temperature gradually, there appear bâtonnets aligning along the direction as illustrated in Fig. 1. They grow and coalesce to form a Sm A monodomain. Complications arise when the phase

TABLE I

Several methods for homogeneouly aligning nematic liquid crystals

	processes
a	Oblique evaporation of SiO etc.
b	Rubbing after coating with polyimide etc.
c	Application of magnetic field
d	Application of electric field

TABLE II

Phase sequences above the Sm C* phase

types	phase sequences
1	Iso → Sm A → Sm C*
2	Iso → N* → Sm A → Sm C*
3	Iso → N* → Sm C*
4	Iso → Sm C*

transition from Sm A to Sm C occurs, because the molecules tend to incline from the layer normal gradually. The complications may be compromised by tiling the molecules and/or the layers themselves properly. These methods, particularly rubbing, must be very important ones from an applicative point of view, specifically in connection with the threshold problems in the switching properties. Since we have not studied these methods, however, we will not mention them any more here.

Actually, we have been using the random planar boundary, where the surface interaction anchors the molecules parallel to the surface but without any preferred direction. Hence we have to apply a field, electric or magnetic, in order to align molecules in a particular direction it specifies. When the Sm A liquid crystals under consideration are dielectrically positive, i.e. $\epsilon_{\parallel} - \epsilon_{\perp} > 0$, an electric field is effective, though it should be applied parallel to the bounding surfaces. Here $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the components of the dielectric constant parallel and perpendicular to the molecular long axis, respectively. A magnetic field is effective for liquid crystals consisting of molecules with benzene rings. In previous papers[5] we reported that, as the temperature decreases, the Sm A phase appears as bâtonnets in the isotropic phase and that the bâtonnets aligning along an applied magnetic field grow and coalesce to form a monodomain; surprisingly, almost all defects, present in bâtonnets or produced during coalescence, disappear when the cell is rather thick. As the cell

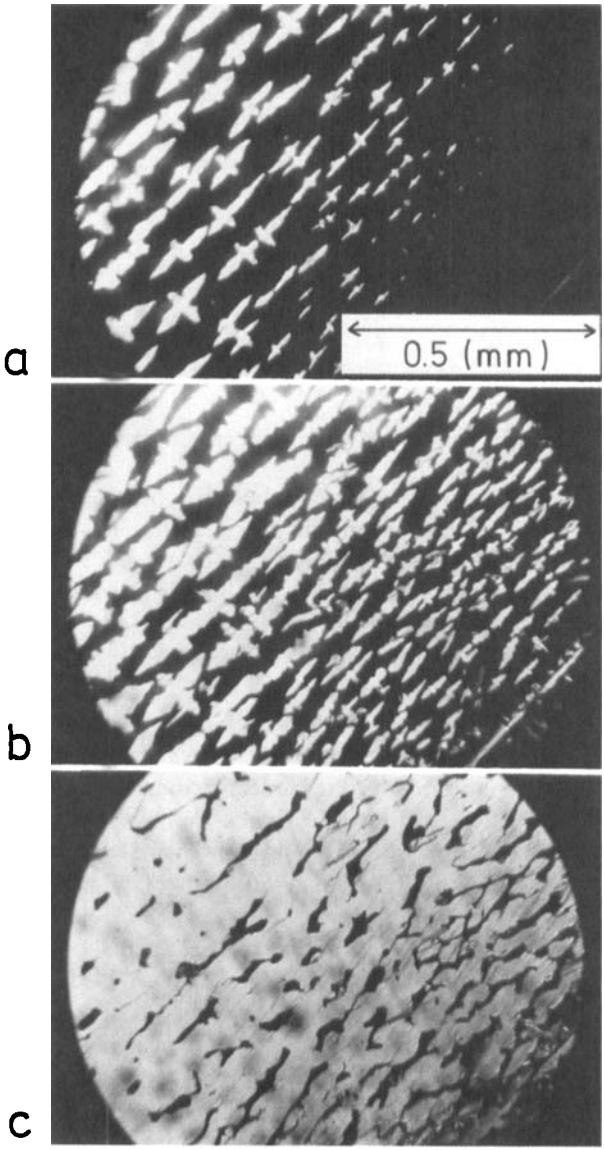


FIGURE 1 Aligning of bâtonnets along a rubbing direction.

becomes thinner, however, it gets more difficult to obtain a cell of high quality, because the bounding surfaces of plates strongly hinder the bâtonnets from aligning along the magnetic field.[6] Practically, the method of aligning bâtonnets by a magnetic field is suitable for preparing cells thicker than several tends of micrometers.

