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Surface and bulk periodical structures in smectic-*C* films with one free boundary

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Textures of achiral and chiral smectic-*C* phases in highly homogeneous samples with one free boundary have been studied. A stripe state has been registered in the smectic-*C* phase of the Schiff base 4-*n*-hexyl-*N*-(4-*n*-pentyloxy-benzyliden)-aniline (5O.6). It is shown that this structure is a surface state analogous to the stripe texture of Langmuir films of fatty acids and is qualitatively different with respect to the stripe texture of free-standing films of the same material. A stripe state has been observed in the bulk chiral smectic-C^* phase with a high spontaneous polarization. Properties of this texture in a sample with one free boundary are analogous to free-standing films, but the formation process of the texture is shifted to lower temperatures.

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Periodical structures in free-standing smectic films and surfactant monolayers have attracted considerable attention recently [1–11]. Investigations of modulated textures give important information about (i) the symmetry of surface stabilized structural states, (ii) new bulk structures suppressed in cells, where the material under study is contained between two solid substrates, and (iii) the interactions that result in these structures.

Modulated textures are observable in liquid-crystalline phases in many situations. For example, we can mention electrohydrodynamic instabilities [12], flexoelectric modulated structures [13], the domain wall instability of ferroelectrics [14], and the striped state in hybrid cells of nematic liquid crystals [15]. The appearance and properties of the above mentioned structures are essentially determined by the geometry of applied fields and boundary conditions. Periodical structures of free-standing films and surfactant monolayers are, on the contrary, thermodynamically equilibrium states [1–11]. Another interesting feature of these structures is their stability only in samples with one or two free boundaries. Two different kinds of periodical textures have recently been observed in free-standing films. One- and two-dimensional periodical structures have been found in free suspended films of the achiral smectic-*C* phase with thicknesses lower than 60 layers [2,10]. These structures were supposed to be due to the chiral symmetry breaking and occurrence of the hexatic-smectic-*L* phase in boundary layers [10]. The chiral symmetry breaking means here the loss of the C_2 rotation axis perpendicular to the tilt plane, because for polar molecules one definite orientation is preferred by the boundary [1–6,10,11]. A qualitatively different type of stripe has been observed in chiral ferroelectric free-standing films [7–9]. This stripe state occurs only in thick free-standing films and is stable in the smectic-C^* phase with high spontaneous polarization.

The following questions remained unresolved in spite of the recent progress in this field: (i) What structure is intrinsic for the free surface in tilted smectic films? (ii) Why do the periodical textures of free-standing achiral smectic-*C* films differ from those of Langmuir monolayers? (iii) What is the influence of the interaction between free boundaries in free-standing films on the pattern formation? To answer these questions, textures of chiral and achiral smectic-*C* phases have been studied in the samples with one free boundary, where smectic planes have been oriented parallel to the substrate. To have comparable experimental conditions with free-standing films, perfect samples with smectic layers parallel to the glass substrate were grown. In smectic-*C* films of the achiral Schiff base 4-*n*-hexyl-*N*-(4-*n*-pentyloxy-benzyliden)-aniline (5O.6) a stripe structure has been observed, which is similar to stripes in surfactant monolayers and qualitatively different from the textures of Maclennan and co-workers [2,10] in free-standing films of the same material. From this observation a conclusion is made that the basic structure of the smectic-*C* free surface in achiral films is a stripe state analogous to Langmuir films. The influence of the substrate on the stripe state of ferroelectric C7 was found in a shift of the stripe formation process to lower temperatures.

Film textures of two substances have been studied in this paper. The first one was achiral Schiff base 5O.6. This material has the following liquid-crystalline phases in bulk phase samples: isotropic (73 °C) *N* (61.4 °C) Sm-*A* (52.8 °C) Sm-*C* (51 °C) Sm-*B* (43.4 °C) Sm-*F* (40.8 °C) Sm-*G* (36 °C) crystalline. The second substance was chiral 4-(2S,3S)-2-(chloro-3-methylpentanoyloxy)-4′ heptyloxybiphenyl (C7). The compound has been characterized in [16] and possesses the following liquid-crystalline phases sequence: isotropic (62 °C) smectic-*A* (54.6 °C) smectic-C^* (43 °C) smectic-*G*.

