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Anticlinic-synclinic transitions in superthin free-standing smectic films

P. V. Dolganov[1)], G. Joly[+], P. Cluzeau[*], V. K. Dolganov, C. Gors[+], H. T. Nguyen[*]

Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow Region, Russia

[+]Laboratoire de Dynamique et Structures des Matériaux Moleculaire, Université de Lille 1, 59655 Villeneuve d'Ascq, France

[*] Centre de Recherche Paul Pascal, CNRS, 33600 Pessac, France

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Anticlinic-synclinic transition was studied in superthin smectic films using polarized light reflected microscopy. The measurements were made in a compound exhibiting the SmC^*_{FI1} subphase in a narrow temperature interval between antiferroelectric SmC^*_A and ferroelectric SmC^* phases. In films we observed series of transitions which numbers increases with increasing film thickness. Surface ordering leads to increasing transition temperatures with decreasing film thickness and to change of orientation of the molecular tilt plane in layers. Succession of transitions results from the competition between the surface and the bulk ordering. We found that line string defects may form in film, their orientation and collective behavior result from elastic deformation of molecular ordering.

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Unique structural quality of thin free-standing smectic films makes them ideal objects for studies of surface phenomena and phase transitions in restricted geometry [1]. Of special interest are the studies of structures with a two-component order parameter, when surface may influence both the modulus and the phase of the order parameter. Such structures are liquid crystals with polar ordering of smectic layers: fundamental ferroelectric Smectic-C^* (SmC^*) [2], the antiferroelectric Smectic-C^*_A (SmC^*_A) [3, 4] phases and intermediate smectic subphases [3, 4]. In smectic-C (SmC) type liquid crystals each layer may be regarded as an orientationally ordered liquid with long molecular axes tilted by an angle θ with respect to the smectic layer normal. Azimuthal orientation of molecules in layers is characterized by the order parameter phase φ. Structure of tilted smectics may be also described by a two-dimensional vector, so-called **c**-director (projection of the nematic **n**-director onto the smectic layer plane) [5]. Different sequences of variation from layer to layer of the phase φ and modulus θ of the order parameter lead to the formation of a variety of smectic structures. In the SmC^* structure the order parameter phase φ in neighboring layers (i and $i+1$) differs insufficiently $\Delta\varphi = \varphi_{i+1} - \varphi_i \approx 0$. In the Sm$C^*_A$ structure molecules in adjacent layers are tilted in nearly opposite directions $\Delta\varphi = \varphi_{i+1} - \varphi_i \approx \pi$. The order parameter modulus is the same in all layers. Difference of $\Delta\varphi$ from 0 and π in these structures is related to the fact that chirality of molecules forming the SmC^* and SmC^*_A induces the formation of a long-wave helix with its axis parallel to the normal to the smectic layers.

Influence of the surface on structure and phase transitions may be divided in two parts. (a) The surface breaks up the translational and rotational symmetry. Smectic layers in the free-standing films are perfectly parallel to the surfaces. Absence of layers from one side of the surface and hence of interactions related to these layers induces a modification of the structure near the surface. In tilted smectic liquid crystals interlayer interaction is anisotropic in the plane of the smectic layer, i.e. the surface influences the modulus and the phase of the order parameter. (b) The second reason for modification of surface structure is related to a change of its dynamics with respect to the bulk. "Freezing" of transverse fluctuations of surface layers leads to increase of the order parameter [6, 7] and to high temperature shift of the surface SmC^*-SmA transition [8]. It is commonly admitted that "freezing" of fluctuations directly influences the modulus of the smectic order parameter. However, in compounds which structure is formed by change of the molecular tilt direction from layer to layer, interaction of order parameter modulus with its phase may also lead to change of the order parameter phase near the surface, i.e. to change of interlayer orientational structure.

In previous studies of the SmC^*_A structure and SmC^*_A – SmC^* transition in thin films a number of principal and important results have been obtained [9 – 12]. Absence of net transverse polarization in SmC^*_A films with an even number of layers [9, 10] was one of the main proofs of anticlinic structure of antiferroelectric. It has

[1)]e-mail: pauldol@issp.ac.ru

been shown that temperatures of the bulk and surface SmC_A^*–SmC^* transitions in films with number of layers $N > 4$ differ [12]. However a number of points remain unclear, in particular the direction of the temperature shift of the SmC_A^*-SmC^* transition in superthin films [9 – 12], the influence of the number of layers on the structural states. The present investigations are the first studies of the antiferro-ferri-ferroelectric transition in superthin films with different number of smectic layers.

