VOLUME 86, NUMBER 20 PHYSICAL REVIEW LETTERS 14 MAY 2001

# Coexisting Nematic and Smectic-*A* Phases in a Twisted Liquid-Crystal Cell

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(Received 6 April 2000)

Twisted homogeneously planar-aligned nematic liquid-crystal cells are cooled into the smectic-*A* phase. The expected defective structure does not form. Instead the cells still show good optical-guiding characteristics. Exploration of the cells using a half-leaky guided-mode arrangement reveals that the liquid-crystal phase separates into three or more regions. Adjacent to both the upper and lower boundaries is a region of highly twisted nematic liquid crystal. In the center of the cell is one or more homogeneous smectic-*A* regions with smectic layers normal to the cell surfaces, separated by twisted nematic. As the cell is cooled so the smectic-*A* regions grow in thickness with the nematic regions progressively thinning but with increased twist gradient. A theoretical model of these novel results is presented.

DOI: 10.1103/PhysRevLett.86.4548 PACS numbers: 61.30.–v, 64.70.Md

Twisted nematic liquid-crystal cells are the important elements of the most widespread electro-optic liquid-crystal display devices which have numerous applications in industry and everyday life. In such cells the surfaces promote homogeneously planar alignment of the nematic director. However, the alignment directions on the two surfaces are generally obliged to be nonparallel resulting in a homogeneous twist of the director across the cell. The corresponding twist deformation is characterized by the twist gradient $d\phi/dz = q$ which is equal to the wave number of the (infinite) homogeneously twisted director profile. Here the azimuthal angle $\phi$ specifies the director orientation in the plane of the cell. The properties of twisted nematic cells are well understood, but there is no information about the structure of such cells below the nematic-smectic transition temperature. In fact, it is difficult to predict *a priori* what will happen to a twisted nematic cell when it passes through the phase transition point into a smectic-*A* or smectic-*C* phase. Since the smectic layers cannot sustain twist does the system become full of defects or can some other defect-free configuration exist? This phase transformation is also interesting from the fundamental point of view because it represents a nontrivial example of a transition in an inhomogeneous soft system in a confined geometry. The properties of such a transition are expected to be strongly dependent on the cell thickness. Moreover, this dependence may be qualitatively different from that observed in freely suspended liquid-crystal films [1–3] and in thin homogeneous liquid-crystal cells [4–7]. In this work we use a very sensitive optical procedure, the half-leaky guided-mode [8] (HLGM) method, to allow accurate characterization of the director profile in thin cells, to study the behavior on cooling of a $S_{C^*}$ material which has the phase sequence: $N^*$-$S_A$-$S_{C^*}$ in twisted cells. We then proceed to develop a theory which explains the primary features of the results.

The sample comprises a twisted homogeneously planar-aligned cell with an angle of 87° between the two polyimide rubbing directions of the top and bottom substrate. The liquid-crystal material is the ferroelectric liquid crystal SCE13. Cells are filled under vacuum in the isotropic phase then slowly cooled to room temperature before being placed onto the computer controlled rotating stage for optical data recording. A coupling prism with the same high index as the top glass plate is optically attached to the cell using index-matching fluid. Then using well-collimated, linearly polarized, monochromatic (632.8 nm) radiation, angle dependent reflectivity data are recorded. First the polarization-conserving signals $R_{ss}$ and $R_{pp}$ in the isotropic phase (~110 °C) are obtained. Upon cooling into the $N^*$ phase a well-aligned monodomain forms. Now, with the rubbing direction on the top substrate aligned in the plane of incidence, the $R_{ss}$, $R_{pp}$, and $R_{sp}$ (polarization conversion) data are recorded at different temperatures. Further cooling takes the cell down into the $S_A$ phase, and finally into the $S_{C^*}$ phase. From close to the $N^*$-$S_A$ phase transition data are taken at intervals of about 1° down to the $S_{C^*}$ phase.

From fitting the angle dependent reflectivity data in the isotropic phase with multilayer optical modeling theory the optical parameters of the boundary layers of the cell are determined. These boundary parameters are then used in the data fitting process which allows the determination of the liquid-crystal director structure in the cell as it is cooled through the $S_A$ region.

