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Formation of string defects at thinning transitions in smectic-C^* free-standing films

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The layer thinning transitions in freely suspended smectic-C^* films have been investigated. The defect structure formed by stringlike lines was observed just before the thinning transitions. The string defects disappear after the thinning transition and appear again near the temperature of the next thinning transition. These results clearly indicate that thin free-standing films at the thinning transitions are slightly below the melting temperature of the interior layers.

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Surface has a strong influence on the structure and phase transitions in thin organic films. Smectic films with two boundary free surfaces in contact with air are ideally suitable to investigate these phenomena. The freely suspended films consist of stacks of molecular layers parallel to the free surfaces and ranging from thousands to only two layers [1]. Heinekamp *et al.* [2] observed the surface smectic-C^* (Sm-C^*) structure well above the bulk Sm-C^*–smectic-A (Sm-A) transition temperature. The surface transition temperature depends on the film thickness. Similar behavior was observed for others phase transitions [3]. For the phase transitions between smectic phases a free surface stabilizes the higher ordered smectic structure. For conventional solids, it is well known that the surface melts below the temperature of the phase transition in the bulk. On the opposite hand, the smectic structures still exist near the free surface well above the bulk smectic-isotropic (I) transition temperature [3,4]. This means that the surface stabilizes the phase with positional order. An excellent demonstration of this phenomenon was given by the experiment of Stoebe, Mach, and Huang [5]. They found that thin Sm-A films neither melt nor rupture when they are heated above the Sm-A–I transition. The temperature range of stability of the Sm-A films increases by decreasing the film thickness N. When the critical temperatures T_N are achieved, the film undergoes thinning transitions where the film thickness decreases. The layer-by-layer thinning regime can start near the bulk transition temperature in films with thickness more than 20 layers [6,7] and a two-layer film ruptures at approximately 30 K above the bulk Sm-A–I transition temperature. To date, the thinning transitions were also observed above the bulk temperatures of the Sm-A–nematic [8,9] and Sm-A^*–I [10] transitions.

The nature of instability of the film near the temperature of the thinning transition is, up to now, the subject of discussions. The first model proposed for the thinning transition [5,8] is based on the assumption that the smectic order occurring on the boundary of the film is characterized by a penetration length ξ. If the film thickness L is less than twice the penetration length, the film is stable in the bulk isotropic or nematic temperature range. When $L > 2\xi$ the isotropic or nematic phase appears in the film interior and removes to the meniscus. The temperature dependence of the thinning transition may be described by a power-law function: $L = L_0 t^{-v}$, where $t = (T_N - T_0)/T_0$ [5,8]. In the model of Go Gorodetsky, Pikina, and Podneks [11] the external compression due to the curvature of the miniscus cannot be balanced by the internal elastic forces when the temperature reaches a critical value and the film undergoes the thinning transition. In that case the interior layers do not melt. In the models [12–14] based on the mean-field theory the interior layers can melt into the nematic [13] or quasismectic [12,14] phases. An alternative dislocation model was proposed to explain the nature of the thinning transition [7,11]. According to this model the thinning transition is initiated by the nucleation of a dislocation. The experimental results can be fitted using equation $N = a_0 t^{-1/2} \operatorname{arcsinh}[a_1 t^{-1}]$, obtained from the dislocation model [7]. T_0, a_0, and a_1 are three fitting parameters. Unfortunately, the results of good fitting have generally not been able to prove the validity of these models. The experimental data can be also described by a simple power law [5,6,8,10,15,16].

In the present Rapid Communication the results of our optical studies of a chiral Sm-C^* phase are reported. We paid particular attention to the behavior of the films near the temperature of the layer-by-layer transition. We found that just before the thinning transitions the continuous orientation of the **c**-director field breaks up. The temperature range of the existence of a defect structure is a few hundredths of a degree. The thinning transition leads to the disappearance of the defect structure.

