Two-dimensional hexagonal smectic structure formed by topological defects

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A two-dimensional hexagonal smectic structure formed by point topological defects and intersecting defect walls was discovered. This unique structure was predicted theoretically about 30 years ago but not observed. For a long time the hexagonal structure was a challenge for experimentalists. A different type of self-organization in smectic films was found and used to form the hexagonal structure. Methods applied for building the hexagonal phase can be used for the formation of complicated liquid-crystal structures.

Free-standing smectic films are unique objects in which the validity of many theories of two-dimensional condensed matter physics was tested and supported [1–4]. These films have two free surfaces and consist of a stack of molecular layers. Nanofilms of only two smectic layers can be drawn. In smectic-C (SmC) liquid crystals the long molecular axes are tilted relative to the layer normal. The projection of the molecular axes onto the layer plane, the so-called **c** director [5,6], can be considered as a two-component order parameter. In chiral smectic phases there is no symmetry with relation to the tilt plane. The reduced symmetry of these phases allows a polarization perpendicular to the tilt plane [7]. Another consequence of the reduced symmetry is the presence of a chiral term $\lambda[\nabla \times \mathbf{c}]_z$ in the free energy [3].

Chirality plays an important role in ferroelectric liquid crystals. Complex equilibrium structures can be formed in chiral materials. In bulk samples chirality leads to the formation of a helix with the axis perpendicular to the smectic plane. Chirality also acts in the plane of two-dimensional smectic layers and leads to nontrivial effects and structures. In free-standing films a simple rotation of the **c** director in the plane of smectic layers does not lead to a decrease in energy with respect to the uniform orientation. However, the uniform orientation in chiral films may become unstable with respect to the formation of a phase with an ordered structure of defects [3,8–13]. A stripe phase formed by periodic arrays of line defects was predicted theoretically in several papers [3,8,9,11]. In a simple model of the stripe phase the **c** director rotates continuously in stripes between defect walls and then jumps back in the wall. A one-dimensional lattice of defect walls is formed when the chiral contribution to the free energy is larger than the energy of the wall $\lambda > \varepsilon$ [3], where ε is the wall energy per unit length. The structure of the domain wall was calculated by using a Landau expansion of the free energy [3,9,11]. Between the walls the modulus |**c**| is approximately constant, and within narrow walls the modulus and orientation of the **c** director change continuously. Stripe structures can be formed also in nonpolar films due to asymmetry related to the surface [14]. Predicted stripe structures in polar films were observed experimentally [8,15–18]. Both the theory describing the stripe phase and the experimental observations are well established.

In the same theoretical papers which described the stripe structure, a more complex phase with a hexagonal lattice

of topological defects and intersecting walls was predicted [3,9,11,13]. This phase is composed of hexagonal domains. At the center of the hexagonal cell there is a point defect of strength $S = +1$. In this phase the director field in the hexagonal cell has C_6 symmetry, in contrast to free point defects with symmetry C_∞. The nearest domains are separated by line walls where the **c** director rotates by π. Point defects with $S = -1/2$ are located at the corners of the cells. However, in spite of the same theoretical approach that successfully predicts the stripe phase, the hexagonal lattice was not observed experimentally. Observation of this structure has remained a challenging problem for several decades. Due to the long history of theoretical predictions, this mysterious phase "remains a theoretical possibility for future experiments" [3].

The question arises as to why this structure was not observed. Kamien and Selinger [3] point out two conditions for the formation of the two-dimensional hexagonal phase: (a) The bend elastic constant K_B must be small in order to decrease the energy of the domains with bend topological defects, and (b) chirality must be high. However, these two conditions may not be met in ferroelectric liquid crystals. In nonpolar SmC and ferroelectric SmC^* with small polarity and chirality, the bend elastic constant K_B is smaller than the splay constant K_S [19–21]. An increase of polarity and chirality in SmC^* leads to an increase of the bend elastic constant due to polarization charges which form at the bend deformation. The bend elastic constant K_B becomes larger than K_S [22–24]. In our opinion, the effect of polarization charges may be one of the reasons why the conditions for the formation of the hexagonal structure have not been obeyed. We also point to another reason why this phase was not observed. The hexagonal lattice is composed of point topological defects with positive energy. At the formation of this phase the nucleus must consist of several domains, that is, its size must be several tens of micrometers in order for the nucleus to be energetically favorable. In our opinion, the possibility of the formation of such a large nucleus is highly improbable.