In the $N^*$ phase we find, as expected, a uniformly twisted director profile in the cell. Because of finite surface anchoring there are small director angle shifts from the rubbing direction (the easy axis) on both surfaces. The angle shifts for the thinnest cell (1.6 $\mu$m) studied are of the order of 9°(88 °C) reducing to about 8° (79 °C). This is due to the increase of the surface anchoring energy at lower temperatures, in accord with the results of Blinov *et al.* [9]. From the data taken on slow cooling it is easy to identify the $N^*$ to the $S_A$ phase transition point by the sudden appearance, between 67.0 and 67.8 °C, of an extra optical mode feature. At the same time we note that the very low

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background signal in the $R_{sp}$ data remains, confirming that the cell is still a monodomain. To fit the angle dependent data in the temperature range below where the extra mode feature appears demands a very different model to the linearly twisted nematic. For the 1.6 $\mu$m cell an untwisted homogeneous region forms in the center of the cell. This we identify as a region of $S_A$ material. This is separated from the walls by thin regions of nematic with a higher twist gradient than before the $S_A$ nucleated. Upon further cooling the thickness of the $S_A$ region grows at the expense of the nematic (Fig. 1). Even more startling, the only way to fit the optical data for the higher thickness cells is for the 2.0 $\mu$m cell to have two regions of uniform azimuthal angle ($S_A$) separated by a twisted nematic with two twisted nematic boundary regions (Fig. 2a), while for the 2.4 $\mu$m cell there are three $S_A$ regions separated by two twisted layers with two twisted boundary layers (Fig. 2b). The uniqueness of this data fitting is confirmed by use both of direct search minimization routines and generic algorithm for establishing the director profile which fits the optical data. One notes that the structure of those cells resembles a simplified (melted) twisted grain boundary phase in which mutually twisted smectic blocks are separated by melted (twisted nematic) layers. Our fits show that the $S_A$ phase exists over a very small temperature range in these twisted thin cells. The phase sequences for the three cells studied are

$$d = 1.6\ \mu\text{m},\quad N^*\text{-67.4 °C-}S_A\text{-65.0 °C-}S_{C^*}\,;$$

$$d = 2.0\ \mu\text{m},\quad N^*\text{-69.0 °C-}S_A\text{-66.0 °C-}S_{C^*}\,;$$

$$d = 2.4\ \mu\text{m},\quad N^*\text{-70.0 °C-}S_A\text{-66.3 °C-}S_{C^*}\,.$$

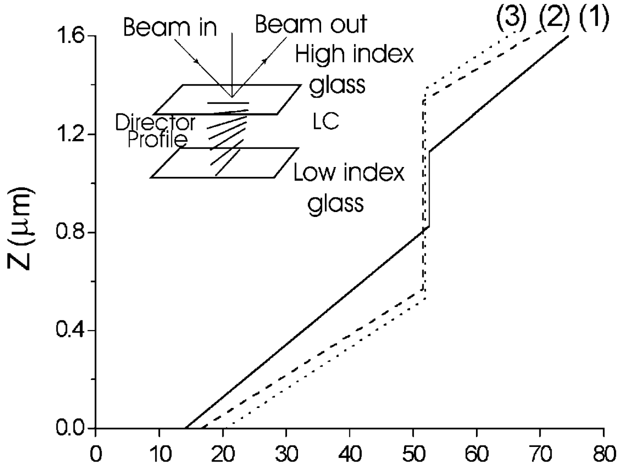

FIG. 1. Director twist angle profiles $\phi(z)$ across the 1.6 $\mu$m twisted liquid-crystal cell obtained using the half-leaky guided-mode method for three different temperatures. (1) $T = 67.0$ °C; (2) $T = 66.3$ °C; (3) $T = 65.8$ °C. Note the untwisted region in the center of the cell which is identified as a region of smectic-$A$ material that grows with decreasing temperature. The inset shows a schematic of the geometry of the experiment.

Comparing the above data with the bulk phase sequence $N^*$-86.3 °C-$S_A$-60.8 °C-$S_{C*}$, we note the huge reduction of the $N^*$ to the $S_A$ phase transition caused by the high twist gradient in the liquid crystal (44° per $\mu$m). This suppression in phase transition has to be expected since the $S_A$ phase cannot tolerate any twist.

This extraordinary phase behavior in the twisted cell demands theoretical interpretation. The essence of this explanation is that there is a delicate balance between the free energies of the twisted nematic plus the interface energies and the free energy of the $S_A$ relative to the twisted nematic. On forming a region of $S_A$ there is an automatic increase of twist energy (the twist has to be accommodated in the nematic region) within the nematic as well as an increase in surface free energy. Hence the system opposes the formation of the low temperature phase. In a thin enough cell the $S_A$ phase may be expelled altogether.

