Periodic structures in ferroelectric freely suspended films with high spontaneous polarization

E. Demikhov

Institute of Physical Chemistry, University of Paderborn, 33095 Paderborn, Germany, and Institute of Solid State Physics RAS, 142432 Chernogolovka, Russia

S. A. Pikin

Institute of Crystallography RAS, 117333 Moscow, Russia

(Submitted 17 March 1995)
Pis'ma Zh. Éksp. Teor. Fiz. **61**, No. 8, 666–672 (25 April 1995)

The nature of the anisotropic and stripe states of free-standing, smectic C* films with high spontaneous polarization is studied. It is demonstrated that these textures are stable only in mixtures with a high spontaneous polarization. A new mechanism of the stripe formation, which phenomenologically takes into account the surface polarization fields, is proposed. © *1995 American Institute of Physics.*

Recently there has been considerable interest in free-standing smectic films consisting of monomolecular layers. Elastic properties, polarization, and viscosities,[1–3] hexatic phases,[4] surface ordering phenomena,[5] and dimensional crossover[6–8] have been successfully studied experimentally. Ferroelectric properties of free-standing films has essentially not been investigated until now, although the first predictions about the new structure transformations due to the dipolar interaction in two-dimensional ferroelectric films appeared in the early 1980s (Refs. 9–11). Texture studies in free-standing films give information about novel structures which is inconsistent with the stationary boundary conditions for the director on solid substrates, free surface-stabilized structures, and basic interactions in films. Unusual anisotropic and stripe states of the free-standing, smectic-C* films with high spontaneous polarization have been observed in Ref. 12. One- and two-dimensional periodic textures in achiral smectic-C films were recently reported in Ref. 17. This stripe state was assumed to be a consequence of the surface-bond orientational order, which exists due to the chiral symmetry breaking.[13] Periodic structures of chiral and achiral films can have the same nature which was discussed in Ref. 13. To verify this statement experimentally, it is important to give a detailed study of the textural transformations in high spontaneous polarization films.

In the present paper we investigated the nature of the anisotropic and stripe states of free-standing, smectic-C* films and compared their properties with relevant structures in achiral films. We showed that the stripe state exists only in chiral-racemic mixtures with a high spontaneous polarization. The stripe state of ferroelectric films has a different nature with respect to achiral films and is a bulky structure. A new mechanism of stripe formation is proposed. This mechanism describes this state as a flexoelectric instability in an electric field induced by surface effects.

We studied chiral 4-[(2S,3S)-2-[chloro-3-methylpentanoyloxy]-4' heptyloxybiphe-

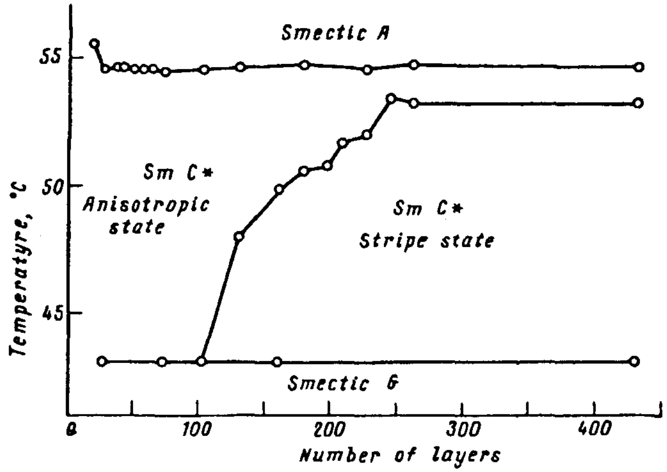

FIG. 1. N/T phase diagram of C7. The dotted line is the boundary between the anisotropic textures in thick and ultrathin films.

nyl (C7) and its chiral-racemic mixtures. This substance, described in Ref. 14, possesses the following sequence of liquid-crystalline phases: isotropic (62 °C)–smectic-A (54.6 °C)–smectic-C* (43 °C)–smectic-G. Spontaneous polarization in the smectic-C* phase of pure chiral C7 varies between 130 and 290 nC/cm^2 with decreasing temperature. The first-order smectic-A–smectic-C* phase transition disappears in free-standing films thinner than $N_c \approx 15$ (Ref. 7).

