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Novel structures of a smectic C* phase with high spontaneous polarization in free-standing films

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New stable structures of the liquid crystalline smectic C* phase are observed in free standing films of a material with high spontaneous polarization. A stable configuration of thick films is a stripe of state with an in-plane rotation of the director. In ultra-thin films an anisotropic state was observed. The director fields of the observed structures are modelled and compared with theoretical predictions.

1. Introduction

Liquid crystalline smectic phases can be prepared in the form of free standing films, which are self-confined between two boundary layers. Recent investigations [1,2] have shown that they are convenient objects for the investigation of phase transitions between partially ordered phases in two dimensions, surface ordering phenomena and finite-size effects. The phase diagram of the free standing films is determined by the number of layers and temperature [3]. The structural parameters of smectic phases in free standing films are strongly influenced by a combination of the surface ordering and the finite-size effects. If we forgot for a while about the ordering on the boundary liquid crystal—air, the main effect of the reduced dimension on the structure is the destruction of the long-range order by thermal fluctuations [4,5]. For example, a plane system of projections of the director on to the smectic C* planes ($\mathbf{c}(x,y)$ director) is predicted to be orientationally disordered [5–8] in a direction parallel to the planes, whereas in an analogous 3D system, a long-range order is possible. A correlator describing the order at large distances is a power law decaying function with a temperature dependent exponent. In free standing smectic films, two effects suppressing the thermal fluctuations can change the structure: the dipolar interaction [6–8] and the surface tension [9,10].

Because of the influence of the surface tension, the boundary layers of the smectic A phase in free standing films are as a rule more ordered than those in the middle [9]. Phase transitions, induced by the change of surface tension, have been observed [10].

As was theoretically predicted [6–8], the suppression of the thermal fluctuations by the dipolar interaction in the smectic C* phase can be observed in the formation of an anisotropic state with a long-range orientational order and a non-zero macroscopic polarization. This state is an analogy of the weak anisotropic state of plane ferromagnets [5].

A competing in-plane structure of the smectic C* phase in thin ferroelectric films with free boundaries can exist because of the lack of symmetry centre in chiral films [11]. A detailed consideration of this problem in the framework of the elasticity theory [12,13] has shown that frustrated striped and hexatic states, combined from defects of the smectic C* phase, can be more stable than the common tilted structure.

Structural forms of the smectic C* phase, mentioned above, have not been investigated systematically until now and effects of the ferroelectricity on the structure of smectic phases were not studied. In our paper we report the observation of new structural modifications of the smectic C* phase—anisotropic, homogeneous isotropic and striped states in a substance with a large spontaneous polarization—and discuss possible director field configurations which can be attributed to them.

2. Experimental

We have studied the structures of the free standing films of 4-(3-methyl-2-chloropentanoyloxy)-4′-heptyloxybiphenyl (C7) [14] with the following phase sequence (temperature in °C):

$$S_G\ 43\ S_C^*\ 55\ S_A\ 62\ I.$$

The phase coexistence region was approximately 0·2°C. Spontaneous polarization in the smectic C* phase varies between 130 and 290 nC cm^{-2} [14]. The first order phase transition smectic A–smectic C* disappears in the free standing films on decreasing the number of layers (N) at $N \approx 15$ [15].

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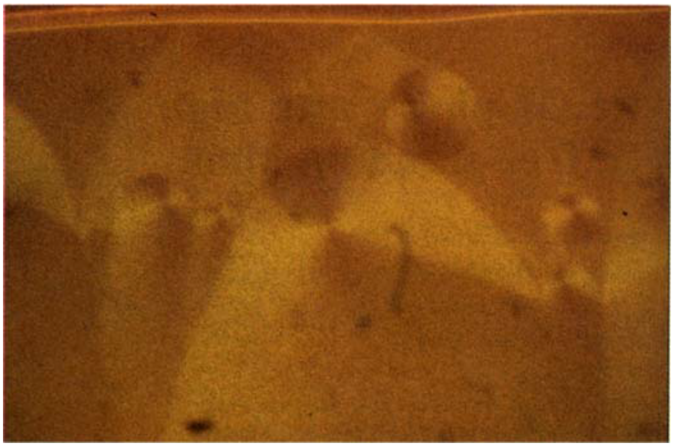