Experiments were carried out on free-standing films of S-4-heptyloxybiphenyl (S)-4-(1-methylheptyloxy) benzoate (7BSMHOB) [17]. The 7BSMHOB exhibits the following phases sequence: Sm-C^*-(92 °C)–cholesteric (N^*)-(135 °C)–I. The measured tilt angle [17] in this material is large: about 45° at the Sm-C^*–N^* phase transition. The helical pitch varies from 130 nm at 73 °C to 300 nm at the temperature of the bulk Sm-C^*–N^* transition. Free-standing films were prepared by drawing a small amount of the liquid crystal across a 4 mm hole in a glass plate. The experimental setup enables simultaneous reflectivity mea-

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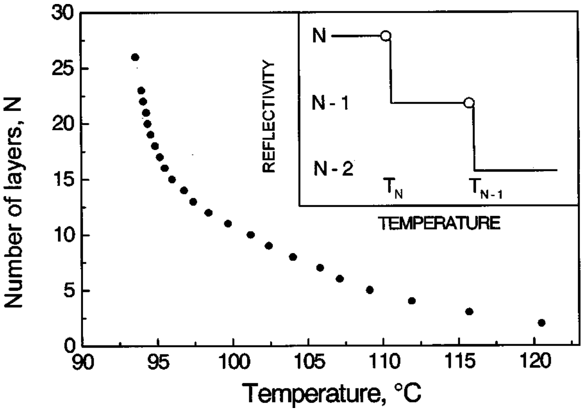

FIG. 1. Number of layers of a freely suspended film N vs temperature T_N for the compound 7BSMHOB. The inset in the figure shows schematically the reflected intensity on heating. T_N is the highest temperature where the N-layer film exists. Stringlike lines appear just before the thinning transitions (open points). In other wide temperature ranges, uniform orientation of the molecular field is observed.

surements and optical observations via reflected light microscope. For an N layer film, optical reflectivity is given by [18]

$$I(\lambda)=\frac{(n^2-1)^2\sin^2(2\pi nNd/\lambda)}{4n^2+(n^2-1)^2\sin^2(2\pi nNd/\lambda)},$$

where n is the average index of refraction and d the layer thickness ($d\approx 3$ nm). For thick films ($N>25$ layers) the thickness is deduced from the reflectivity spectrum. For thinner films the relative reflectivity at a constant wavelength was used to determine their thickness. The thinning transitions were recorded as sharp steps of the optical reflectivity on heating. The temperature was controlled to within ± 5 mK. For determination of the temperature dependence of the thinning transitions in films with $N<25$, heating rates of $\leqslant 200$ mK/min were used. It was shown [6] that long series of single-layer transitions were observed more easily with fluorinated liquid-crystal compounds. In our experiments a nonfluorinated compound was used. We will demonstrate that a long series of single-layer transitions can be also observed with a nonfluorinated compound.

Free-standing films from 5 to 20 layers were prepared in the Sm-C^* phase at $T=89\,°\mathrm{C}$. Then the films were heated up to 93 °C and cooled down to 86 °C. At this temperature a part of the material moves from the meniscus towards the center of the film. Such a method allows us to prepare uniform films with thicknesses of up to 10 μm (about 3300 layers). This thickening of the films can be repeated after thinning at high temperature. After the below described series of thinning transitions the thin Sm-C^* films can be cooled to low temperature and thick Sm-C^* films can be again obtained. We started our measurements with these thick films (1–10 μm). After the preparation of a thick film, its thickness remains unchanged over the bulk Sm-C^* temperature range for a long time. At 92 °C the Sm-C^*–N^* transition can be easily observed. In the N^* phase the material becomes more mobile and can move in the plane of the film. Through some time the material moves to the meniscus and the film thickness decreases. This first thinning transition enables the film to come back to the smectic structure. The reached thickness of the film, as a rule, was from 35 to 50 layers. A further heating of this film leads to a series of thinning transitions which preserve the Sm-C^* structure.