The textures from a film area 400 μm in diameter were observed in a polarized Leitz–Orthoplan microscope between slightly decrossed polarizers. These textures were recorded photographically. The frame for the production of the free-standing films consisted of two brass rails and two movable brass blades. The number of smectic layers was determined by multiple beam interferometry technique, as described in Ref. 15. This method gives an exact number of layers in a broad interval of film thicknesses, as demonstrated in Ref. 8. The films were produced in the smectic-A phase and then cooled down to the smectic-C* phase. The configurations of the plane director field in free-standing films of C7 were studied in a large number of layers (from 10 to 500).

Figure 1 shows the N/T phase diagram of the smectic-C* structural modifications in C7. In thick films ($N \geqslant 85$) two states have been observed. An anisotropic state occurs just below the phase transition Sm A–Sm C* after the annihilation of defects. This state is characterized by a uniform contrast between crossed polarizers, which can be changed by rotating the microscope table (Fig. 2). The temperature interval of the anisotropic state increases with decreasing number of layers. At $N_c \approx 85 \pm 10$ the stripe state of pure chiral C7 disappears. We found that the anisotropic state in thick films possesses a different defect structure with respect to ultrathin films ($N \leqslant 30$). Walls of discontinuous defects are typical for the ultrathin films immediately upon cooling from the smectic-A phase. A possible configuration of the director field is the "chessboard" texture observed in Ref. 12. However, we were not able to produce this texture over the whole film area. The

FIG. 2. The sealed anisotropic state in a 25-layer film at $T=48.06$ °C. Analogous structures can be seen in thick sealed films.

variation of contrast near the defects in thick films was always smooth. Pseudostripes produced by the motion of point defects were observed in thick films in the temperature interval of the anisotropic state. Such stripes can be topologically stable when the point defects move from one point on the film contour to the other. They were not reproducible, however, and they have not filled the whole film area.

A stable stripe state formed spontaneously in thick films ($N_{cr} \geqslant 85$) upon cooling to a temperature T_s below the Sm A–Sm C* phase transition. The dependence of T_s on the number of layers is shown in Fig. 1. The structural transformation from the anisotropic state to the stripe state is reversible: the stripe state disappears as a result of heating 1–3 °C above T_s. This behavior is reminiscent of the hysteresis of structural transformations by first-order phase transitions. The best way to record the stripe state is to look at the film contour. Elongated stripe sources 100–200 μm in length produce stripes when T_s is reached. Interaction of stripes of different sources results in a typical texture, which is called here the striped state. The usual stripe texture is deformed and it is difficult to attribute a characteristic periodicity to this state. Typical values of an interstripe distance are relatively large (~80–150 μm). Figure 3 shows a typical stripe state near a source in a 420-layer film. The stripe texture can be deformed and aligned by the motion of the movable side of the film frame parallel to it.

It was found that the striped state completely disappears in chiral–racemic mixtures with a concentration of chiral C7 less than 75%. Figure 4 shows the shift of T_s with respect to T_{AC^*} which depends on the number of layers for mixtures with 100, 95, 87.5, and 85 wt. % chiral C7. According to Ref. 16, the spontaneous polarization P_s, which is measured 2 °C below $T_A C^*$, decreases from 195 nC/cm^2 to 90 nC/cm^2 as a result of decreasing the chiral C7 concentration from 100% to 75%. The critical spontaneous polarization, which is necessary for the formation of the stripe state, was found to be 175 nC/cm^2 and independent on the C7 concentration in the region[16] 100–75%. We found that a variation of the composition influences textures of the anisotropic state. The anisotropic state with discontinuous walls was observed only in mixtures with more than 95% chiral C7. Figure 5 shows the texture of a 150-layer film in a 75% chiral C7 mixture with