2.2. Epitaxial growth from a spacer edge under a temperature gradient

In the method mentioned above, we are trying to align molecules or, more properly, aggregates of molecules (bâtonnets) just as in nematic liquid crystals. Since smectic liquid crystals are one dimensional solids (crystals), however, there should exist another method based on the concept of crystal growth. A temperature gradient is essential for growing crystals. We have tried two arrangements in producing a temperature gradient. One is an orthodox arrangement shown in Fig. 2, where the two ovens are placed in tandem and a temperature gradient is produced between them by controlling their temperatures independently; passing a sample cell through the temperature gradient, we grow a monodomain in it. The other is a sophisticated novel arrangement, where one of the two bounding surfaces has a special pattern of nesa film electrodes illustrated in Fig. 3, a part of which acts as a local heater producing a temperature gradient as large as several tens of degrees in centigrade per millimeter. This is an improved version of the previous one.[8] An electric current flows through ABCD, which is completely separated from the other electrode EFG for applying switching voltages; the BC part acts as a local heater.

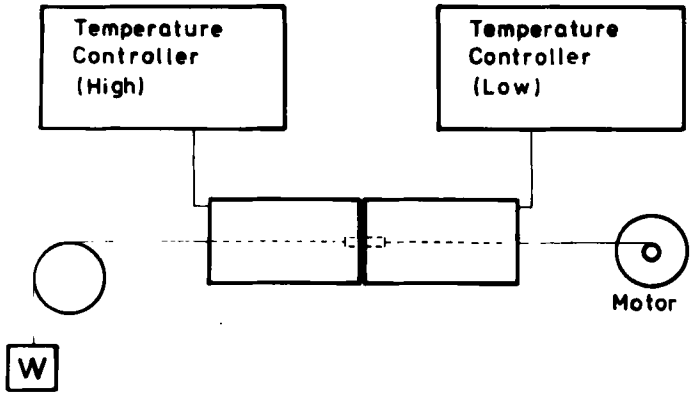


FIGURE 2 An orthodox arrangement for producing a temperature gradient.

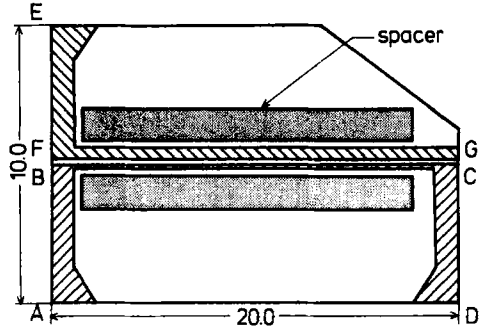


FIGURE 3 A sophisticated novel arrangement using a special pattern of nesa film electrodes as a local heater.

Another important thing to be considered is the control of nucleation. In previous papers,[7,8] we pointed out that the edge of a polyethylene terephthalate (PET) film cut by a sharp knife is favorable for the aligned nucleation of the Sm A phase with their layers perpendicular to the edge and the bounding surfaces. At the beginning, we thought that a spacer edge cut parallel to the main drawing direction forces the molecules parallel to it while an edge cut perpendicular to it does not. Recently, however, we found that even an edge cut obliquely to the main drawing direction can align the molecules parallel to itself; rubbing the spacer edge and/or realigning the polymer chains appear to be associated with the cutting process, giving it an ability to align the molecules parallel to the edge.

