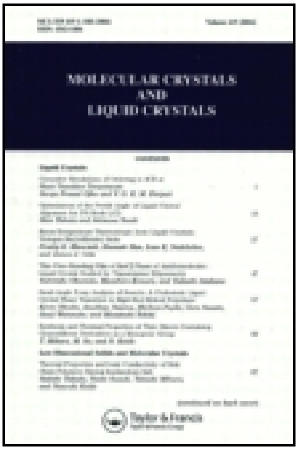

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Surface-Freezing Transitions and Novel Tilted Hexatic Phases in Smectic Liquid-Crystal Thin Films

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We report the first unambiguous identification in a thermotropic liquid crystal of a hexatic smectic-*L*, a phase with molecular tilt direction intermediate between those of the smectic-*I* and smectic-*F*, using electron diffraction in free-standing films of 5-(4"-hexyl, 3'-fluoro-*p*-terphenyl-4-oxy)-pentanoic acid ethyl ester. Our structural data directly support the proposed explanation of the unusual stripe phase observed optically. The films show a rich phase diagram as a function of thickness and temperature. A novel phase transition within the surface smectic-*L* phase is also observed.

Keywords: hexatic smectic-*L* phase; liquid-crystal thin films

INTRODUCTION

The defect-mediated two-dimensional melting theory predicts the existence of the hexatic phase, with quasi-long-range bond-orientational but short-range crystalline order [1-3]. Hexatic phases have been found in smectic liquid crystals, with the molecules either normal[4,5] or tilted [6,7] relative to the smectic plane. Tilted hexatic liquid crystals offer a rich variety of possible phase transitions with which to study the melting process in reduced dimensions and on surfaces. In the smectic-*I* (Sm-*I*) phase, the tilt direction is along a local bond. In the smectic-*F* (Sm-*F*) phase, the tilt direction is halfway between two adjacent bonds. Furthermore, a new smectic-*L* (Sm-*L*) phase, with the tilt direction between those of the Sm-*I* and Sm-*F* phases, is predicted [8,9]. Recently, the optical textures observed in 5-(4"-hexyl,3'-fluoro-*p*-terphenyl-4-oxy)-pentanoic acid ethyl ester (FTE1) pointed to the possible occurrence of a surface Sm-*L* phase [10,11]. We report electron-diffraction and optical experiments on free-standing FTE1 films which not only provide the structural evidence for the first observation of hexatic Sm-*L* order in a thermotropic liquid crystal, but also reveal a novel phase transition involving the surface Sm-*L* phase.

For the electron-diffraction studies, free-standing FTE1 films 1 mm in diameter were drawn at about 86 °C in the smectic-*C* (Sm-*C*) phase. Electron diffraction was performed in an electron microscope equipped with a pressurized and temperature-controlled sample chamber [12]. The electron-beam diameter was about 5 μm. The intensity distribution of the electron-diffraction pattern in a hexatic phase is very sensitive to the symmetry of the tilt order relative to the underlying hexatic bond axes. The diffraction pattern is a uniform diffuse ring for the smectic-*A* phase, six sharper diffuse arcs of equal intensity for the hexatic-*B* phase, and six sharp Bragg spots for the crystal-*B* phase. For tilted phases, additional intensity modulations are present, resulting in a diffuse ring with twofold intensity modulation for the Sm-*C* phase, a pair of strong arcs and two pairs of weak ones for the Sm-*I* phase, and two pairs of weak arcs and a pair of weaker ones for the Sm-*F* phase. In the case of the Sm-*L* phase, the expectation is that the diffraction pattern consists of three pairs of arcs of different intensity, and this has been confirmed qualitatively using computer simulation [13]. The diffraction patterns for the Sm-*C* tilted liquid and all tilted hexatic phases are shown schematically in Fig. 1.

