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PERIODICAL STRUCTURES IN FERROELECTRIC FREE SUSPENDED FILMS WITH HIGH SPONTANEOUS POLARIZATION

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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 is proposed which phenomenologically takes into account surface polarization fields.

Recently there has been considerable interest in free standing smectic films combined 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 in series of experimental works. Ferroelectric properties of free standing films has practically not been investigated until now, although first predictions about new structure transformations due to the dipolar interaction in two-dimensional ferroelectric films appeared in early 80th [9–11]. Texture studies in free standing films give information about novel structures inconsistent with fixed boundary conditions for the director on solid substrates, free surface stabilized structures and basic interactions in films. Unusual anisotropic and stripe states of the smectic-C* free standing films with high spontaneous polarization have been observed in [12]. One- and two-dimensional periodical textures in achiral smectic-C films were recently reported in [17]. This stripe state was supposed to be a consequence of the surface bond orientational order, which exists due to the chiral symmetry breaking [13]. Periodical structures of chiral and achiral films can have the same nature which has been discussed in [13]. To verify this statement experimentally it is important to give a detailed study of textural transformations in high spontaneous polarization films.

In the present paper we investigated nature of the anisotropic and stripe states of smectic-C* free standing films and compared their properties with relevant structures in achiral films. It is shown that the stripe state exists only in chiral-racemic mixtures with 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 which describes it as a flexoelectric instability in an electric field induced by surface effects.

Chiral 4-[(2S,3S)-2-[chloro-3-methylpentanoyloxy]-4' heptyloxybiphenyl (C7) and its chiral-racemic mixtures have been studied in this paper. The substance has been characterized in [14] and 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 $N_c \approx 15$ [7].

Textures from a film area 400μm in diameter have been observed in a polarized Leitz-Orthoplan microscope between slightly decrossed polarizers and registered 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 [15]. This method gives an exact number of layers in a broad interval of film thicknesses, as it was demonstrated in [8]. Films were produced in the smectic-A phase and then cooled down to the smectic-C* phase. Configurations of the plane director field in free standing films of C7 have been studied in a broad interval of number of layers (from 10 to 500).

Fig.1 shows the N/T phase diagram of the smectic-C* structural modifications in C7. In thick films ($N \geq 85$) two states have been observed. An anisotropic state occurs close below the phase transition Sm A – Sm C* after the annihilation of defects. This state is characterized by a homogeneous contrast between crossed polarizers, which is changed by the rotation of the microscope table (fig.2). The anisotropic state temperature interval increases with decreasing number of layers. At $N_c \approx 85 \pm 10$ the stripe state of pure chiral C7 disappears. We have found that the anisotropic state in thick films possesses a different defect structure with respect to ultrathin films ($N \leq 30$). Discontinuous defect walls are typical for the ultrathin films just after the cooling from the smectic-A. One of the possible configurations of the director field is the 'chess-board' texture observed in [12]. However we have not succeded in producing this texture on the whole film area. The variation of contrast around defects in thick films was always smooth. Pseudostripes produced by motions of point defects have been 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, but they were not reproducible and have not filled the whole film area.

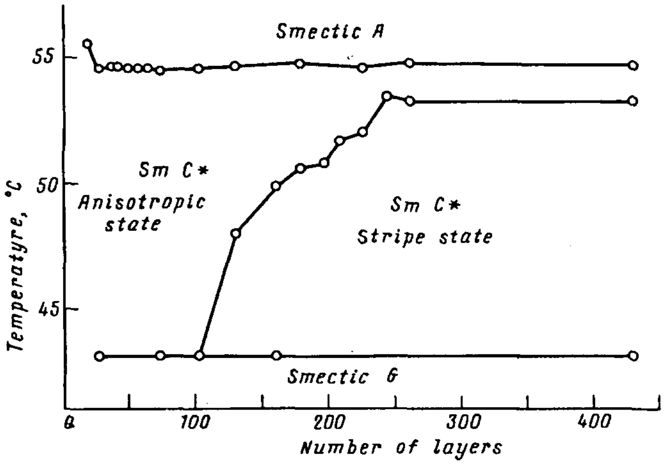

Fig.1. N/T phase diagram of C7. The dotted line is the boundary between anisotropic textures in thick and ultrathin films