Conflicting evidences exist, though; Kevlar (poly paraphenylene terephthalamide) fibers whose surface must consists of well aligned polymer chains have little ability to nucleate the Sm A phase when the temperature decreases rather uniformly without producing a temperature gradient intentionally. When a sharp temperature gradient exists across the Kevlar fibers, on the other hand, the aligned nucleation of the Sm A phase occurs apparently at the surfaces and a monodomain of high quality is produced as shown in Fig. 4. Even an aluminum foil and a glass fiber whose edge or surface was not treated intentionally appear to have an ability to align the molecules in the temperature gradient. Moreover, a temperature gradient itself appears to control the aligning direction at least after a large area of the Sm A phase has been formed; there is a tendency that the Sm A and isotropic boundary becomes perpendicular to the temperature gradient. The tendency appears to cause focal conics when the boundary is not perpendicular to the gradient as seen in Fig. 3 of ref. 8.

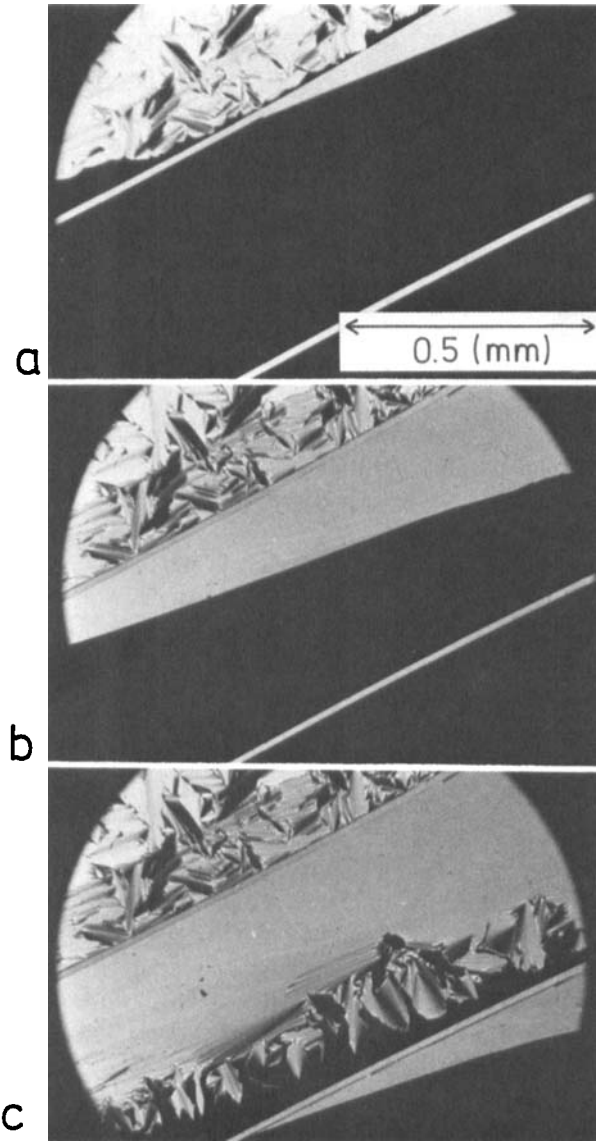


FIGURE 4 When a temperature gradient exists across the Kevlar fibers, the aligned nucleation of the Sm A phase occurs apparently at the surfaces, forming a mono-domain of high quality.

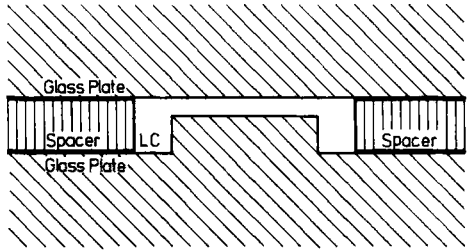
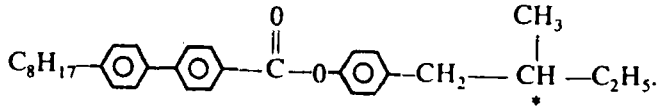


FIGURE 5 A method for obtaining a cell as thin as 1 μm. A step is prepared on one of the bounding surfaces to compensate the thickness of PET films.