In this paper investigations of free-standing films have been performed in antiferroelectric liquid crystal 4-(1-methylheptyloxycarbonyl)-3-fluoro-phenyl – 4′[4-dodecyloxybenzoyloxy]-benzoate (MHOFPDC) exhibiting the following phase sequence: SmC_A^* (109.5 °C) SmC_{FI1}^* (110 °C) SmC^* (123 °C) SmA. Formation of subphases between SmC_A^* and SmC^* is typical for antiferroelectric liquid crystals [3, 4]. In the bulk sample of MHOFPDC the transition from the anticlinic to synclinic ordering occurs via the 3-layer SmC_{FI1}^* structure [13 – 16]. Symmetry of the SmC_{FI1}^* and numerical calculations [17, 18] show that this structure is formed by change of both the phase and modulus of the order parameter from layer to layer. Investigations of phase transitions and defects in thin films were performed using polarized and depolarized reflected light microscopy. The films were prepared by spreading a small amount of the compound in the SmC^* phase over a 3mm hole in a thin glass plate. The number of smectic layers in the film was determined by the intensity of reflected light in the backscattering geometry [19]. For orientation of the tilt plane we used a magnetic field which direction could be changed with respect to the film plane [20]. Studies of phase transitions and structure of defects were performed using a digital camera.

In thin films we observed a series of transitions with transformation of anticlinic structure to synclinic (Fig.1). At higher temperatures we also observed transformation of the film structure related to the bulk SmC^*–SmA transition. It is known that these transitions in films occur near and above the bulk transition temperature [12, 21 – 24]. In the present paper we discuss the results of investigations of the SmC_A^*–SmC_{FI1}^*–SmC^* transitions in thin films. In a two-layer film we observed the transition at temperature about 140 °C. This is not only higher than the transition to the SmC^* phase, but also above the phase transition in the bulk sample from the SmC^* to untilted SmA phase. However the two-layer film both below and above the transition possesses the in-plane optical anisotropy, i.e. upon heating the transition from antiferroelectric to the tilted synclinic structure occurs with a sufficient high temperature shift (about 30 °C) with respect to the bulk sample. With increasing the film thickness the number of transitions increases (Fig.1). In a three-layer film we observed 2 transitions, in a four-layer film 3, in five-, seven-layer film 4 transitions. Transition temperatures decrease with increasing film thickness. In thick films the four transitions are grouped into two pairs and the temperature range of the transitional region between anticlinic and synclinic structures is about 10 °C (Fig.1).

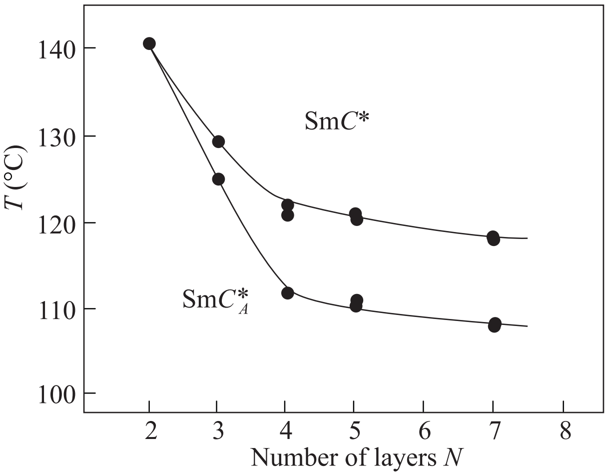

Fig.1. Transitions in thin free-standing films of MHOFPDC. In thick films, the low-temperature branch is related to two interior transitions in films, the high-temperature branch to two surface transitions. In five- and seven-layer films there are two pairs of transitions with close temperatures of transition. N is the number of smectic layers in the films