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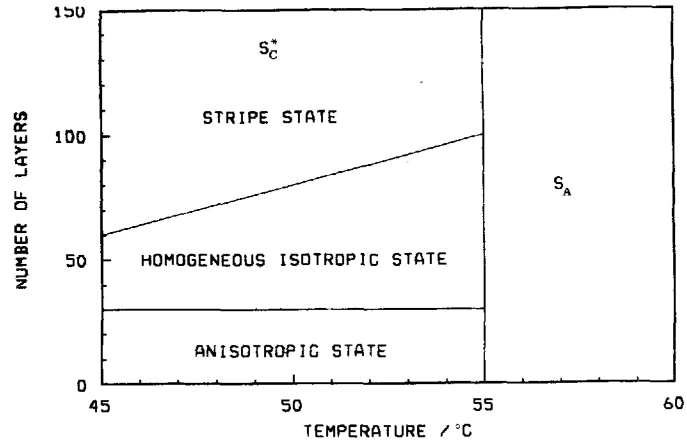
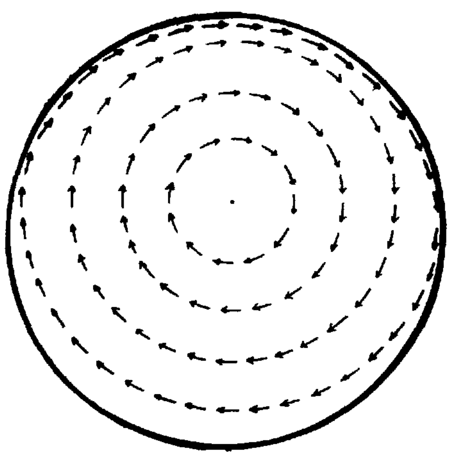


Figure 3. Schematic phase diagram of the structural forms of the smectic C* phase.



(*b*)

Figure 1. (*a*) Smectic C* droplets of C7 occurring in the co-existence region for the phase transition smectic A–smectic C* ($N = 20$)*, and (*b*) scheme of the two-dimensional director field.

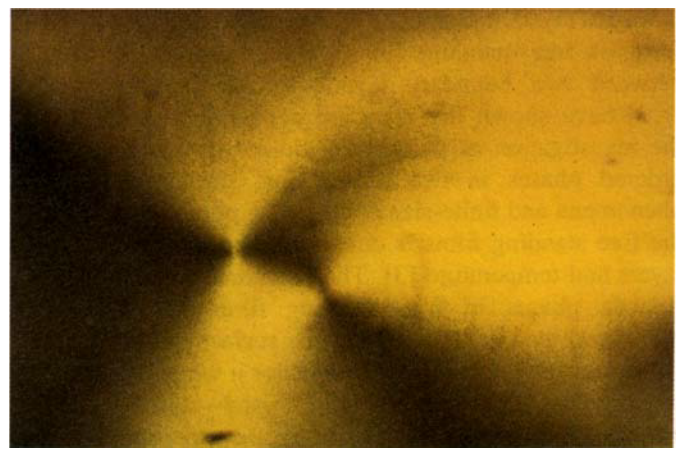


Figure 4. Unstable point defects in a 210-layer film just below the transition temperature into the smectic C* phase ($T = 53°C$).

Figure 2. Schlieren texture of the smectic A phase of C7 at 0·5°C above the phase transition to the smectic C* phase ($N = 20$).

Figure 5. Striped state of the plane director field of the smectic C* phase in the 'bulk' free standing film ($N = 380$).