In all events, this method based on the epitaxial growth of the Sm A phase from a spacer edge under a temperature gradient works quite well. We can obtain a monodomain cell as thick as several hundreds micrometers by using the Bridgman type oven shown in Fig. 2. As for thin cells, the novel method with nesa film electrodes is very effective, but some problems arise. It is difficult to handle the spacers when they are less than 6~4 μm in thickness. Moreover, the thinnest PET films commercially available is about 2 μm. To avoid these difficulties, we tried to make a step on one of the bounding surfaces to compensate the thickness of PET films as illustrated in Fig. 5. Actually this was done by photo-resist technique using dilute HF solution as etchant. Thus we can prepare cells as thin as 2 μm or less, but it is still not easy to obtain cells as thin as 1 μm or less.

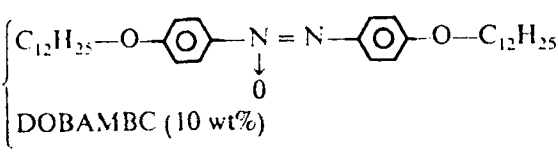
2.3. Epitaxial growth in the phase sequences other than type 1

Epitaxial growth from a spacer edge under a temperature gradient must also be effective for phase sequences other than type 1. Under the random planar boundary, the helical axis of the N^* phase is perpendicular to the bounding surfaces. Since the helical pitch diverges at the phase transition, however, the Sm A phase with the layers perpendicular to the bounding surfaces must grow from the spacer edge without trouble; hence the method works quite well in type 2 as actually confirmed using 8SI*[10]

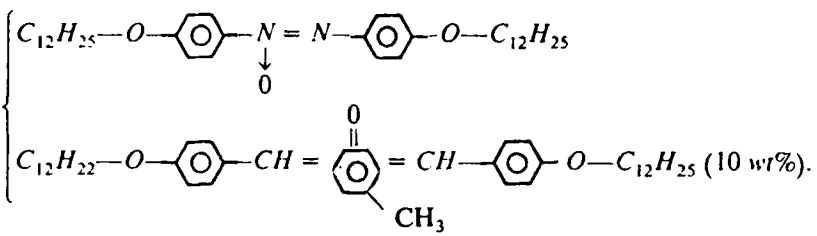


In the case of type 4, one problem needs to be solved; the aligned nucleation at the spacer edge is compatible with the two possible layer

orientations. Either of these two possibilities is selected by applying an electric field perpendicularly to the bounding surfaces. In fact, we can prepare a monodomain cell of high quality as demonstrated using two mixtures,[11]



and



Type 3 is slightly complicated. Since the helical pitch does not appear to diverge at the phase transition, the twisting power may hinder the aligned nucleation at a spacer edge. When the N^* phase is dielectrically negative, $\epsilon_{\parallel} - \epsilon_{\perp} < 0$, however, we may be able to use epitaxial growth from a spacer edge under a temperature gradient with applying an electric field perpendicularly to the bounding surfaces. When it is dielectrically positive, $\epsilon_{\parallel} - \epsilon_{\perp} > 0$, an electric field applied for selecting either of the two possible layer orientations may align the molecules in the N* phase perpendicularly.

3. SOME FINDINGS OBTAINED USING THE HIGH QUALITY SSFLC CELLS

3.1. Dislocations decorated with director singularities[12]

Now we mention three findings obtained using the high quality SSFLC cells. The first one relates to the identification of characteristic "zigzag line" defects appearing in SSFLC cells. Since the cell is almost free from other defects, such as focal conics, the defects under consideration reveal their typical aspects as shown in Fig. 6. They consist of thin lines perpendicular to the smectic layers and of rather thick lines connecting the thin lines at their ends alternately. The