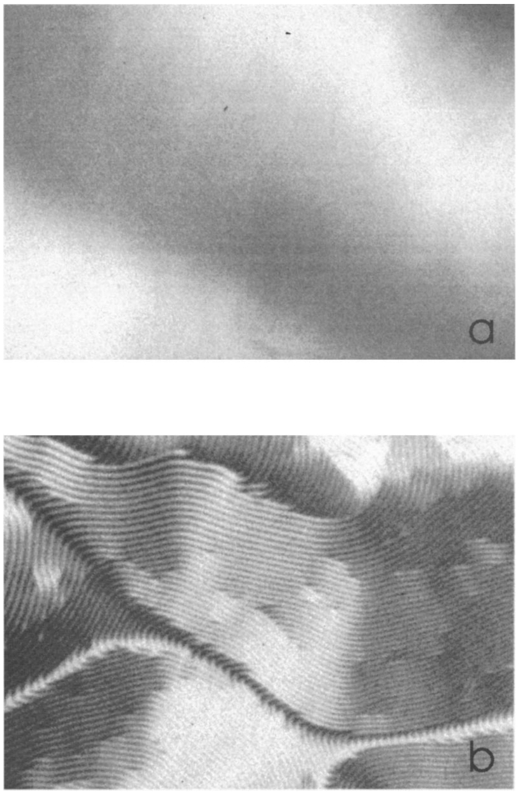

FIG. 2. Texture in the 18-layer free-standing film, observed far (a) and near (b) the temperature of the thinning transition, $T_N=94.90\,°\mathrm{C}$. (a) Director field is continuous, $T=94.70\,°\mathrm{C}$; (b) Modulated phase just before the thinning transition, $T=94.88\,°\mathrm{C}$. Polarizers are crossed. The horizontal size of each image is about 300 μm.

For thick films ($N\geqslant 24$) the thinning transitions occur through multilayer steps. For thinner films heating runs with layer-by-layer transitions may be observed. Figure 1 shows heating run with series of the layer-by-layer transitions in which the film losses a single layer per each thinning. Optical observations with a microscope used in reflection showed that in thick films ($N\approx 50-30$ layers) the thinning transition results from the nucleation of cholesteric droplets in the films. This behavior was previously observed in other compounds [9,10].

Another essential phenomenon was found in thinner films in which the layer-by-layer transitions could be observed. Figure 2(a) is a photograph of white light reflected on an 18-layer thick film at $T=94.70\,°\mathrm{C}$. This texture is typical for freely suspended Sm-C^* films. Dark and bright regions emanate from smooth angular variations of the two-dimensional **c**-director across the film. However, just below the temperature of the thinning transition $T_N=94.90\,°\mathrm{C}$, a dramatic change in the film was observed. The two-dimensional molecular orientational field breaks up into modulated structure formed by stringlike lines [Fig. 2(b), $T=94.88\,°\mathrm{C}$].

Figure 3 shows the detail of the appearance and evolution of stringlike lines in a 21-layer film. As in an 18-layer film, usual Sm-C^* texture is observed over a wide temperature range of the Sm-C^* phase. When the temperature is increased nothing happens until the temperature is close to the layer-by-layer transition temperature ($T_N=94.28\,°\mathrm{C}$ for a 21-layer film). Upon heating, sharply defined line defects

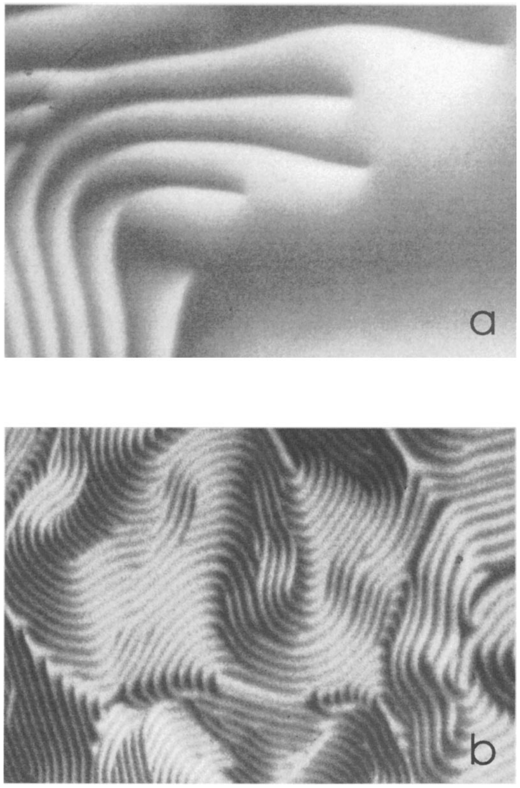

FIG. 3. Appearance and evolution of modulated texture near the temperature T_N of the thinning transition ($N=21$, $T_N=94.28$ °C). (a) Network of line defects developing at $T=94.25$ °C; (b) Modulated texture at $T=94.26$ °C. Polarizers are slightly uncrossed in order to increase the reflected intensity. The horizontal size of each image is about 300 μm.