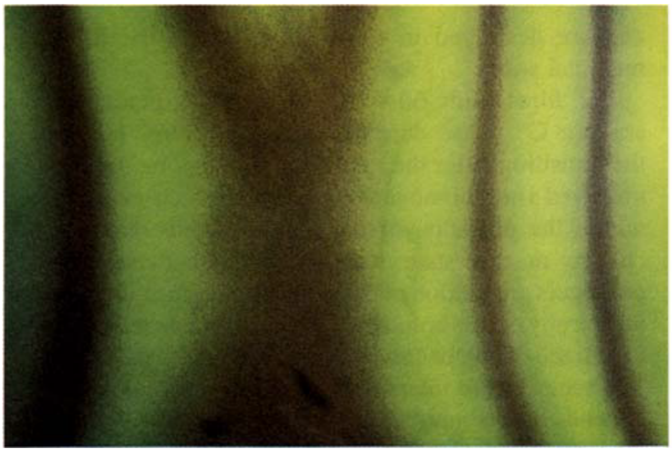


Figure 6. Destruction of the striped state in the middle of the film due to mechanical distortions ($N = 350$).

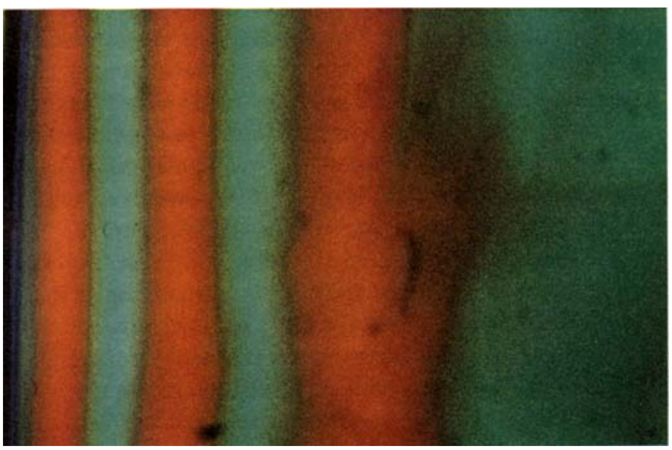
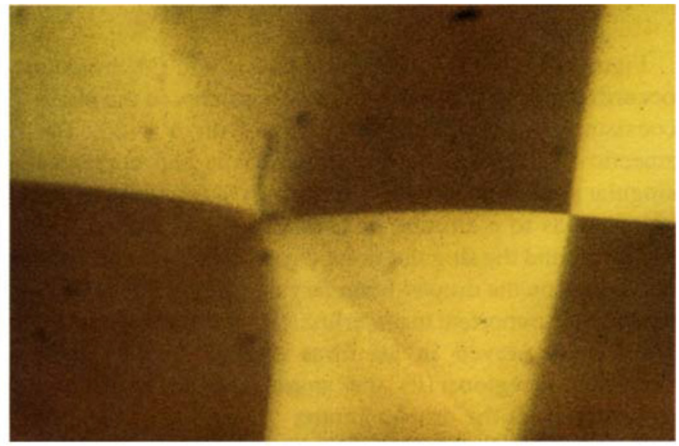


Figure 7. Formation of the striped state from the isotropic state in the smectic C* phase at $T = 48°C$ ($N = 72$).

Textures in the free standing films have been observed using a Leitz–Orthoplan polarizing microscope between slightly uncrossed polarizers and registered photographically for a broad range of number of layers (N = 5–400). Colour of the films arises from a combination of interference and selective reflection, which for this substance corresponds to the visible region of the spectrum. The frame for the production of the free standing films consisted of two brass rails and two movable brass film holders. The number of smectic layers was determined by multiple beam interferometry measurements as previously described in [16, 17]. Films were produced in the smectic A phase and cooled down to the smectic C* temperature interval.