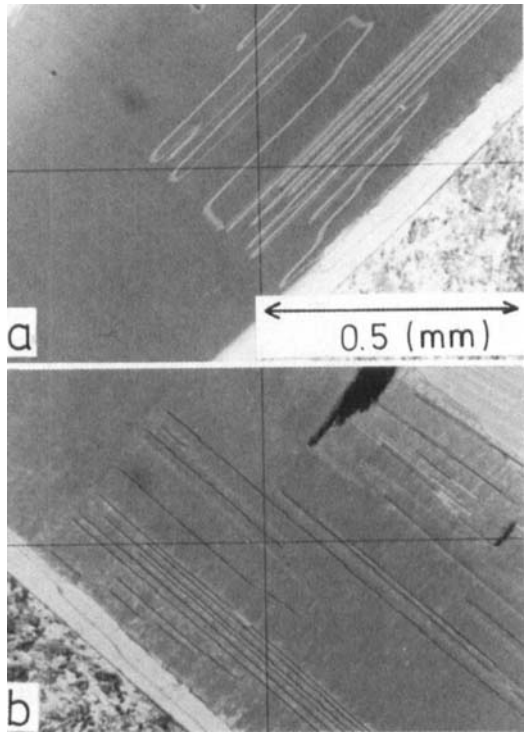


FIGURE 6 Characteristic "zigzag line" defects observed in a SSFLC cell. (a) 13 V is applied, and (b) no voltage is applied. The cell thickness is about 4 μm. See Color Plate V located in the final volume of these Conference Proceedings.

neighboring thin lines look different one after the other and these appearances alter to each other by reversing the C-director field; there exist two kinds of thin lines. One kind of lines sometimes consist of two kinds of segments, which are slightly laterally moved each other.

The pattern of the defects is so regular that we strike on the following model. The thin and thick lines are assigned to the screw and edge dislocations decorated with the singularity of C-directors.[12] The difference in appearances of the thin lines is attributed to the relation of handedness between the screw dislocations and the $s = +1$ disclinations. The handedness also plays an important role in causing discontinuous lateral shifts to produce the two kinds of segments. In all events, we can plausibly argue that the dislocations decorated with the disclinations and other singularities of C-directors are responsible for the characteristic "zigzag line" defects appearing in SSFLC cells.

3.2. The number and the structure of surface stabilized states

The second finding is concerned with the number and the structure of surface stabilized states. There exist two kinds of twisted states with splayed polarization in addition to the two uniform, up and down, states (UU and UD).[1-4] The polarizations at the bounding surfaces are directed outwards in one twisted state (TO),[2,3] while they are directed inwards in the other twisted state (TI).[4] All the four states, uniform and twisted, are observed as shown in Fig. 7, which was obtained by cooling a cell constituting a monodomain in the Sm A phase to the Sm C phase with the electrodes short-circuited. The probability that each of these states appears critically depends on samples used, surface conditions, voltages applied now and before, etc. Aging also seems to affect the probability; the adsorption of some charged molecules contained in samples as impurities may be responsible for the aging effect. The UU state borders the UD state directly or via either of the TO or TI state. The transitions between these states induced by an electric field does not occur as a movement of clear-cut walls, specifically when the cell is not really thin; instead, many spotted favorable states appear here and there in unfavorable states and grow gradually until all areas are covered by the favorable states.

Clear-cut walls are frequently observed within the TI state. Figures 8 (a) and (b) were obtained with the crossed polarizer and analyzer combination by rotating the layer normal by $\pm\Theta$ from the polarizer direction, respectively. The black (blue) region in Fig. 8 (a) and the blue (black) region in Fig. 8 (b) represent the UD (UU) state. When the analyzer is rotated by $+2\Theta$, the pink and white (black and blue) regions in Fig. 8 (a) and (b) become dark (light) as shown in Fig. 8 (c); hence both the pink and white regions are in the TI state. In other words, the TI state has two substates, which are quite symmetric in the sense that the pink (white) region in Fig. 8 (a) transforms into the white (pink) region in Fig. 8 (b) and that the border between the two substates is very vague when the layer normal is parallel to the polarizer direction.

When we apply a voltage favorable to one of the uniform states, e.g., the UU state in Fig. 9 (a), the border between the two substates moves as a clear-cut wall. The wall movement expands the pink region into the white region as illustrated in Fig. 9 (b). Then the wall enters into the black region, changing it into the red region as shown in Fig. 9 (c). Finally the red region transforms into the pink region as seen in Fig. 9 (d). Handschy[3] observed the similar wall in the twisted