nucleate in the film just before the layer-by-layer transition. At $T=94.24$ °C defects may exist in the film as isolated thin lines with a few to several hundred micrometers length. As the temperature is further increased, new director field defects nucleate and grow [Fig. 3(a)]. Defects form a quasiperiodic structure that completely fills the film [Fig. 3(b)]. The range of existence of this defect structure is a few hundredths of a degree. Above that, the film undergoes the thinning transition, in which the thickness decreases in a stepwise manner. After the thinning transition the usual Sm-C^* structure [Fig. 2(a)] reappears in the film. These processes repeat upon heating. The next formation of the defect structure occurs again in the film just before the next thinning transition. Open points in the inset of Fig. 1 show the regions where the defect structures occur. It should be noted that the thinning transitions are monotropic, i.e., the film thickness does not increase upon cooling, whereas the defect structure formation is reversible. Cooling down the film when the defect structure exists leads to its disappearance. We did not observe crossing of the line defects. This means that the lines are not localized independently at two surfaces.

In the films with $N<23$, with a polarizing microscope used in reflection mode, the thinning transition can be observed as the motion of the step of the thinning front. This step is associated with edge dislocation which crossed the film [7,8]. In intermediate thickness films ($30>N>23$) both the formation of defect lines and nucleation of the droplets from the defect lines were observed. Such type of the nucleation occurs also in thinner films at relatively high heating rates (>200 mK/min).

On heating, the distance between lines decreases from about 20 μm to several micrometers in very narrow temperature interval (a few hundredths of degree). At the temperature of the thinning transition the period of modulated texture is less in thinner films. But as the distance between lines near the thinning transitions is close to the microscope resolution, it was impossible to perform quantitative measurements of the film-thickness dependence of the stripe period. In thin films ($N<13$) we did not observed modulated texture. However, one has to note that the distance between lines and optical contrast decreases with the decreasing of film thickness. Thus, in thin films the defect spacing may be below the microscope resolution (~2 μm).

Various defect textures have been found in the smectic films of chiral and nonchiral liquid crystals [19–23]. In slightly uncrossed polarizers, strings look like sharp line defects characterized by the strength $\Omega=\frac{1}{4}$ [21], but due to limited microscope resolution it is impossible to determine the line structure. It must be pointed out that in our case the defect structure exists only in very narrow temperature intervals in which the inside of the films is a very soft material. Similar behavior was previously observed in thin droplets with one free surface [24,25]. Defect structures were found in the Sm-C phase in a very narrow temperature range (about 0.1 K) near the bulk melting temperature of the Sm-C–nematic transition. In our case the line defects appear below the film melting temperatures. So we may assume that the reasons of the appearance of the line defects have the same nature.

There are no theories predicting the appearance of the line defects near the temperature of the thinning transition. However, it is clear that the nucleation of the line defects is connected with the changes in the interior layers near the thinning transition temperature. At high temperature the smectic order parameter ψ and compressive modulus of the smectic lattice depend on the distance from the surface of the film [7,11]. The latter leads to the appearance of an elastic deformation field inside the film and to a long-wavelength mechanical instability of the film when heated above some critical temperature [11]. Mechanical instability repeats near every thinning transition temperature. Moreover, above the bulk transition temperature the tilt angle of the molecules depends on the distance of the smectic layer from the surface [2,3]; that means a strong bend deformation of the **n**-director [26,27]. Mechanical instability and bend deformation of the **n**-director may result in the appearance of defects in the smectic film near the thinning transition temperatures.

In conclusion, we have observed iterative unusual formation of modulated texture in the Sm-C^* films. String defects appear below the thinning transitions and disappear after thinning of the film. We speculate that the deformation field inside the films near the temperature of the thinning transition is favorable to the appearance of the defects. Further experimental and theoretical studies are necessary to understand the nature of these defects and layer-thinning transitions in freely suspended films.

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