In this paper we report the observation of a hexagonal defect structure. We describe the procedure that leads to the formation of a structure with ordered point topological defects and defect walls. The hexagonal structure was built from smectic islands that were formed in a smectic nanofilm. An antiferroelectric SmC_A^* liquid crystal
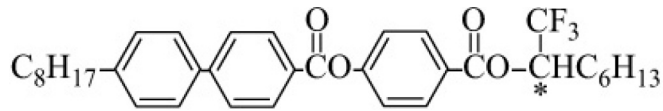
FIG. 1. Molecular structure of compound TFMHPBC. An asterisk indicates the chiral center.

was used for the formation of the hexagonal structure. The investigations were made on liquid-crystal 4-(1-trifluoromethylheptyloxycarbonyl)phenyl 4′-octylbiphenyl-4-carboxylate (TFMHPBC) [25], whose chemical structure is given in Fig. 1. The sequence of phase transitions in the bulk sample is SmA-(75 °C)-SmC$_\alpha^*$-(74.3 °C)-SmC$_A^*$. Two peculiarities of this material are appropriate for the preparation of the hexagonal phase. First, free-standing films of antiferroelectric liquid crystals have a small polarization related to the surface in films with an even number of layers or noncompensated polarization of one smectic layer in films with an odd number of layers [26–29]. Second, the wavelength of the selective reflection in the bulk sample is about 500 nm, that is, the chirality of TFMHPBC is rather high.

Free-standing smectic films were prepared in a rectangular hole. The frame used to prepare the films had two immovable rails with a fixed distance between them (about 0.5 cm) and two movable metal plates. The movable plates can be in contact and moved apart up to several centimeters. Observations between the crossed polarizers and using depolarized light-reflected microscopy (DLRM) [30] were made to map the **c**-director orientation. The photographs presented in this paper were taken in the antiferroelectric phase at about 60 °C, when the contrast of DRLM images was high. The images of the films were taken with a digital video camera.

The hexagonal structure was prepared in several steps. First, we prepared a two-layer film in the temperature range of the SmC$_A^*$ phase. Such a thin smectic nanofilm is the starting point of our experiment. The typical size of the films was about 0.5 × 1 cm^2. Then, the distance between the movable plates was decreased sharply. The area of the hole decreased so fast that the material of the film had no time to move into the meniscus. Circular islands of a larger thickness are formed in the thin film as the size of the film decreases [Fig. 2(a)]. The islands of homogeneous thickness are, as a rule, up to six times thicker than the nanofilm. The configuration of the **c** director in the island is shown in Fig. 2(b). The circular orientation of the **c** director on the island border requires the existence of a point topological defect with strength $S = +1$ in the island or on its boundary. Similar islands were investigated earlier [22,23,31–36]. In most previous investigations [22,23,32–34] the formation of the islands was induced by small particles that were located in the center of the topological defects and changed their energy. In our studies the centers of the topological defects had a natural structure.

There are several stable and metastable configurations of the **c** director in the circular island [22,33,36]. Further, we deal with pure bend islands with a point topological defect located near their center (Fig. 2). In order to conserve the topological charge in the system simultaneously with the island ($S = +1$), a topological defect with $S = -1$ nucleates in the film [37]. The island and the $S = -1$ defect form a topological dipole.
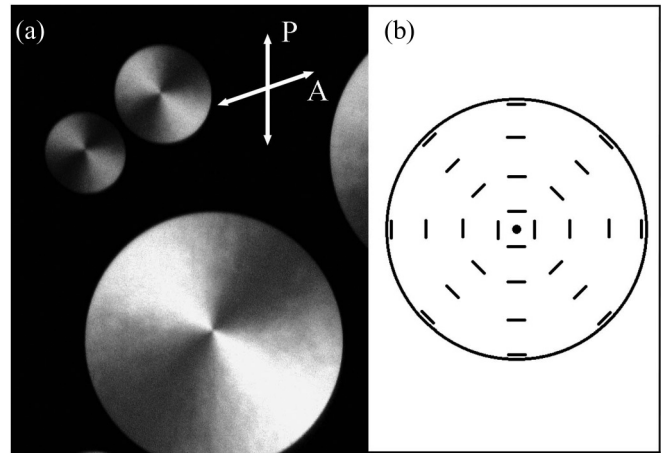

FIG. 2. (a) Islands with point topological defect, $S = +1$. The islands were created in a smectic nanofilm with a thickness of two molecular layers. (b) Schematic representation of the director orientation in an island. The islands are viewed in reflection using DRLM. The orientation of the polarizer (P) and the analyzer (A) is shown in the figure. The horizontal size of (a) is 367 μm.

The dipoles attract and can self-organize in linear chains [38–40]. However, another scenario is possible. In thin nanofilms the repulsive interaction between islands is small and they can come into contact (Fig. 3). Moreover, the length of the contact line increases. Some islands fuse, especially in the case when the material of the film and the islands move. However, in many cases the islands remain in contact for a long time. Chirality leads to the same sense of **c**-director rotation at the inner boundary of different islands, which prevents their fusion. An increase in the defect wall length when islands enter in contact suggests that the wall has a negative energy with respect to the energy of two free boundaries of the islands. This conclusion is important for the further formation of defect structures and for the theory of the hexagonal structure.