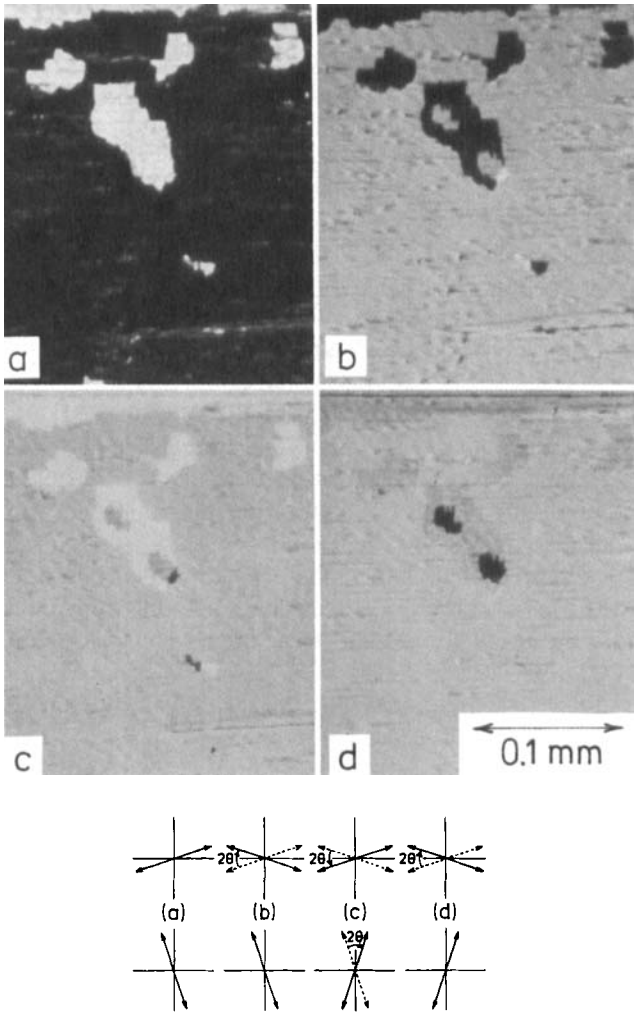


FIGURE 7 All the four states, uniform and twisted, are observed in a cell when cooling a Sm A monodomain to the Sm C phase with the electrodes short-circuited. The black regions correspond to (a) UD, (b) TI, (c) TO, and (d) UU, respectively. A polarizer and an analyzer are set as indicated in the lower part, where Θ is the tilt angle of the Sm C phase. The cell thickness is about 10 μm. respectively. For details, see text. See Color Plate VI, located in the final volume of these Conference Proceedings.

state and tried to explain it by introducing the circular conical boundary with and without tilting the smectic layer normal away from the bounding plates. When a transition requires to rotate the molecules on the boundary surfaces, however, it does not appear to occur as a movement of clear-cut walls as pointed out above. There-

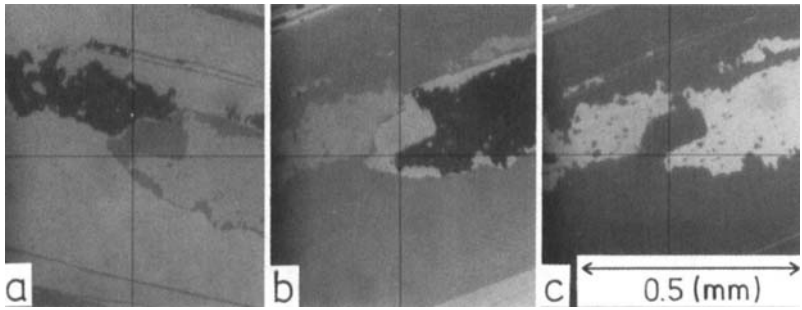


FIGURE 8 Clear-cut walls (the boundary between pink and white in (a) and (b)) observed within the TI state. The polarizer and analyzer directions in (a) and (b) coincide with cross-hairs; in (c) the polarizer direction coincides with the horizontal cross-hair but the analyzer direction is rotated by twice the tilt angle from the vertical cross-hair. Black and blue in (a) and (b) and white in (c) are the uniform (UD and UU) states; pink and white in (a) and (b) and black in (c) are the twisted (TI) state. The cell thickness is about 5 μm. See Color Plate VII, located in the final volume of these Conference Proceedings.