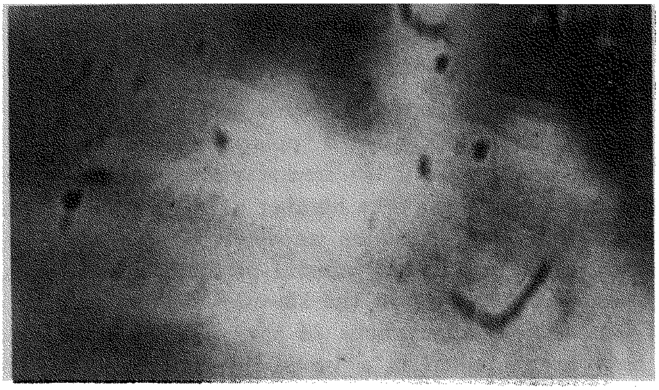

Fig.2. Sealed anisotropic state in 25-layer film at $T = 48.06\,^\circ$C. Analogous structures are observed in thick sealed films

A stable stripe state occured spontaneously in thick films ($N_{cr} \geq 85$) on cooling at 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 anisotropic state – stripe state is reversible: the stripe state disappears on heating 1-3 °C above T_s. This behaviour is reminiscent of the hysteresis of structural transformations by first order phase transitions. The best way to register the stripe state is to look at the film contour. Prolongated 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 ascribe some characteristic periodicity to this state. Typical values of interstripe distance are relatively large ($\sim$ 80-150 μm). Fig.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.

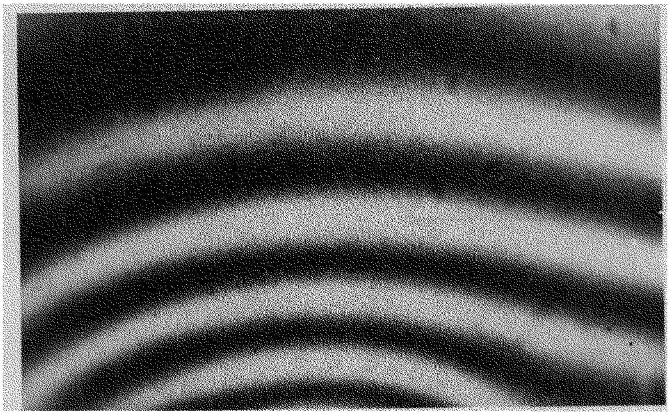

Fig.3. Stripe state near a stripe source on 420-layer film contour at $T = 49.5\,^\circ$C

It was found that the striped state completely disappears in chiral - racemic mixtures with a concentration of chiral C7 less than 75%. Fig.4 shows the shift of T_s with respect to T_{AC^*} dependent on the number of layers for mixtures with 100, 95, 87.5, 85 wt. % chiral C7. According to [16] the spontaneous polarization P_s measured 2 °C below T_AC^* decreases from 195nC/cm^2 to 90nC/cm^2 by decrease of chiral C7 concentration from 100% to 75%. The critical spontaneous

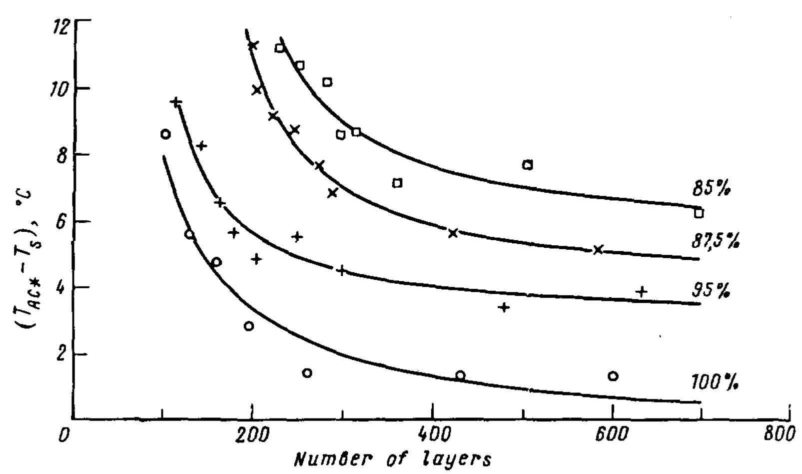

Fig.4. Dependence of the transition temperature anisotropic state – stripe state on the concentration of the chiral component of C7

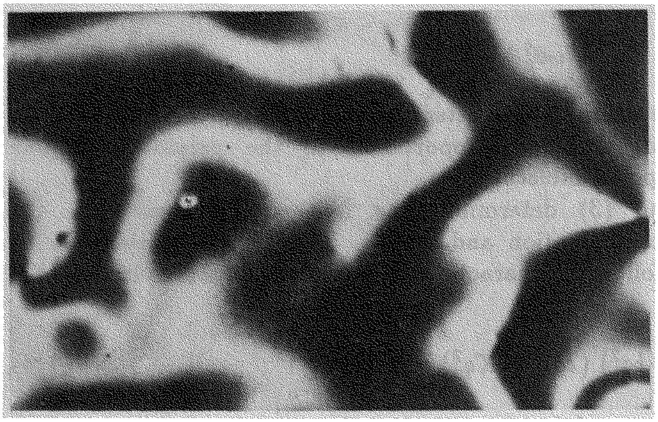

Fig.5. Anisotropic texture of the smectic-C* phase in a mixture of 75% chiral C7 with its racemat, $N = 150$, $T = 53.85\,°C$