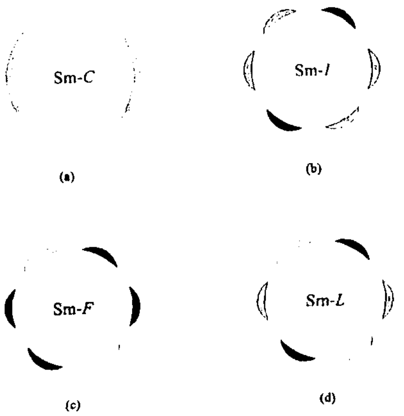

FIGURE 1 Electron-diffractions pattern expected in the (a) Sm-*C*, (b) Sm-*I*, (c) Sm-*F*, and (d) Sm-*L* phases.

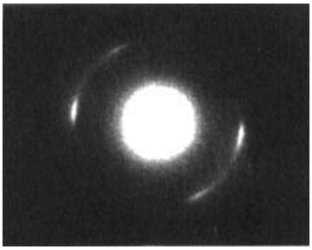

FIGURE 2 Electron-diffraction pattern from a ten-layer FTE1 film in the Sm-*L*/Sm-*C* phase at 70.3°C.

We have studied the structures of films between three and fifteen molecular layers thick on successive cooling and heating runs. The behavior is typified by that in a ten-layer film [14] as follows. The diffraction pattern above 81°C consists of a diffuse ring with a twofold intensity modulation characteristic of oriented Sm-*C* ordering in the probed region. On further cooling, there is a transition at around 81°C which is characterized by an enhancement of the in-plane positional order on the surfaces while the interior remains in the Sm-*C* phase. Detailed analysis of the intensity scans both radially and around the diffraction circle confirms that the Sm-*I* phase is now present in the outermost layer on either surface with the interior remaining in the Sm-*C* phase [14]. At 76°C, the film undergoes another surface transition, giving a diffraction pattern shown in Fig. 2, in which two pairs of sharper arcs of different intensity are superimposed on the diffuse Sm-*C* modulated ring. A χ scan around the diffraction circle, as shown in Fig. 3(a), reveals two pairs of uneven hexatic arcs 60° apart and a broad, twofold Sm-*C* background. It has been suggested [15] and confirmed by numerical simulation [13] that the in-plane diffraction pattern of the Sm-*L* phase is characterized by three pairs of arcs of different intensity, as indicated in Fig. 1(d). Thus Fig. 2 signifies the existence of the Sm-*L* surface layers on top of the Sm-*C* interior. The absence of a third pair of arcs in the observed Sm-*L* signal is probably due to their diffraction rods being tilted too far away from the detection plane, as indicated in theoretical simulation [13]. The χ-scan intensity after subtraction of the interior Sm-*C* contribution is shown as a function of temperature in Fig. 3(b). The gradual shift in the intensity ratio of the two adjacent arcs on cooling suggests a continuous change of the tilt direction of the Sm-*L* surfaces from the Sm-*I*-like to Sm-*F*-like, as expected theoretically [8,9]. Our data represent the first structural identification of a *hexatic* Sm-*L* phase in a thermotropic liquid-crystal system. An earlier observation of Sm-*L* symmetry in a lyotropic liquid-crystal system could not discern whether the phase is hexatic or multi-crystalline [15]. At 65°C, the entire film transforms into the Sm-*F* phase, characterized by a diffraction pattern with two pairs of arcs of equal intensity similiar to Fig. 1(c).

Unusual stripe textures were observed optically in free-standing FTE1 films using a polarizing microscope with slightly decrossed polarizers. Our electron-diffraction structural data directly support the earlier suggestion that the stripes are due to the existence of a surface Sm-*L* phase [10,11]. Uniform stripes separated by sharp, weakly fluctuating walls with Sm-C-like director fluctuations in the background were observed optically from 76°C to 65°C in FTE1 films of about fifteen layers thick, in precisely the same temperature range in which the diffraction pattern in Fig. 2 was observed. The stripe width, which was initially about 3 μm, increased with decreasing temperature. We were able to obtain single-domain diffraction below 73°C, when the typical stripe width in FTE1 films is larger than the electron-beam diameter of 5 μm [10].