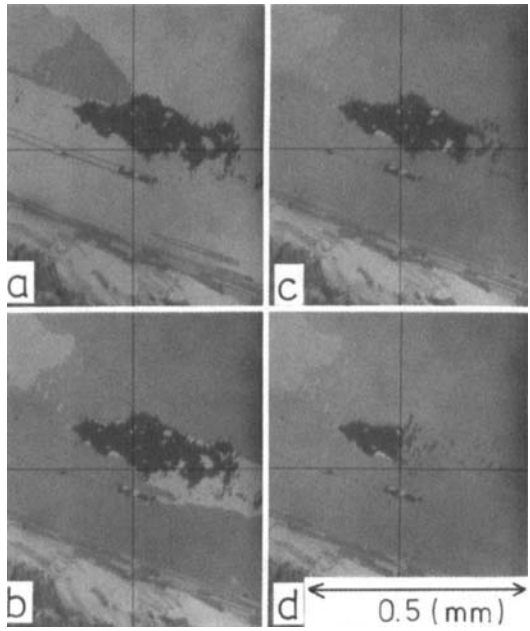


FIGURE 9 Electric field induced movement of clear-cut walls. The applied electric field first spreads pink into white. Then the wall enters into black, changing black into red. Finally, red further transforms into pink. In (d), about 0.7 V is applied. The cell thickness is about 5 μm. See Color Plate VIII, located in the final volume of these Conference Proceedings.

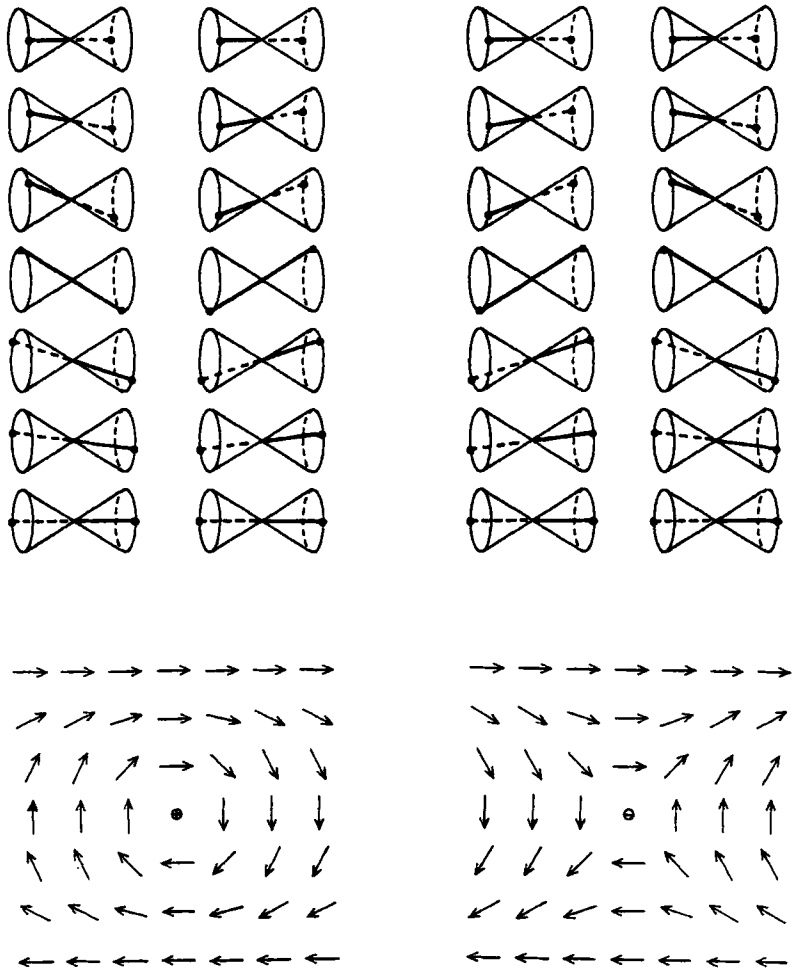


FIGURE 10 A model of the clear-cut walls.

fore, we suspect that the wall movement under consideration does not involve the molecules on the bounding surfaces. Rather, the molecules in the middle must be responsible for the wall movement.