Textures in free-standing films have been observed in a polarized Leitz-Orthoplan microscope in reflection mode and registered photographically. Orientation of smectic planes parallel to the substrate has been achieved by the following procedure. First, a small amount of substance has been sheared between two glass slides without spacer in the temperature interval of the smectic-*A* phase and one slide has been removed. This has given an imperfect orientation of smectic-*A* planes parallel to the substrate and only several places were of a satisfactory quality. Orientation of smectic-*A* planes of thermotropic liquid crystals by shearing is qualitatively analogous to lamellar lyotropic liquid crystals

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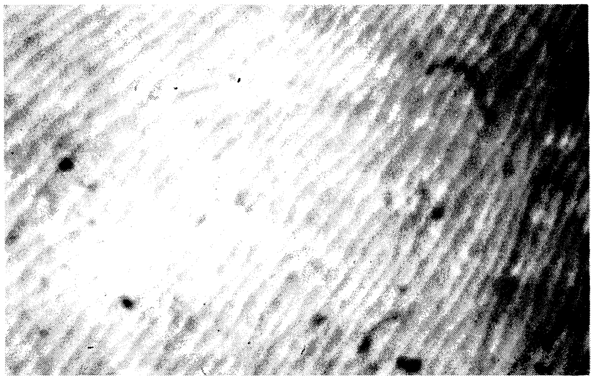

FIG. 1. Stripe state in smectic-*C* phase of 5O.6 at $T = 51.5\,^\circ\mathrm{C}$ in films with one free boundary. The long side dimension of the image is 300 μm.

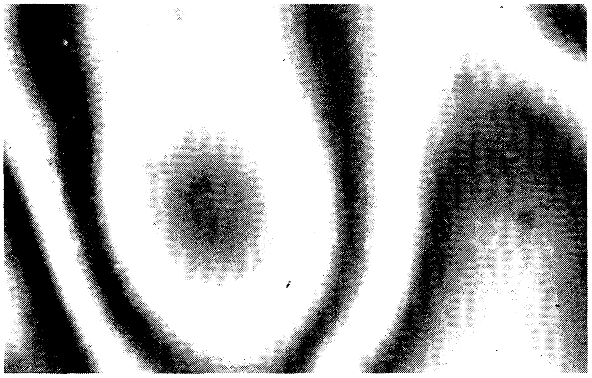

FIG. 2. Schlieren texture of the smectic-C^* of C7 at $T = 52.79\,^\circ\mathrm{C}$. The magnification is the same as in Fig. 1.

studied in [17]. To improve the orientation of the samples, they were heated to a temperature just above the clearing point and after that cooled down to the smectic-*A*. Such a procedure improves the quality of the smectic planes' orientation drastically. This property can be explained by a tendency of molecules to be oriented perpendicular to the free boundary as observed by Oswald and co-workers [18]. Repeating of heating and cooling 2–3 times results in a perfect orientation of smectic-*A* planes parallel to the glass substrate. The smectic-*A* phase has no visible defects on a large area and is completely dark between crossed polarizers. The thickness of such films was 1–3 μm. The homogeneity of the film thickness has been controlled in a Leitz-Orthoplan interference microscope with a precision of ±5 smectic layers [19]. The film thickness was not uniform on the whole substrate area and smooth variations of thickness could be recorded by the interference microscope. Texture observations have been carried out on parts with approximately constant thickness in the microscope field (≈ 300 μm in diameter) which could always be found.

Figure 1 shows a stripe state, which has been observed in the temperature interval 51–52.3 °C in samples with one free boundary of 5O.6. The contrast of the pattern was very low close below the phase transition Sm-*A*–Sm-*C*, therefore it was difficult to register the stripe state at higher temperatures in the smectic-*C*. The stripe texture consists of equidistant discontinuous defect walls separated by 5–10 μm. The interstripe spacing increases by decreasing the temperature, which is similar to free-standing films [2], and does not depend on the film thickness. The stripes can be observed only in slightly decrossed polarizers, whereas in crossed polarizers the film is dark. This observation means that the stripe texture is a surface state. The two-dimensional director $\mathbf{c}$ (a projection of the director onto smectic planes) rotates inside of each stripe by approximately $50^\circ \pm 10^\circ$ and jumps on the defect wall by approximately the same value. No modulation of the film thickness due to the stripes was recorded by the interference microscopy. Introduction of planar boundary conditions on the glass substrate destroys the stripes and results in the focal conic structure of smectic-*A* phase which remains unchanged in the smectic-*C* phase.

A qualitatively different behavior was observed in films of C7. After the phase transition from the smectic-*A* the smectic-C^* phase possesses a schlieren texture shown in Fig. 2. At $T \approx 48\,^\circ\mathrm{C}$ this texture spontaneously transforms into a striped structure (Fig. 3). This striped structure is a bulk phase state of the films because it is observable in crossed polarizers. The periodicity of the stripe texture was about 50 μm which is independent of the film thickness. The interstripe spacing decreases on cooling. The appearance and properties of this stripe texture are analogous to the free-standing films.