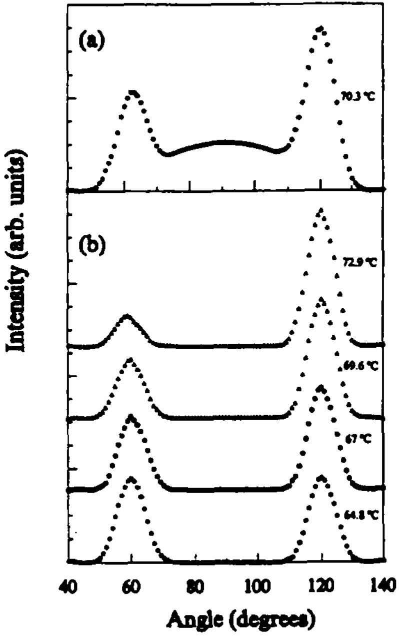

FIGURE 3 Diffraction intensity along a χ scan for a ten-layer film (a) at 70.3°C and (b) at various temperatures after subtraction of the background Sm-*C* contribution [14].

We have conducted numerous temperature runs with electron diffraction, and have compared our results with optical observations of free-standing FTE1 films of thickness from two to forty layers. The optical phase sequence on heating is shown in Fig. 4 for different layer thicknesses. This phase diagram for FTE1 thin films is surprisingly rich, since the bulk material only shows a transition from the Sm-*C* phase to an unknown crystal [11]. Electron diffraction shows that the high-temperature region of the optical phase diagram in which line textures were observed corresponds to the Sm-*I* surfaces in the presence of a Sm-*C* interior (Sm-*I*/Sm-*C*). The stripe phase region is confirmed to consist of a surface Sm-*L* phase and an interior Sm-*C* phase (Sm-*L*/Sm-*C*). The low-temperature region below the Sm-*L*/Sm-*C* phase where lines are again observed is a Sm-*F* phase. Optically, the film loses its modulated texture at the transition from the Sm-*L*/Sm-*C* to the Sm-*F* phase. The lowest temperature region in Fig. 4 has been shown by electron diffraction to consist of novel surface crystal phases with tilted hexatic interiors [14]. Apart from increasing transition temperatures with decreasing thickness, the phase diagram does not change qualitatively from forty to three layers. Two-layer films are anomalous in that they do not show stripes at any temperature. The same number of phase transitions is observed optically as in thicker films, but since we did not conduct structural studies on two-layer films, the phase indentifications are somewhat speculative.

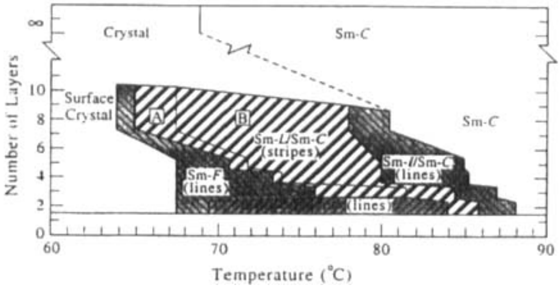

FIGURE 4 Phase diagram of FTE1 films of different thicknesses based on optical textures.

An interesting optical observation is that the surface Sm-*L* region, in which stripes are observed, appears to be divided into two regions, labeled *A* and *B*, separated by a textural transition denoted in Fig. 4 by a dashed line. Upon cooling, the stripes disappear momentarily at this transition and then reappear below it, but in regions *A* and *B* the film textures are optically indistinguishable. For a ten-layer film, this novel phenomenon occurs at 68°C. The presence of a structural transition at this temperature is indicated by the temperature behavior of the tilt direction of the surface Sm-*L* phase obtained from electron diffraction.