Considering the symmetry observed in Figs. 8 (a) and (b), we tentatively assign this wall to the boundary between the twisted states shown in Fig. 10. The simplest of such a boundary must contain a disclination. The existence of a disclination favors to explain the fact that the wall crosses the boundary and enters into the UD state and that it stays rather stably. The transformation from the red to the pink

region must involve the rotation of the molecules on the bottom surface, because the transition from the UD to the TI states needs to occur. Actually, the spotted unfavorable red region disappears here and there, while the pink and red regions as a whole are separated by a clear-cut wall from the black and white regions as a whole. The molecules on the top and bottom bounding surfaces in the red region stay in the same positions as in the black region, while only the molecules in the middle rotates accordingly.

3.3. Polarization realignment corresponding to transitions among surface stabilized states

The third finding is concerned with the method of measuring spontaneous polarization. In a previous paper,[13] we proposed to apply the direct measurement of spontaneous polarization using triangular waves to ferroelectric liquid crystals. This allows us to observe a bump due to the polarization realignment appearing on a straight line. When the cell is thin and its quality is really good, we can observe at least two kinds of wall movement induced by the applied triangular wave; one is due to the transition from the uniform to the twisted state and the other to that from the twisted to the uniform state. When we try to measure the spontaneous polarization in such a cell, the bump due to the polarization realignment shows two peaks as illustrated in Fig. 11. When the cell is not of high quality, consisting of multi-domains, we could not observe the two peaks and instead a

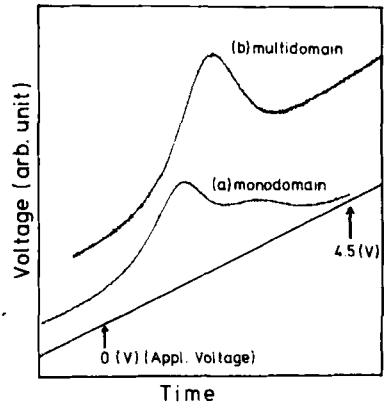


FIGURE 11 A bump due to the polarization realignment caused by a triangular voltage wave of 5 Hz, (a) for a monodomain cell of high quality and (b) for a multidomain cell. The cell thicknesses are 10 μm thick. Note that the areas of both bumps in (a) and (b) are nearly the same.

single broad peak located in between appears. The two peaks must reflect the polarization realignment corresponding to the transitions from the uniform to the twisted state and then to the opposite uniform state.

References

1. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.* **36**, 899 (1980).
2. M. A. Handschy, N. A. Clark and S. T. Lagerwall, *Phys. Rev. Lett.* **51**, 471 (1983).
3. M. A. Handschy, Thesis (University of Colorado, 1983).
4. M. Glogarová and J. Pavel, *J. de Phys.*, **45**, 143 (1984).
5. K. Kondo, F. Kobayashi, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.* **20**, 1733 (1981).
6. K. Kondo, Y. Sato, K. Miyasato, H. Takezoe, A. Fukuda, E. Kuze, K. Flatischler and K. Skarp, *Jpn. J. Appl. Phys.* **22**, L13 (1983).
7. K. Kondo, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.* **22**, L85 (1983).
8. K. Ishikawa, K. Hashimoto, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.* **23**, L211 (1984).
9. R. B. Meyer, L. Liébert, L. Strzelecki, P. Keller, *J. de Phys.* **36**, L69 (1975).
10. H. R. Brand and P. E. Cladis, *J. de Phys. Lett.* to be published. (1984).
11. J. Pavel, M. Glogarová, D. Demus, A. Mädicke and G. Pelzl, *Cryst. Res. Technol.* **18**, 195 (1983).
12. K. Ishikawa, T. Uemura, H. Takezoe and A. Fukuda, *Jpn. J. Appl. Phys.* **23**, L666 (1984).
13. K. Miyasato, S. Abe, H. Takezoe, A. Fukuda and E. Kuze, *Jpn. J. Appl. Phys.* **22**, L661 (1983).