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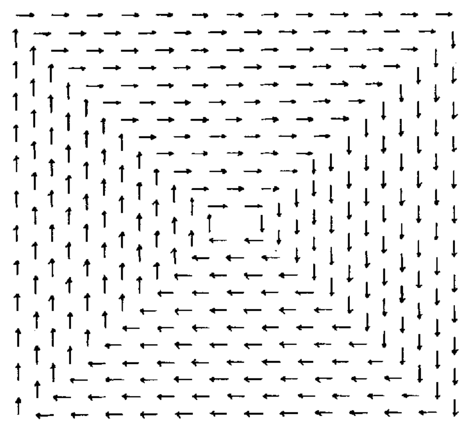

(*b*)

Figure 8. (*a*) Chessboard texture in the smectic C* phase at $T = 52°C$ in an $N = 25$ film, and (*b*) schematic representation of the director field.

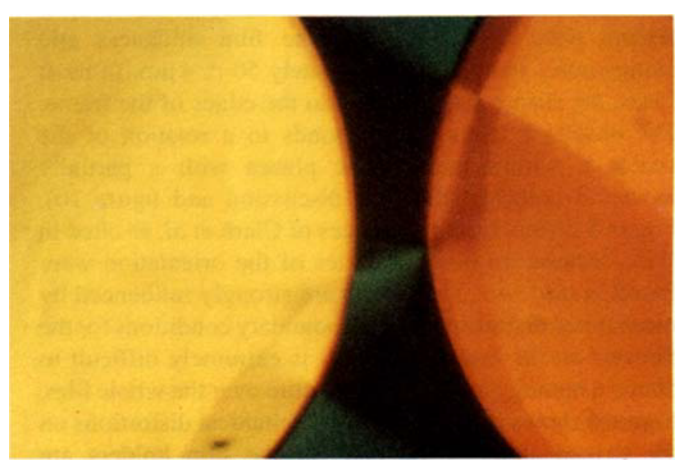

Figure 9. Chessboard texture in the smectic C* phase formed during film production at $T = 49{\cdot}8°C$.

3. Results

Figure 1 (*a*) shows the texture in smectic C* droplets occurring during the phase formation process in the phase coexistence region S_A/S_C^* in a film with $N = 20$. The smectic C* droplets have a round shape and contain a singular point. The variation of contrast inside the droplets corresponds to a circular distribution of the vector field $\mathbf{c}(x, y)$ around the singular point with tangential anchoring conditions on the droplet boundary (see figure 1 (*b*)). Two features are important to underline: (i) such a configuration has been observed in all films studied in the phase coexistence region; (ii) the singular point is usually displaced from the droplet centre.

As already shown [18], the boundary layers in the smectic A phase are tilted. Because of that, one observes a schlieren texture viewing perpendicularly to the planes. Figure 2 shows a texture of the smectic A phase 0·5°C above the phase transition to the smectic C* phase. This image consists of a set of singular point with a variation of contrast similar to that in figure 1 (*a*). Singular points build up a stable structure without any long-range orientational order in the direction parallel to the film. An initial diameter of the smectic C* droplets, occurring in the coexistence region, approximately equals the distance between the singular points in figure 2.

Figure 3 summarizes different structures of the smectic C* phase observed in this work on a schematic *N*/*T* phase diagram for C7.

A general feature of all smectic C* films of C7 is the formation of a system of unstable point defects (see figure 4) which originate from the singular points inside the droplets in the figure 1. These defects recombine over several minutes and a stable texture occurs.