The equilibrium thickness $d_A$ of the single $S_A$ region inside a twisted cell corresponds to a minimum of the total free energy which includes the energies of $S_A$ and twisted nematic regions plus the energy of all interfaces. The total

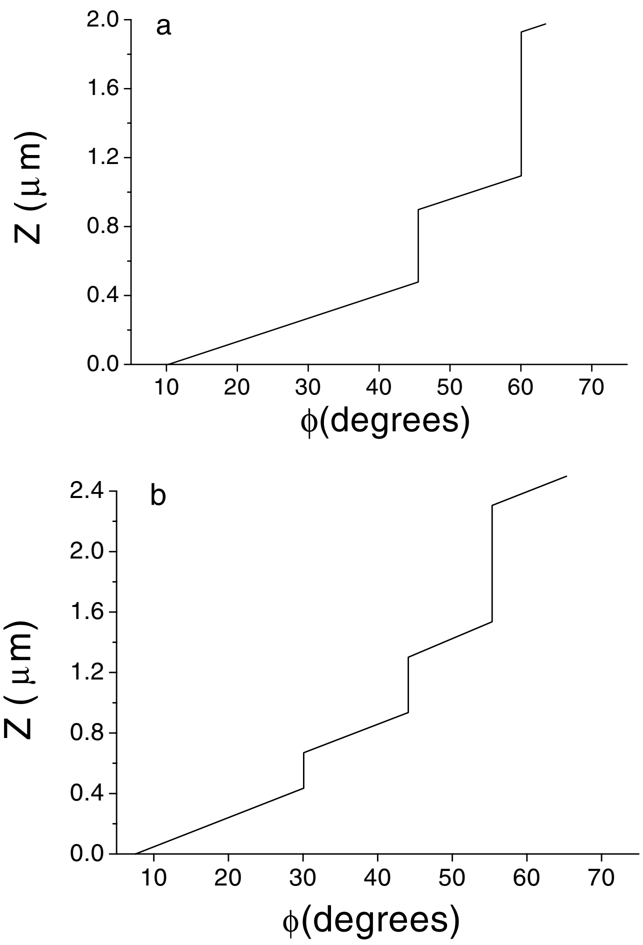

FIG. 2. Director twist angle profiles $\phi(z)$ in the 2.0 $\mu$m twisted cell with two separate smectic-$A$ regions (a), and in the 2.4 $\mu$m cell with three smectic-$A$ regions (b).

free energy of the cell per unit surface area (with respect to that of the untwisted nematic phase) can be written as

$$\Delta F_{N+A}/s = d_A\left[\frac{1}{2}\,\alpha(T - T^*)\psi^2 + \frac{1}{4}\,b\psi^4 + \frac{1}{6}\,c\psi^6\right] + \frac{1}{2}\,d_N K_{22} q^2 + 2\sigma_{NA} - 2W_S \cos^2\delta\phi\,. \tag{1}$$

In Eq. (1) the first term represents the free energy of the $S_A$ slab expanded in powers of the smectic order parameter $\psi$. The second term is the distortion energy of the nematic regions where $K_{22}$ is the twist elastic constant, $d_N = d - d_A$ is the total thickness of the nematic regions, $d$ is the cell thickness, and $q$ is the wave number of the homogeneous twist deformation in the nematic layers. The third term is the free energy of two equivalent $N$-$S_A$ interfaces, and the last term is the azimuthal anchoring energy of the nematic at the two surfaces of the cell written in a simple Rapini form. Here $\delta\phi$ is a director angle shift from the rubbing direction at the surface caused by the torque from the bulk, and $W_s$ is the anchoring strength. It should be noted that for simplicity we have omitted the natural twist term $\sim q$ in Eq. (1) which is related to the chirality of the material. Such a term does not influence the qualitative behavior of the system.

One readily obtains $q = (\Delta\phi_{12}^0 - 2\delta\phi)/d_N$, where $\Delta\phi_{12}^0 = 87°$ is the angle between the two rubbing directions of the top and bottom surfaces. The deviation from the rubbing direction $\delta\phi$ can be determined from the familiar boundary condition at the surface: $K_{22}(d\phi/dz) = K_{22}q = W_S \sin 2\delta\phi$. Experimentally $\delta\phi$ is rather small, $\delta\phi < 10°$, and therefore $\sin 2\delta\phi \approx 2\delta\phi$. Now there are two linear equations for $q$ and $\delta\phi$ and one obtains

$$\delta\phi = \Delta\phi_{12}^0/2(1 + y/\Delta), \quad q = \Delta\phi_{12}^0/d(y + \Delta), \tag{2}$$

where $y = d_N/d$ is the dimensionless thickness of the nematic regions and $\Delta = K_{22}/W_s d$. The parameter $\Delta$ can be estimated using the director twist angle profile presented in Fig. 1. For the 1.6 $\mu$m cell at $T = 66.3\,°\mathrm{C}$, $\delta\phi \sim 15°$, and $y \approx 0.53$. Substituting these data into Eqs. (2) one obtains $\Delta \sim 0.3$.