Comparison of Fig. 1 with images of the stripe state in surfactant monolayers [6] shows that these structures are very similar. In both cases stripes are restricted by discontinuous defect walls; the rotation angle of the tilt plane inside of each stripe is of the same order of magnitude. This is a natural result and is combined with identity of symmetry and molecular packing in surface layers on the free surface of achiral smectic-*C* phase and Langmuir films of fatty acids. 5O.6 molecules possess a longitudinal dipole moment and the head-tail symmetry is broken on the free boundary. This means that smectic layers on the free surface possess a net electric dipole moment, which is also true for Langmuir films. Some difference can exist in the value of the surface polarization and elastic constants which determine the stability and periodicity of the stripe state on the free surface. The mechanism of the stripe formation described in [20] does not work in this case because it does not describe the variation of

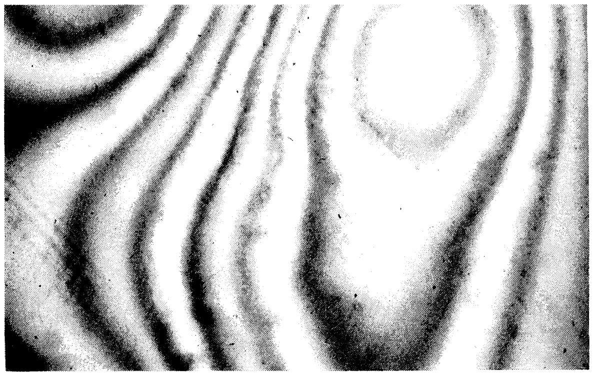

FIG. 3. Spontaneous formation of the stripe state from the schlieren texture at $T = 45.45\,^\circ\mathrm{C}$. The region of the sample and the magnification are the same as in Fig. 1.

the director orientation inside of the stripes. The images observed by Maclennan and co-workers [2,10] in the smectic-C free-standing films of 5O.6 differ from the results of this paper and the stripe state in Langmuir films [6] in the following points: (i) The stripe state in free-standing films [2,10] is combined from two different stripe systems. In the model of [10] the stripes were considered to be smectic L_1 and smectic L_2 alternating domains. The contrast inside of each stripe was constant. On the contrary, the smectic-C stripes contrast in one free boundary sample of 5O.6 studied in the present paper changes continuously, which corresponds to a bend-splay deformation of the two-dimensional director field. All stripes are equivalent and there is no need to introduce Sm-L_1 and Sm-L_2 domains in our case. (ii) No structure with two-dimensional periodicity (brick walls, honeycomb structure) has been observed in the present paper.

The stripe state in achiral smectic-C films is a surface state which is shown in the present paper by microscopic observation. The second argument for this statement is the spontaneous director rotation inside of the stripes. Such textures possess no center of symmetry, are forbidden for the bulk smectic-C phase, and can be due only to the chiral symmetry breaking on the boundary. Let us discuss what structures are inherent to the free surface of smectic-C. If some of the textures of smectic-C free-standing films [2,10] were intrinsic for the boundary layers, one should observe them in samples with one free boundary too. The results of the present paper contradict such an assumption. Therefore we can make an important conclusion that the one- and two-dimensional periodical structures of free-standing films observed in [2,10] should be explained by molecular interactions. This interaction changes the configuration of the basic structural states of the free boundary and is combined with chiral symmetry breaking (Fig. 1). To model the observed periodical textures in the smectic-C free-standing films one has to construct centroasymmetric patterns with an essential account of interaction between free boundaries. Boundary layer structure can correspond to the hexatic-smectic-L phase where the director is tilted between the nearest neighbor and next-nearest neighbor directions 30° with respect to the next neighbor [21]. In ultrathin free-standing films the interaction gives a centrosymmetric structure and the stripes disappear as reported in [10]. In thick free-standing films with more than 60–70 layers the interaction of net dipoles is not strong enough to produce a periodic structure across the whole film. Periodic textures of both boundaries are out of phase, therefore a structureless image in the smectic-C is observed.