As a rule transitions occur with thermal hysteresis. In states overheated or overcooled with respect to equilibrium transition temperature the transition occurs in a short time interval in the whole film (less then 0.1 s). The reason for the existence of this hysteresis seems to be related to a substantial potential barrier between anticlinic and synclinic orientations. In the case of large thermal hysteresis in some of the experiments a smaller number of transitions than shown in Fig.1 were observed due to their combination. For example, in a five-layer film three or only two transitions can occur: one in the region of the low-temperature branch of transitions and one in the high-temperature region. When we are able to observe the transitions at an equilibrium temperature they look like a sharp front moving in the plane of the film (Fig.2a). Figure 2b shows the transition in a film upon motion of fronts formed by two germs of the new structure. Besides a boundary between two structures (1-2 and 1-2′) in a number of cases we could observe

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Fig.2. Sharp front of transition from anticlinic (*1*) to intermediate (*2*) structure in a five-layer film (a). Meeting of two transition fronts (*2-1*) and (*2′-1*) may lead to formation of a boundary (*2-2′*) with breaking of the **c**-director orientation (b), four-layer film. $T = 120.5\,^\circ$C (a), $T = 111.3\,^\circ$C (b). The horizontal size of the images is 710μm

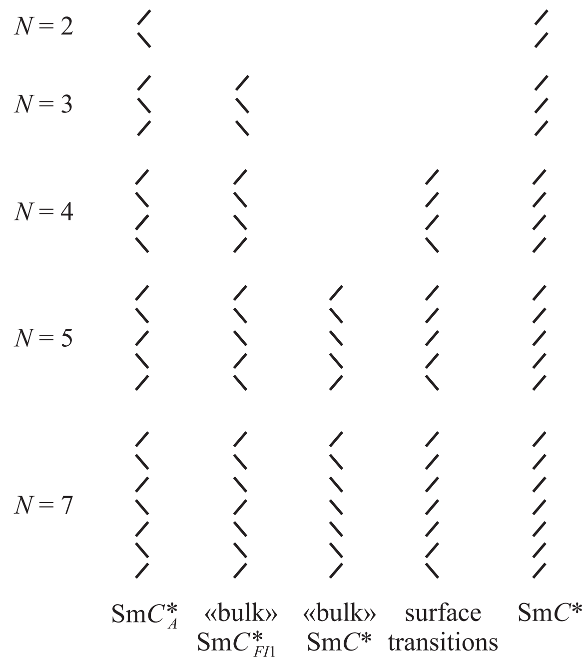

Fig.3. Structures formed during the transition of the film from the anticlinic ordering (SmC^*_A) to synclinic (SmC^*). N is the number of smectic layers in the films

a breaking of **c**-director orientation in the same structure in the place of meeting of two fronts (2-2′, Fig.2b). Such sharp boundaries are not typical for liquid crystals with in-plane orientation ordering, in which the transition from one orientation to another occurs, as a rule, by continuous change of **c**-director orientation. We shall return to this question later when we shall discuss orientational defects forming in films.

Comparing the number of observed transitions with possible orientation of molecular tilt planes in different smectic layers we may deduce practically unambiguously structure of superthin films and with a large degree of probability structures of thicker films. As was mentioned before, in a two-layer film the transition between in-plane anisotropic structures could be only an anticlinic-synclinic transition (Fig.3). In a three-layer film the transition between the SmC^*_A and SmC^* occurs via an intermediate structure with anticlinic orientation of surface layers (Fig.3). In the center of thick films the sequence and temperature range of the phases should correspond to the bulk sample. Two low-temperature transitions in thick films should be interpreted as transitions from anticlinic structure to a three-layer one and then to a synclinic state (Fig. 3). Surface transitions are shifted to the high temperature region (high temperature branch). As a rule these transitions occur independently on the two surfaces at close temperatures.