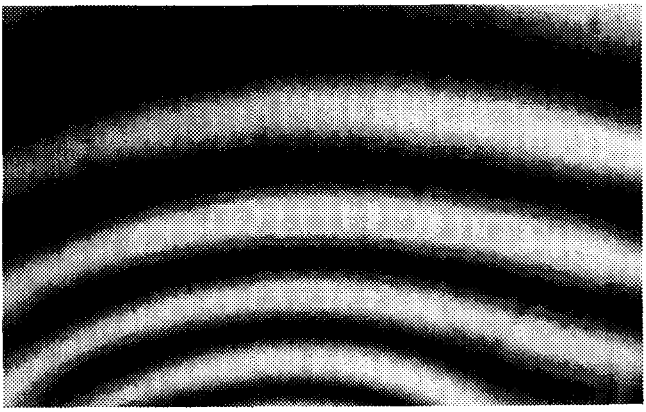

FIG. 3. Stripe state near a stripe source on a 420-layer film contour at $T = 49.5$ °C.

its racemat. It can be characterized by a gradual loss of quality of the uniaxial orientation. This texture is the intermediate state between the anisotropic structure in the chiral C7 and a classic schlieren observed in a 50% chiral C7 mixture.

To explain properties of observed textures we have considered the effects of external fields on the in-plane modulations for thin smectic-C films. The external field E is applied normally to the film surface; i.e., the component E_z should be included in the flexoelectric invariant:[11]

$$\beta' E_z n_z \left(\frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y} \right). \tag{1}$$

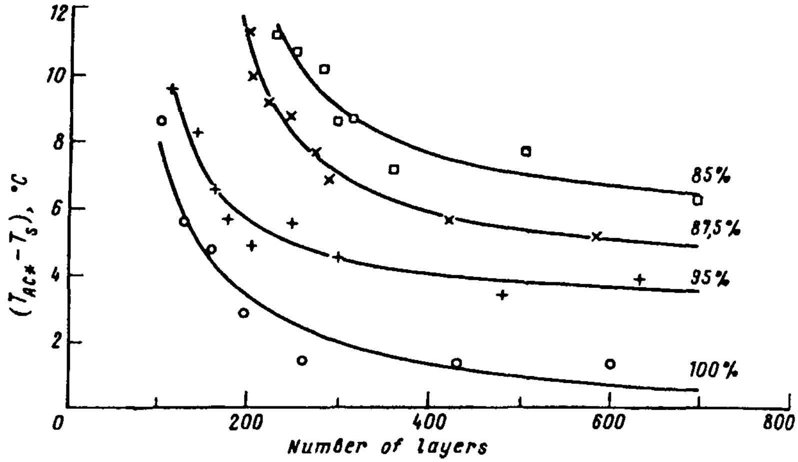

FIG. 4. Dependence of the temperature of the transition from the anisotropic state to the stripe state on the concentration of the chiral component of C7.

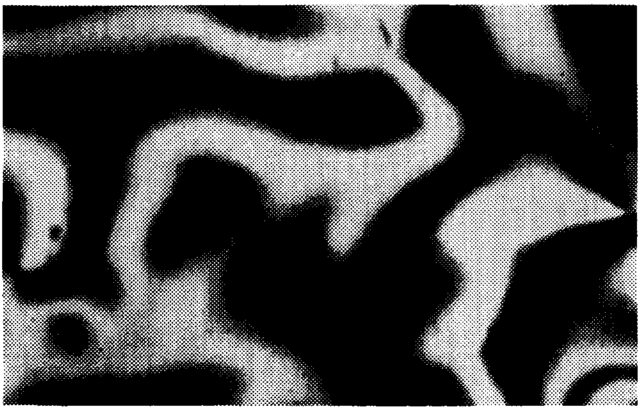

FIG. 5. Anisotropic texture of the smectic-C* phase in a mixture of 75% chiral C7 with its racemat, $N=150$, $T=53.85$ °C.

Here the director components are $n_x=\theta\sin\varphi\approx\theta\varphi$, $n_y=\theta\cos\varphi\approx\theta$, and $n_z\approx 1-\theta^2$. It is assumed that the tilt angle θ and the aximuthal angle φ are small, and β' is the flexoelectric coefficient. We assume that the field E is electric in nature. For example, such a field can be created by the elastic stress σ at the expense of increasing the density of the surface charge as a result of decreasing the surface area of the polar heads of molecules. For free-standing thin films, the elastic stress can be caused by the film weight w if the film thickness, i.e., the number of smectic layers $N(w\sim N)$, is sufficiently large. Thus $E\sim\sigma\sim w\sim N$.