The free energy of the $N$-$S_A$ interface $\sigma_{NA}$ is qualitatively determined by the gradient term $(1/2)g(d\psi/dz)^2$ in the $S_A$ free energy density expansion in the boundary region. Thus, in the first approximation, $\sigma_{NA} = \sigma_0\psi_0^2$ where $\psi_0$ is the average smectic order parameter. In the present system the bulk and surface free energies in Eq. (1) can be clearly separated because the thickness of the boundary region, which is of the order of the parallel coherence length $\xi_\parallel$ [10], is much smaller than that of the $S_A$ slab which is formed well below the bulk $N$-$S_A$ transition temperature.

Substitution of Eqs. (2) into Eq. (1) yields

$$\Delta F_{N+A}/d = (1 - y) \times \left[\frac{1}{2}\,\alpha(T - T^*)\psi_0^2 + \frac{1}{4}\,b\psi_0^4 + \frac{1}{6}\,\psi_0^6\right] + \sigma_0\psi_0^2 + \frac{\tilde{K}}{\Delta + y} - \tilde{W}\,, \tag{3}$$

where $\tilde{K} = K_{22}\phi_{12}^2/2d^2$, and $\sigma_0 = \sigma_{NA}^0/d$. Smectic order parameter $\psi_0$ and the equilibrium thickness of the nematic layer $y$ can be determined by minimization of the free energy (3) with respect to $y$ and $\psi_0$:

$$-\frac{1}{2}\,\alpha(T - T^*)\psi_0^2 - \frac{1}{4}\,b\psi_0^4 - \frac{1}{6}\,\psi_0^6 - \frac{\tilde{K}}{(\Delta + y)^2} = 0\,, \tag{4}$$

$$(1 - y)[\alpha(T - T^*)\psi_0 + b\psi_0^3 + \psi_0^5] + 2\sigma_0\psi_0 = 0\,. \tag{5}$$

Solutions of Eqs. (4) and (5) are globally stable if the free energy density (3) is lower than the free energy of the twisted nematic cell without $S_A$ regions $F_N^{tw}/d = \tilde{K}/(1 + \Delta)$. The transition temperature in the twisted cell $T_0^*$ and the critical thickness of the $S_A$ region at the transition point are determined from equation $F_{N+A} = F_N^{tw}$ and Eqs. (4) and (5). At $I = T_c^*$ the smectic-$A$ region of thickness $y_c$ is spontaneously formed inside a twisted nematic cell. One notes that the temperature $T_c^*$ is different from the $N$-$S_A$ transition temperature $T_0(y_c)$ in the liquid-crystal layer of thickness $y_c$ with *fixed boundaries*. $T_0(y_c)$ is determined from the equation $d_A f_A + 2\sigma_{NA} = 0$ where $f_A$ is the free energy density difference between the $N$ and the $S_A$ phases [see the first three terms in Eq. (1)]. This condition is different from the one which determines $T_c^*$. In the case of a first order transition in the bulk $T_0(y) = T^*(y) + 3b^2/16\alpha c$, where the instability temperature $T^*(y) = T^* - G'/(1 - y)$ is shifted with respect to its bulk value $T^*$ due to the presence of the surface term [see Eq. (5)], and where $G' = 2\sigma_0/\alpha$. The $N$-$Sm_A$ transition in the bulk occurs at $T = T_0 = T^* + 3b^2/16\alpha c$.

One can obtain a simple approximate equation for $y(T)$ from Eqs. (4) and (5). Equation (5) has the following stable solution for the smectic order parameter $\psi_0^2(\tau) = (b/2c)1 + [1 + \tau^*(y) - \tau]^{1/2}$ where the dimensionless temperatures $\tau^*(y) = (4\alpha c/b^2)T^*(y)$ and $\tau = (4\alpha c/b^2)T$. The dimensionless $N$-$Sm_A$ transition temperature in the bulk $\tau_0 = \tau^* + 3/4$. Substituting this expression into Eq. (4) one obtains an explicit equation for $y(\tau)$ which depends on the difference $\delta\tau = \tau - \tau_0$. After the order parameter $\psi_0$ is expressed in terms of $\delta\tau$ and $G_0$, Eq. (4) can be expanded in powers of $\delta\tau$ assuming that the dimensionless temperature difference $\delta\tau$ is small. Equation (4) may also be expanded in powers of $G_0$ because the term $G_0/(1 - y)$, which represents the dimensionless surface energy, remains to be a correction if the smectic region is not too thin, i.e., if $y$ is not too close to 1. In our experiments $y < 0.8$. Performing the expansion simultaneously in $G_0$ and $\delta\tau$, keeping the linear terms and returning to the dimensional temperature $T$, one obtains a simple approximate equation for $y$:

$$\frac{\kappa}{(\Delta + y)^2} = T_0 - T - \frac{G}{1 - y}, \tag{6}$$

where $\kappa = 6\tilde{K}c/5\alpha b$ and $G = \sigma_0/5\alpha$. The solution of Eq. (6), which describes the temperature variation of the dimensionless thickness of the nematic region $y(T)$, is presented in Fig. 3 for $\Delta = 0.32, G = 0.1, T_0 = 65.5$ °C, and $\tilde{\kappa} = 1.8$. Stable solutions are represented by the lower branch of the solid curve in Fig. 3 while the upper branch is unstable. One can numerically calculate the free energy of the cell with $N$ and $S_A$ coexisting regions using Eq. (3) and a stable solution for the thickness $d_N$, and compare it with the free energy of the homogeneously twisted nematic cell. Calculations show that for the whole branch of stable solutions presented in Fig. 3 the free energy $F_{N+A}$ is lower then $F_N^{tw}$ and therefore the twisted cell with an $S_A$ region is globally stable in the corresponding temperature interval. In this case the $N$-$S_A$ transition in the twisted cell occurs at the turning point of the solid curve in Fig. 3 where the derivative $d\,(d_N)/dT$ diverges. This point determines the transition temperature $T_0^*$ and the critical thickness $y_c$. The transition is strongly first order and is accompanied by a spontaneous formation of the $S_A$ region of finite thickness $d_A^c$ comparable with that of the whole cell (in our case $d_A^c < 0.2d$). The experimental data for the temperature variation of the thickness $d_N$ for the 1.6 $\mu$m cell are also presented in Fig. 3 (squares). These data are quantitatively described by the present model. The model, however, does not describe the formation of more than one smectic region in thicker cells. One expects that several $S_A$ slabs always possess higher total free energy than the single slab of the total thickness because the additional $N$-$S_A$ interfaces are energetically unfavorable while the total elastic energy remains the same. It is reasonable to suppose that these structures are nonequilibrium ones and appear as a result of nucleation kinetics. Such structures, once formed, are locally stable because two neighboring $S_A$ slabs cannot coalesce without overcoming a high potential barrier. Two $S_A$ slabs begin to repel each other when the separation is decreased because the elastic energy in the nematic gap is increasing.

In conclusion, using the HLGM technique we have found the existence of well-aligned $S_A$ phase regions in thin, twisted homogeneously planar-aligned liquid-crystal cells. The strong twist gradient causes a large reduction in the phase transition from the $N^*$ to the $S_A$ phase in the cells studied. The $S_A$ phase exists in thin layers, separated by a $N^*$ region, the number of such layers appearing to depend upon the cell thickness. For the thinnest cell a thermodynamic model of the phase behavior provides a complete explanation for the temperature dependence of the thickness of the single smectic-$A$ region observed.

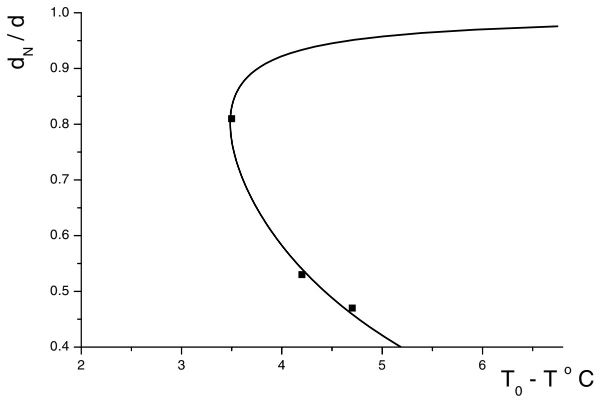

FIG. 3. Predicted temperature variation of the thickness of the smectic-$A$ region in the twisted 1.6 $\mu$m cell obtained from Eq. (6) (solid curve). Stable solutions correspond to the lower branch of the curve. Experimental points are denoted by squares.

The authors acknowledge the support of the Engineering and Physical Sciences Research Council and the Defence Evaluation and Research Agency.

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