Besides symmetry arguments we can apply a physical model of [9] to explain qualitatively general features of the observed textures. The idea of this model is to describe phenomenologically flexoelectric instabilities which can occur in free-standing films under the influence of electric fields produced by films (see also [22]). Because of breaking of the C_2 rotation axis the electric polarization field on the boundary can be large and should be proportional to the number of layers with broken symmetry. This model would work in this case, if the flexoelectric coefficient is large enough. This model predicts periodicity of the stripe state which is comparable with the results of this paper, and explains the rotation of the tilt plane inside of each stripe.

The stripe state of the smectic-C^* phase of the ferroelectric C7 demonstrates a qualitatively different behavior. It was shown in [8] that this kind of modulated structure appears only in thick free-standing films with high spontaneous polarization. As already mentioned, this stripe state is a periodical structure of the bulk smectic-C^* phase. This stripe texture cannot be explained by theories [23,24] because they include no ferroelectric and flexoelectric terms. The stripe state in thick free-standing films with high spontaneous polarization is a flexoelectric instability in a field produced by the film as was shown in [9]. Using the results of [7] we can suppose that the surface layers in ferroelectric films possess a spontaneously anisotropic texture. The stripe state appears in free-standing films of comparable thickness at $T \approx 53.5$ °C or 1.1 °C below the phase transition temperature Sm-A–Sm-C^*. The shift of the stripe formation to lower temperatures in samples with one free boundary can be ascribed to the coupling of the director field with the substrate. This fact demonstrates that the energy gain of the stripe state formation with respect to the uniform orientation of the director field in the smectic-C^* phase has the same order of magnitude as the coupling energy of the director with the substrate. This explains why the stripe state was not observed in samples contained between solid substrates.

Conclusions. Periodical stripe textures are observed in films with one free boundary of chiral and achiral smectic-C phase. The basic structural state of the free surface of the achiral smectic-C is the stripe texture described in the current paper. This texture is analogous to the corresponding one of the surfactant monolayers of fatty acids. One- and two-dimensional periodical textures of free-standing smectic-C achiral films are supposed to be due to electrostatic long range interactions. The stripe state in the ferroelectric smectic-C^* films with high spontaneous polarization is a bulk phase state analogous to that of free-standing films. Its formation is shifted to lower temperatures in films with one free boundary with respect to free-standing films.

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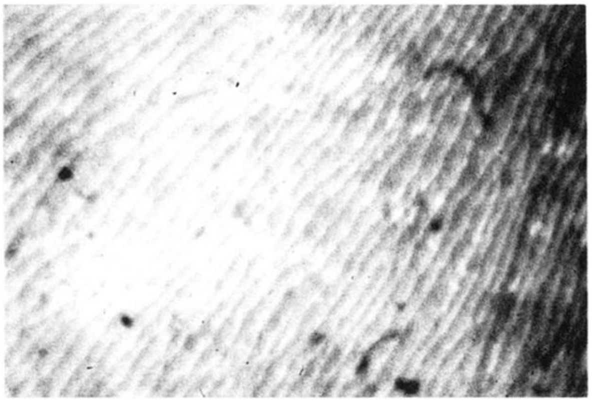

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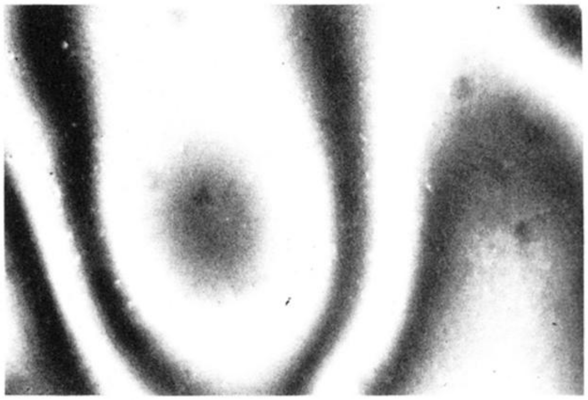

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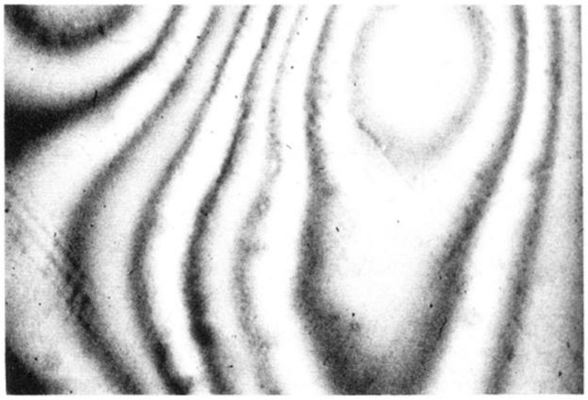

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