Let us consider a free-standing smectic film under the condition when its weight causes the mechanical stress σ_{xx}, and the perturbations $\theta'=\theta-\theta_0$ and φ are uniform along the y axis but heterogeneous along the x axis. The values $\theta=\theta_0$ and $\varphi=0$ correspond to an unperturbed smectic-C. In such a case we should take into account the following invariants in the free energy density:

$$g'\varphi_{xx}n_x^2\approx gw\theta_0^2\varphi^2, a\theta_0^2\theta'^2, \frac{1}{2}K\theta_0^2\left(\frac{\partial\varphi}{\partial x}\right)^2, \frac{1}{2}b\left(\frac{\partial\theta'}{\partial x}\right)^2, \tag{2}$$

where the constants a, b, g, and K are positive. For simplicity, we ignore the effects of free charges, the internal fields, and the boundaries. The invariant (1) can be written in the form

$$\beta w\theta_0^2\theta'\frac{\partial\varphi}{\partial x}, \tag{3}$$

which results in a nonzero free energy value after the integration over the x coordinate. Here $\beta' E\sim\beta w$, and the coefficient β is proportional to the permanent dipole moment and to the concentration of polar molecules.

The sum of the terms (2) and (3) determines the free energy density in the framework of the considered approximation and results, after its minimization with respect to θ' and φ, in the following characteristic equation under this assumption that the waves for θ' and φ are sinusoidal:

$$(2a\theta_0^2+bq^2)(2gw+Kq^2)=\beta^2\theta_0^2q^2w^2, \tag{4}$$

where q is the wave vector of the modulated structure. The physical solution $w(q^2)$ for positive values of q^2 can be written as follows:

$$w(q^2)=\frac{g(2a\theta_0^2+bq^2)+\sqrt{g^2(2a\theta_0^2+bq^2)^2+K\beta^2\theta_0^2q^4(2a\theta_0^2+bq^2)}}{\beta^2\theta_0^2q^2}. \tag{5}$$

The function $w(q^2)$ has a minimum value $w_{\rm cr}=w(\mathrm{a}_{\rm cr}^2)$,

$$w_{\rm cr}=\frac{gb}{2\beta^2\theta_0^2}\left(1+\sqrt{1+2(2aK)^{1/2}(|\beta|\theta_0^2/bg)}\right)^2, \tag{6}$$

for the value of the wave number squared, $q^2 = q_{\rm cr}^2$:

$$q_{\rm cr}^2=\frac{1+\sqrt{1+2(2aK)^{1/2}(|\beta|\theta_0^2/bg)}}{(K/2a)^{1/2}(|\beta|/g)}. \tag{7}$$

Equations (4)–(7) show that there is a threshold weight value $w=w_{\rm cr}$ (or a critical number of layers $N_{\rm cr}$) for the smectic-C film, above which the one-dimensional in-plane modulation (stripe state) can appear with the threshold wave number $q_{\rm cr}$ (the spatial period $h_{\rm cr}$ is equal to $2\pi q_{\rm cr}^{-1}$). The threshold $w_{\rm cr}$ strongly depends on the flexoelectric coefficient β and on the tilt angle θ_0:

$$w_{\rm cr}\sim N_{\rm cr}\sim\frac{1}{\beta^2\theta_0^2}\sim\frac{1}{\beta^2(T_{AC}-T)}. \tag{8}$$