A number of qualitative conclusions about the interlayer interactions could be deduced from the view of the phase diagram (Fig.1). In a two-layer film the high temperature shift of the transition between synclinic SmC^* and untilted SmA with respect to the bulk sample is about 30 °C [8, 25]. Surface ordering also leads to increase of the anticlinic – synclinic transition temperature in a two-layer film (Fig.1). The same value of temperature shift means that the transition between tilted structures in the two-layer film occurs at the same value of molecular tilt angle as in the bulk sample. Antiferroelectric - ferroelectric transition results from competition between F_a and F_s interactions stabilizing anticlinic and synclinic ordering in nearest neighboring (NN) layers. These interactions alone cannot lead to formation of intermediate structure in a three-layer film. To form the structure with both anticlinic and synclinic orientations in a three-layer film interaction between next-nearest neighboring (NNN) layers is necessary. Such interac-

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Fig.4. Linear defects in MHOFPDC films. The tilt plane is oriented by magnetic field in horizontal direction. (a) π-walls with continuous change of **c**-director orientation. Two walls are separated by a point topological defect. The polarizers are crossed. (b) Strings with breaking of orientation of the **c**-director in the center of the line defect. Strings are oriented perpendicular to the **c**-director. The polarizer and the analyzer are slightly decrossed. (c) Orientation of the **c**-director near the string ending with two $|s| = 1/4$ point defects. (d) Strings attract and link by ends having point defects of opposite signs, forming longer strings. $N = 6$, $H = 2\,\mathrm{kG}$, $T = 115.2\,^\circ\mathrm{C}$. The horizontal size of the photographs is about 500μm

tion in the discrete phenomenological theory [26, 27] is the so-called frustrating interaction (F_f), stabilizing anticlinic orientation in NNN layers. In a three-layer film the surface ordering (i) increases the region of existence of anticlinic structure due to NN interaction F_a and (ii) stabilizes the intermediate structure at higher temperatures with respect to the bulk sample through NNN interaction F_f. In thick films before the transition to the SmC^* the surface structure is anticlinic if one considers two surface layers and SmC^*_{FI1}-like, if we take into account three layers (Fig.3), i.e. surface ordering makes a contribution to stabilization of the surface structure both via NN and frustrating NNN interaction. Description of the SmC^*_A–SmC^*_{FI1}–SmC^* transitions in thick films needs consideration of NNNN interaction [16, 28]. Until now such theoretical description of the transitions in films has not been made.

In thin films we observed two types of linear orientation defects: walls with continuous change of **c**-director orientation across the defects (Fig.4a) and string defects with a sharp core (Fig.4b). Strings were first found in films by J. Pang et al. [29] but up to now their internal structure and origin remain unclear. Appearance of string defects is also connected with thinning transitions [30]. We investigated strings in oriented samples and found that strings orient perpendicular to the **c**-director (Fig.4b) and interact even at large distances. In the present case, the nucleation of defects is connected with structural transition. Figure 4c shows the distribution of the **c**-director near an isolated string obtained by depolarized light reflected microscopy. This is a so-called 1/4-string [29] with **c**-director oriented by an angle $\pm\pi/4$ to the string near its core and with a discontinuous change of orientation on the angle $\pi/2$ upon crossing the string. The **c**-director orientation near the string ends corresponds to two point topological defects with strengths $s = +1/4$ and $s = -1/4$. Short strings may be considered as a topological dipole [31]. Long strings repel in the direction perpendicular to the strings due to same direction of the bend deformation of the **c**-director orientation between neighboring strings. Such strings are situated at substantial distances. With time the average length of the strings increases (Fig.4d). It occurs not due to elongation of isolated strings, but as a result of their head to tail adjoining and formation of longer strings. Strings shifted with respect to each other by a distance of the order of their length interact more like topological defects with strength $\pm 1/4$. These strings attract to each other and adjoin by ends having topological defects of opposite signs.

Several proposals have been made concerning the structure of the core [29], in particular that it is formed by small particles of impurities. We observed formation of strings after a fast transition in a film and their disappearance as a result of a next transition. We may propose that string core consists of nuclei of another structure like a boundary formed as a result of transitions starting in two different parts of the film (Fig.2b). Particles of impurities trapped on this linear defect may prevent string collapse from its ends.

In summary, we have reported optical reflection measurements of compound possessing SmC^*_A, SmC^* phases and SmC^*_{FI1} subphase with a small temperature interval. Our results show that surface ordering effectively interacts with phase of the order parameter leading to increase of transition temperature in thin films and to formation of two branches of transitions (interior and surface transitions). In film besides conventional walls we observed narrow string defects with total topological strength zero. Their orientation in anisotropic film and collective behavior are determined by elastic deformation of the in-plane molecular ordering.

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