polarization which is neccessary for the stripe state formation was found to be 175nC/cm^2 and independent on the C7 concentration in region 100-75% [16]. We have found that composition variation influences textures of the anisotropic state. The anisotropic state with discontinuous walls has been observed only in mixtures with more than 95 % chiral C7. Fig.5 shows a texture of a 150-layer film in a 75 % chiral C7 mixture with its racemat, which can be characterized by a gradual loss of quality of uniaxial orientation. This texture is intermediate state between the anisotropic structure in chiral C7 and a classic schlieren observed in 50% chiral C7 mixture.

To explain properties of observed textures we have considered 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]

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

where the director components are $n_x = \theta \sin\varphi \approx \theta\varphi$, $n_y = \theta\cos\varphi \approx \theta$, $n_z \approx 1 - \theta^2$, it is assumed that the tilt angle θ and azimuth angle φ are small, β^f is the flexoelectric coefficient. We assume the electric nature of the field E. For example, such a field can be created by the elastic stress σ at the expense of increasing density of the surface charge at decreasing surface area of polar heads of molecules. For free-standing thin films, the elastic stress can be provoked 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 smectis film at the conditions when its weight causes the mechanical tension stress σ_{xx} and the perturbations $\theta' = \theta - \theta_0$ and φ which are homogeneous along y-axis but heterogeneous along x-axis, the values $\theta = \theta_0$ and $\varphi = 0$ correspond to a non-perturbed smectic-C. In such a case, one should take into account the following invariants in the free energy density:

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

where the constants a, b, g and K are positive. For a simplicity, we neglect effects of free charges, internal fields and 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 non-zero free energy value after the integration over x-coordinate, here $\beta' E \sim \beta w$, the coefficient β being proportional to the permanent dipole moment and concentration of polar molecules.

The sum of 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 asumption of sinusoidal waves for θ' and φ:

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

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

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

The function $w\left(q^2\right)$ has the minimum value $w_{cr} = w\left(q_{cr}^2\right)$,

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

at the value of wave number squared $q^2 = q_{cr}^2$,

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

Eqs. (4)-(7) show that there is the threshold weight value $w = w_{cr}$ (or critical number of layers N_{cr}) for the smectic-C film, above which the one-dimensional in-plane modulation (stripe state) can appear with the threshold wave number q_{cr}

(the spatial period h_{cr} being equal to $2\pi q_{cr}^{-1}$). The threshold w_{cr} substantially depends on the flexoelectric coefficient β and the tilt angle θ_0:

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

i.e., the values w_{cr} and N_{cr} must strongly increase near the phase transition temperature T_{AC} where $\theta_0^2 \sim (T_{AC}-T)$. At a fixed weight w, Eq.(7) determines the corresponding critical temperature T_s below of which the stripe state arises,

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

Presented theory describes qualitatively good the N_s/T phase diagram of the smectic-C* structural modifications. Solid lines of figure 4 show the best mean square fitts of the T_s dependence on the number of layers with expression (9) taking into account that N is determined there up to some constant N_0. The stripe state of ferroelectric free standing films has obviously a different nature compared to that of achiral films [17]: i) the contrast in stripes observed in present work changes continuously, ii) no defect walls has been observed, iii) periodical textures of achiral films were found only in thin films ($N \leq 60$), whereas the stripe state of smectic-C* is stable only in thick films with $N \geq 85$. The surface bond-orientational order is predicted to exists in 2-3 boundary layers [18]. Therefore effects combined with it should be enhanced by decreasing the number of layers. This is not the case with the stripe state of high spontaneous polarization free standing films. Predictions of [19] can not 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 explains similarity of images of the anisotropic state in thick films before the stripes are formed and that of sealed ultrathin films with thickness below N_{cr}. A more precise model should take into account fluctuation effects similar to described in [9] - [11], which will be published elsewhere.

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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. **A21**, 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. **B16**, 2191 (1977).
10. R.A.Pelcovits and B.I.Halperin, Phys. Rev. **B19**, 4614 (1979).
11. S.A.Pikin, Structurnye prevrasheniya v shidkih kristallah, Nauka, Moskva, p. 178 (1981); english translation: Structural Transformations in Liquid Crystals, Gordon and Breach Science Publishers, New York , p. 229 (1991).

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 **37**, 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).