Figure 5 shows a stable texture of a film with 380 layers at $T = 51$°C in the smectic C* phase. A periodic system of stripes is observed after the relaxation of the point defects. Such a configuration of the director field is typical for films with $N \geqslant 100$. The periodicity of the striped texture does not depend on the film thickness and temperature, and was approximately $50 \pm 4\,\mu$m. In most cases, the stripes were parallel to the edges of the frame. The observed texture corresponds to a rotation of the vector $\mathbf{c}$ within the smectic planes with a partially unwound conical helix (see discussion and figure 10). Figure 5 differs from the images of Clark *et al.* as cited in [12], because no discontinuities of the orientation were found in our case. The stripes are strongly influenced by mechanical distortions and the boundary conditions for the director on the brass holders. It is extremely difficult to obtain a homogeneous striped texture over the whole film. Figure 6 shows the influence of mechanical distortions on the striped state. If the ends of the film holders are positioned far apart, films are slightly curved. In such large films, the stripes are seen only in the vicinity of the holders and are destroyed in the middle, where the films are maximal stress.

For films with $60 \leqslant N \leqslant 100$, the structure of the smectic C* phase depends on temperature. Just below the transition, after the relaxation of the point defects, we observed a new homogeneous texture, which was isotropic within the precision of our measurements. No contrast change in this state was registered between crossed polarizers on rotation of the microscopic stage. The optical anisotropy of this homogeneous state, measured by means of a Brace–Koehler compensator, was less than 2×10^{-3}. The temperature interval, where this texture was found, depends on the number of layers. At lower temperatures, the isotropic state was destroyed by the formulation of the striped state, as shown in figure 7, where both states are seen.

For films with $30 \leqslant N \leqslant 60$, the homogeneous isotropic state is stable over the whole temperature interval of the smectic C* phase.

The last region of the phase diagram corresponds to thin films with $N \leqslant 30$. A stable configuration of two-dimensional director field is a new 'chess-board' texture, shown in figure 8. Such a texture develops spontaneously from the smectic C* droplets with a singular point inside (see figure 1). The chess-board texture consists of several singular points, like those shown in the figure 8, with homogeneous fields between them. We have not succeeded in producing a periodic array of quadrangles in the whole film. The chessboard texture has been also found in films thicker than 30 layers, but was unstable and relaxed to the isotropic state. The chessboard texture was observed in the film production process in the smectic C* as shown on figure 9. This image displays a film with a nonuniform thickness, where the yellow part (left) approximately corresponds to 24 layers and the orange part (right) to 30 layers. One can see that the chessboard texture is 'pushed' out of the thicker part in the middle (green colour) into the thinner parts. The area around the singular point consists of the four fields with an anisotropic orientation of the director inside each field; the boundaries between domains are sharp and the director orientation jumps by 90 degrees at each boundary. The director field possesses a fourfold symmetry axis perpendicular to the films. The chessboard texture is a configuration of the anisotropic state with a minimum of polarization around the singular point. This state is analogous to the anisotropic state described in the theory [7, 8].

4. Discussion

To describe the configurations of the director field in the free standing films of the smectic C* phase in the case of zero external field, we use the following free energy

$$F = F_{\mathrm{ch}} + F_{\mathrm{fr}} + F_{\mathrm{P}}, \tag{1}$$

where $F_{\rm ch}$ are additional terms, which exist because of chiral symmetry breaking, $F_{\rm fr}$ is the Frank elastic free energy for an achiral film, and $F_{\rm P}$ is the term describing the long-range dipolar interaction in chiral films.

Let us analyse stable configurations which correspond to different terms in equation (1). Because of the lack of a centre of symmetry in the chiral films, terms proportional to ($\mathbf{c}\cdot$curl $\mathbf{c}$) have to be taken into account in the elastic free energy. Such an analysis was done for the first time by de Gennes [11] and later developed in [12, 13]. A detailed consideration of [12, 13] has shown that the director $\mathbf{c}$ can build-up a one-dimensionally periodic system of discontinuous defect walls (striped state), or a two-dimensional array of intersecting $+1$ walls and $-1/2$ disclinations with a hexagonal symmetry (hexagonal state) [13]. The discrepancy between the observations of figures 5 and 6 and the predictions of theory [11–13] is that no defect walls have been found in our case. This feature can be explained, if we consider the conical spiral structure of the smectic C* phase with an axis perpendicular to the layers. In films thicker than $p/4$, where p is the pitch of the conical spiral, we should not see any stripes. Figure 10 shows a structural model, which corresponds to the double-rotation of the director parallel and perpendicular to the smectic planes, for the case in which no stripes are observable. Both rotations are shown as continuous for the sake of simplicity. The development of this idea leads us to the conclusion that the conical spiral in our case is partially unwound, because in accordance with our estimation we should not see any stripes in films thicker than 100 layers. The unwinding of the conical helix can be analogous to the effect of the polarization field in a planar cell discussed in [19].