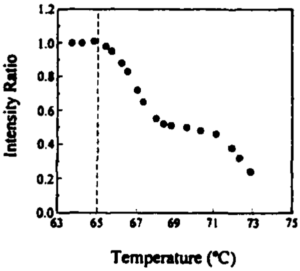

FIGURE 5 Temperature dependence of the ratio of the integrated intensity of the surface Sm-*L* arc at 60° to that at 120° in Fig. 3 for a ten-layer FTE1 film.

Figure 5 shows the relative intensities of two hexatic arcs versus temperature for a ten-layer film, computed by taking the ratio of the integrated χ-scan intensities of arcs at 60° and 120° shown in Fig. 3. This ratio is sensitive to the azimuthal tilt direction relative to the hexatic bond axes. Below 65°C, the entire film goes into the Sm-*F* phase, so the ratio is close to unity, as shown in Fig. 5. This ratio was not determined above 73°C because the stripes in the Sm-*L* phase at higher temperatures are rather narrow, causing multi-domain diffraction. It can be seen that the temperature dependence of the intensity ratio in Fig. 5 exhibits a distinct change in slope at about 68°C, which corresponds to the temperature at which the stripes disappear and then reappear. The intensity ratio at this temperature is about 0.5, indicating that the tilt direction of the surface Sm-*L* phase is midway between the Sm-*I* and Sm-*F* configurations. The reason for this apparent transition remains mysterious, but is likely related to a symmetry change. Above the transition (in region *B*), the Sm-*L* tilt $\hat{c}$-director points closer to the Sm-*I* (nearest-neighbor) direction, whereas below the transition (in region *A*), the $\hat{c}$-director is closer to the Sm-*F* (next-nearest-neighbor) direction. The momentary disappearance of the stripes at 68°C may mean that the chiral Sm-L_1 and Sm-L_2 domains that comprise the stripes [10] are energetically equivalent at this temperature.

Acknowledgments

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References

[1] J.M. Kosterlitz and D.J. Thouless, *J. Phys.*, **C6,** 1181 (1973).
[2] B.I. Halperin and D.R. Nelson, *Phys. Rev. Lett.*, **41,** 121 (1978).
[3] A.P. Young, *Phys. Rev. B*, **19,** 1855 (1979).
[4] R. Pindak, D.E. Moncton, S.C. Davey, and J.W. Goodby, *Phys. Rev. Lett.*, **46**, 1135 (1981).
[5] M. Cheng, J.T. Ho, S.W. Hui, and R. Pindak, *Phys. Rev. Lett.*, **61,** 550 (1988).
[6] J.D. Brock et al., *Phys. Rev. Lett.*, **57,** 86 (1986).
[7] E.B. Sirota, P.S. Pershan, L.B. Sorensen, and J. Collett, *Phys. Rev. A*, **36,** 2890 (1987).
[8] J.V. Selinger and D.R. Nelson, *Phys. Rev. Lett.*, **61,** 416 (1988).
[9] J.V. Selinger and D.R. Nelson, *Phys. Rev. A*, **39,** 3131 (1989).
[10] J.E. Maclennan and M. Seul, *Phys. Rev. Lett.*, **69,** 2082 (1992).
[11] J.E. Maclennan et al., *Phys. Rev. E*, **49,** 3207 (1994).
[12] M. Cheng, J.T. Ho, S.W. Hui, and R. Pindak, *Phys. Rev. Lett.*, **59,** 1112 (1987).
[13] R. Pindak, M. Seul, and S. Heinekamp, to be published.
[14] C.Y. Chao, S.W. Hui, J.E. Maclennan, C.F. Chou, and J.T. Ho, *Phys. Rev. Lett.*, **78,** 2581 (1997).
[15] G.S. Smith, E.B. Sirota, C.R. Safinya, and N.A. Clark, *Phys. Rev. Lett.*, **60,** 813 (1988).