In other words, the values $w_{\rm cr}$ and $N_{\rm cr}$ must increase rapidly near the phase transition temperature T_{AC}, where $\theta_0^2\sim(T_{AC}-T)$. For a fixed weight w, Eq. (7) determines the corresponding critical temperature T_s below which the stripe state is formed:

$$(T_{AC}-T_s)\sim\frac{1}{\beta^2w}\sim\frac{1}{\beta^2N}. \tag{9}$$

The theory presented above is a good qualitative description of the N/T phase diagram of the smectic-C* structural modifications. The solid lines in Fig. 4 show the best mean-square fits of the T_s dependence on the number of layers. Expression (9) takes into account that N is determined up to a certain constant N_0. The stripe state of the ferroelectric free-standing films has obviously a different nature compared to that of achiral films:[17] i) the contrast in stripes observed by us changes continuously; ii) no defect walls have been observed; iii) periodical textures of achiral films were found only in thin films ($N\leqslant 60$), whereas the stripe state of smectic-C* is stable only in thick films with $N\geqslant 85$. Since surface bond-orientational order is predicted to exist in 2 or 3 boundary layers,[18] the effects combined with it can be enhanced by decreasing the number of layers. This is not the case with the stripe state of high spontaneous polarization, free-standing films. The predictions of Ref. 19 cannot be used in our case, because no ferroelectric terms are taken into account. According to our model, the stripe state disappears in thin layers, because the electric field E_z is not strong enough to produce stripes. This circumstance explains the similarity of images of the anisotropic state in thick films before the stripes are formed and the similarity of sealed, ultrathin films with thickness below N_{cr}. A more precise model should take into account the fluctuation effects such as those described in Refs. 9–11. The results of this study will be published elsewhere.

Acknowledgments. The authors wish to thank Prof. H. Stegemeyer and E. Hoffmann for the cooperation. We also thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and INTAS project of EC for financial support.

[1] C. Young, R. Pindak, N. A. Clark, and R. B. Meyer, Phys. Rev. Lett. **40**, 773 (1978).

[2] C. Rosenblatt, R. B. Meyer, R. Pindak, and N. A. Clark, Phys. Rev. A **21**, 140 (1980).

[3] R. Pindak, C. Young, R. B. Meyer, and N. A. Clark, Phys. Rev. Lett. **45**, 1193 (1980).

[4] J. D. Brock, R. J. Birgenau, J. D. Litster, and A. Aharony, Contemp. Phys. **30**, 321 (1989).

[5] C. C. Huang and T. Stoebe, Adv. in Physics **42**, 343 (1993).

[6] S. Heinekamp, R. Pelkovits, E. Fontes *et al.*, Phys. Rev. Lett. **52**, 1017 (1984).

[7] Ch. Bahr and D. Fliegner, Phys. Rev. A **46**, 7657 (1992).

[8] I. Kraus, P. Pieranski, E. Demikhov, and H. Stegemeyer, Phys. Rev. E **48**, 1916 (1993).

[9] D. R. Nelson and R. A. Pelcovits, Phys. Rev. B **16**, 2191 (1977).

[10] R. A. Pelcovits and B. I. Halperin, Phys. Rev. B **19**, 4614 (1979).

[11] S. A. Pikin, *Structural Transormations in Liquid Crystals*, Gordon and Breach Science Publishers, New York, 1991, p. 229.

[12] E. Demikhov, Europ. Lett. **25**, 259 (1994).

[13] J. V. Selinger, Z.-G. Wang, R. F. Bruinsma, and C. M. Knobler, Phys. Rev. Lett. **70**, 1139 (1993).

[14] Ch. Bahr and G. Heppke, Mol. Cryst. Liq. Cryst. **148**, 29 (1987); B. R. Ratna, R. Shashidhar, Geetha G. Nair *et al.*, Phys. Rev. A **27**, 1824 (1984).

[15] P. Pieranski *et al.*, Physica A **194**, 364 (1993).

[16] E. Demikhov, E. Hoffmann, H. Stegemeyer *et al.*, Phys. Rev. E, in press.

[17] J. E. Maclennan and M. Seul, Phys. Rev. Lett. **69**, 2082 (1992); J. E. Maclennan, U. Sohling, N. A. Clark, and M. Seul, Phys. Rev. E **49**, 3207 (1994).

[18] J. V. Selinger and D. R. Nelson, Phys. Rev. A **39**, 3135 (1989).

[19] S. A. Langer and J. P. Sethna, Phys. Rev. A **34**, 5035 (1986); G. A. Hinshaw, R. G. Petschek, and R. A. Pelcovits, Phys. Rev. Lett. **60**, 1864 (1988).

Published in English in the original Russian journal. Reproduced here with stylistic changes by the Translation Editor.