The striped state of the smectic C* phase was observed in several earlier experiments [20, 21] without discussing their nature. The essential point for the observation of the striped state is the ability of the molecules to rotate freely at the limiting surfaces [11]. This is the reason why the striped state has not been found in common cells with strong anchoring of the director at the solid substrates. No stripes have been observed in free standing films of materials with a ten times smaller spontaneous polarization—DOBAMBC [16] and ALLO [17]. The influence of spontaneous polarization on the properties can be observed in two ways: first, Frank coefficients can be changed so that the 'elastic' mechanism of stripe formation [11–13] becomes possible; second, some specific ferroelectric effects can constitute the reason for the striped state. Among the theoretical results concerning the influence of the long-range dipolar interaction on the film structure [22–24], we refer to recent calculations by Pikin [24], where the periodical structures are predicted to be stable due to the flexoelectric effect.

In the case of achiral films, the following expression for $F_{\rm fr}$ can be used [7]:

$$F_{\rm fr} = \int dA[\tfrac{1}{2}K_s(\nabla\cdot\mathbf{c})^2 + \tfrac{1}{2}K_b(\nabla\times\mathbf{c})^2], \qquad (2)$$

where K_b and K_s are two-dimensional bend and splay elastic constants; the integration is carried out over the whole area of the film.

It has been shown [6, 7] that the ground state of an achiral film is disordered in two dimensions. That means, that the $\mathbf{c}$ vectors are correlated in orientation only over some distance l_0 [7]

$$l_0 \sim d\exp\left[\frac{\pi K_b(1+\Delta)^{1/2}}{k_BT}\right], \qquad (3)$$

where $\Delta = (K_s - K_b/K_b)$ and d is the film thickness.

The correlation function describing the orientational order in the low temperature phase decays algebraically at large distances as

$$\langle c_\alpha(0)c_\beta(r)\rangle \sim \delta_{\alpha\beta}r^{-\Delta(T)}, \qquad (4)$$

where c_α are components of the $\mathbf{c}$ director, $\delta_{\alpha\beta}$ is the Kroneker symbol, r is the distance between two points and $\Delta(T)$ is a temperature dependent exponent.

Let us now discuss the influence of ferroelectricity [7, 8] on the structure of the two-dimensional smectic C* phase. The main effect of the long range dipolar interaction is the suppression of the thermal fluctuations of the director in thin films, because of the appearance of polarization charges with density $\rho \sim -\operatorname{div}\mathbf{P}$, where $\mathbf{P}$ is the polarization vector which is parallel to the plane of the film and perpendicular to the molecular long axes. The stability