Not only two but a larger number of islands can enter in contact. In order for the hexagonal structure to be formed, islands of approximately the same size must be prepared.
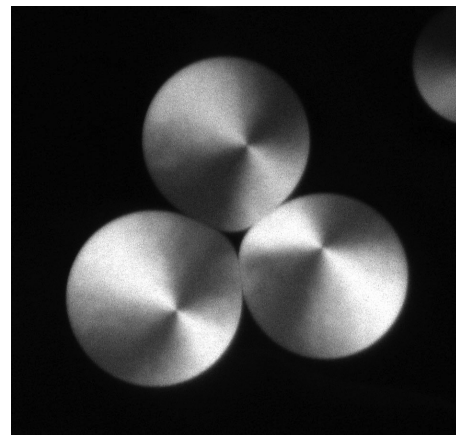

FIG. 3. A cluster formed by three islands. The islands attract due to a decrease of the boundary energy. The photograph was taken in DRLM. The horizontal size of the image is 427 μm.
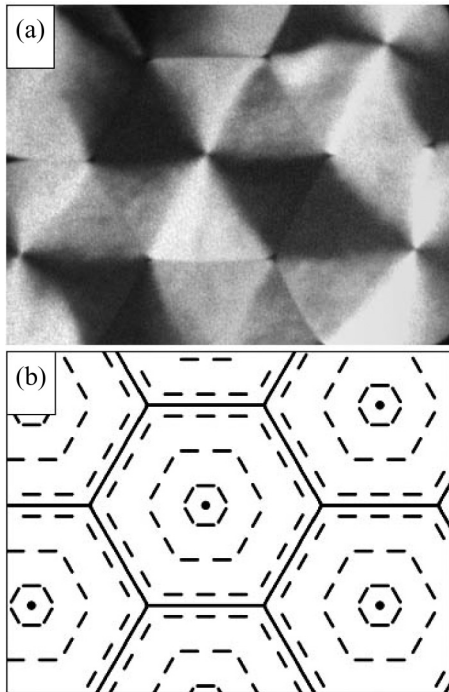
FIG. 4. (a) Hexagonal structure formed by point topological defects and intersecting defect walls. The microscope image was obtained in DRLM. The orientation of the director in the hexagonal structure is shown in (b). The horizontal size of the image is 167 μm.

After several attempts we succeeded in preparing such islands. The remarkable self-organization of the islands and the transformation of their form from circular to hexagonal occur. These processes lead to the formation of ordered structures of point topological defects and walls. Figure 4(a) shows an image of the two-dimensional structure formed by the islands. Figure 4(b) shows the configuration of the **c** director in this structure. The formed structure is the hexagonal lattice of topological defects. In each domain formed by one island the **c** director has a hexagonal symmetry (Fig. 4). The **c** director orients parallel without deformation in each sector. Then, on the boundary with the nearest sector, the **c** director sharply rotates by $\pi/3$, in accordance with the change of the orientation of the defect wall. This structure is the same as was predicted theoretically [3,9,11,13]. The **c** director rotates in opposite directions in the vortex (the center of the hexagonal domain) and in the antivortex where three defect walls meet. In the area where three domains meet, as a rule, a small piece of the initial nanofilm remains. It decreases the core energy of the defect.

Let us repeat why we have succeeded in the observation of the hexagonal structure formed by topological defects. First, we prepared the islands as components of the hexagonal structure. These islands were prepared in a thin nanofilm whose elasticity does not prevent the formation of the two-dimensional structure. The energy of the defect wall is negative with respect to two separate boundaries of the islands, which leads to a self-organization of the islands in a two-dimensional structure. The core of the antivortex (the $S = -1/2$ disclination) consists of a thin film that decreases the energy of the defect. A SmC_A^* liquid crystal with a small bend elasticity and high chirality was used. All these factors are favorable for the formation of the unique structure of the hexagonal lattice of topological defects.

In summary, we directly observed the hexagonal modulated structure in free-standing smectic films. The procedure to obtain a hexagonal lattice of topological defects was developed and described. We demonstrate that smectic islands can self-organize in a two-dimensional ordered structure. The distinguishing feature of this structure is the presence of a regular network of both point topological defects and wall defects. Chirality stabilizes the hexagonal structure. Our observations of the hexagonal structure are consistent with theoretical predictions. The strategies used for the formation of the hexagonal structure can be applied to building other structures. These may be clusters with a different number of particles and symmetry, and two-dimensional structures in which thin films and islands are different materials. Using the dispersion of materials in films and laser tweezers, together with describing the mechanism of self-organization, can extend the possibility of the preparation of different structures.

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