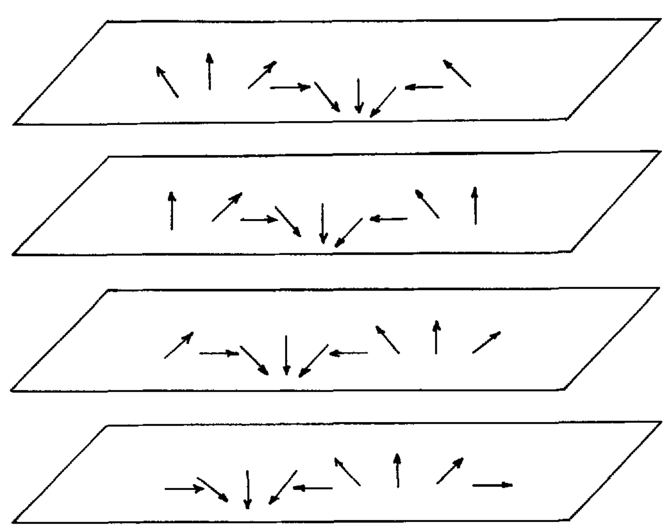

Figure 10. Model of the structure of the smectic C* phase in thick free standing films ($N \geqslant 100$) showing a combined rotation of the director parallel and perpendicular to the smectic planes.

and origin of the chessboard singular points is not clear now, because (div **P**) has a maximum in the configuration of figure 8 (*b*).

The experimental results of this work confirm the general predictions of [7], related to the possible change of structure of the smectic C* phase in films. The orientation at short distances is perturbed by the thermal fluctuations and at large distances our system possesses a long-range orientational order. Let us remark that the correlator analogous to equation (4) is asymptotically equal to a constant for this state [8]. The typical length L_g, characterizing the size of the disturbed region L_g, was estimated in ref. [7] by the following expression:

$$L_g \sim \frac{K}{2\pi P_S^2}, \qquad (5)$$

where K is an elastic constant and P_S is the value of the spontaneous polarization. The condition for the observation of the anisotropic state is that L_g is smaller than the film thickness d. Taking for K the same value as in [7] and for P_S the experimentally measured values in [14], we obtain $L_g \approx 100$ nm. This value corresponds approximately to 25–30 layers, which correlates excellently with our experimental findings.

This estimation shows the importance of the large value of P_S in C7 for the observation of the anisotropic state of the smectic C* phase. The chess board texture in figure 8 is locally anisotropic. Because in the case of the structure with the algebraic decay of the correlator (4) the director field configuration can remain orientationally ordered at small distances within the film size, from our measurements it is impossible to distinguish the anisotropic state of ferroelectrics [7, 8] from the orientationally disordered state (4).

Finally, it is important to emphasize, that the anomalous director field configurations shown in figures 1–8 have not been observed in substances with a ten times smaller spontaneous polarization [16, 17]. The structure inside droplets occurring in the S_A/S_C^* coexistence region of these substances corresponds to a homogeneous orientation of the director [17]. The stable configuration of the smectic C* phase in this case is a common schlieren texture without any periodic modulations in the director field, walls and singularities.

A complete theoretical description of the phase diagram of free standing films with high spontaneous polarization deserves future work. Here we underline the main features of the observed new structures. The stable configuration of the smectic C* phase in thick films ($N \geqslant 100$) is a combination of the in-plane striped state with a partially unwound conical helix perpendicular to the smectic planes. The observation of the striped state in thick films does not contradict the theory of modulated phases as mentioned in [13], but effect of the large value of the spontaneous polarization have to be considered accurately.

In ultrathin films ($N \leqslant 30$), the smectic C* phase forms an anisotropic state which can be regarded as analogous to the weak anisotropic state of plane ferromagnets. Intuitively, it is clear that the critical number of layers N_{cr}, where the stripes disappear, as well as the periodicity of the striped state, depends on P_S (cf. for example, a standard consideration for the smectic C* phase in [8]). This statement follows from the condition of minimization of the free energy in equation (1), but a concrete form of such dependences has to be evaluated. The shift of the phase boundary between the striped and isotropic states at lower temperatures to a range involving smaller numbers of layers (see figure 3) can be explained by the stabilization of the long-range striped order by the dipolar interaction.

This work has revealed a qualitatively new class of structure transformations between liquid crystalline smectic phases in systems with confined dimensions. The investigation of this phenomenon is now in progress and a more detailed description of new structures will be given elsewhere.

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