Dimensional crossover of the phase diagram in ferroelectric smectic free-standing films

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A phase diagram of the surface melting type, qualitatively new for liquid crystals, has been observed in free-standing films: the SmC*– Sm C_{ferri} and Sm C_{ferri}–SmC_A phase transitions can be shifted to lower temperatures by decreasing the number of layers. This phenomenon is explained by the influence of the depolarizing fields. © *1995 American Institute of Physics.*

The phenomenon of surface reconstruction is well known in liquid crystal systems. Quantized layer growth was found in high-resolution synchrotron measurements on the free surface of the isotropic liquid of dodecylcyanobiphenyl (12CB) in Ref. 1, where the first smectic layer has been recorded at approximately 10 °C above the isotropic–smectic A phase transition. Analogous behavior was observed for the isotropic–nematic phase transition.[2,3] Positional order corresponding to several smectic A layers on the boundary[4] occurs in the nematic phase above the nematic–smectic A phase transition. In free-standing films the existence of surface hexatic smectic I layers on the smectic C films has been reported in Ref. 5. Layer-by-layer phase transitions in free-standing films has been studied calorimetrically and optically in Refs. 6 and 7. All situations mentioned above correspond to the surface freezing in liquid-crystal phases, where the boundary regions are more ordered than in the bulk.

Qualitatively different behavior can be expected for the ferroelectric films.[8,9] The boundary layers in films with homogeneous in-plane distribution of dipoles should be less ordered with respect to the films interior. This effect occurs as a result of taking into account the electrostatic interaction of the dipoles with the depolarizing fields. In this case the phase transition to the ferroelectric phase can be shifted to lower temperatures by decreasing the film thickness. From this point of view, it is extremely interesting to determine what kind of surface ordering is relevant to the ferroelectric films with a high spontaneous polarization.

The other salient feature of the films with high spontaneous polarization is the textural transition between the in-plane stripe instability and the anisotropic state, which occurs as a result of lowering the number of layers in the SmC* phase.[10–14] The stripe state is stable in thick, highly polar films. The anisotropic state is formed spontaneously in thin films and corresponds to the predictions of the Pelcovits–Halperin–Pikin theory.[15,16] A model was proposed[13] to explain the stripe texture. In this model the stripe texture was considered to be a flexoelectric instability in an electric field produced by the

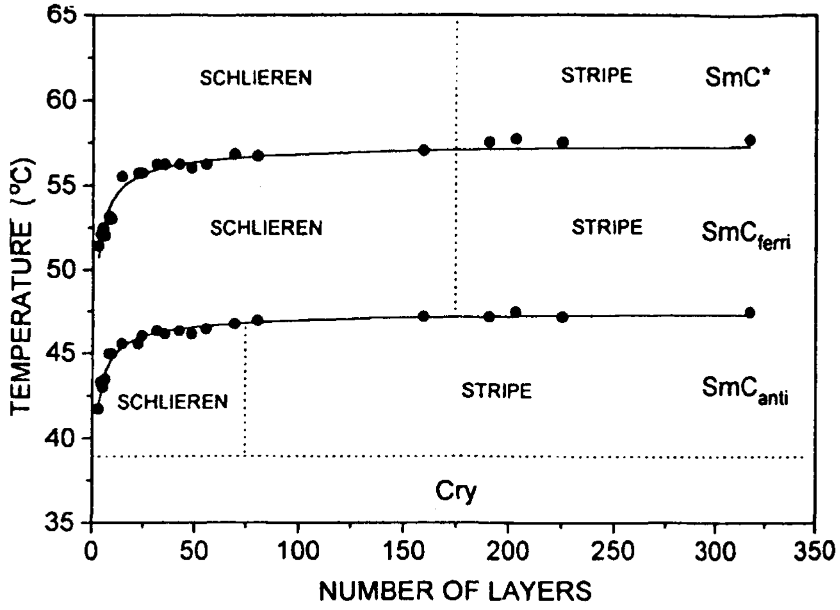

FIG. 1. Phase diagram of 14P1M7.

film. Thus, both the phase diagram and the film textures can depend on the depolarizing electric fields.

In this article we show that the phase diagram of the compound 14P1M7 possessing the SmC*–$\mathrm{SmC_{ferri}}$–$\mathrm{SmC_{anti}}$ phase sequence has the surface melting character. The textural transition stripe state (schlieren) has been observed in ferro-, ferri-, and antiferroelectric phases as a result of decreasing the number of layers. The features of this transition are discussed by using the structural models of dipolar phases and the model of the stripe state.[13,14]

A highly spontaneous polarization material 14P1M7 reported in Ref. 17 was studied by us. It possesses the following phase transitions in the bulk [$T(\infty)$] (Ref. 18: I (94.5) Sm A* (90.5) Sm C* (57.7) Sm $\mathrm{C_{ferri}}$ (47.7 (Sm $\mathrm{C_{anti}}$ (40) Cry.

The spontaneous polarization of this material was measured in Ref. 17. It lies between 30 and 100 $\mathrm{nC/cm^2}$ in the SmC*.

The films were produced int he smectic C* phase and sealed in 20–30 minutes in order to obtain a uniform thickness. The number of layers was determined at $T = 87$ °C by the light diffraction measurements, as described in Refs. 19 and 20. The interlayer spacing was 4.2 nm and $n = 1.6$ taken from Ref. 17. The film textures were studied at temperatures below 88 °C and $N = 2-1000$.

Figure 1 shows the phase diagram of 14P1M7. The stripe texture was observed in thick smectic C* films. The properties of this texture are similar to those of C7 (Ref. 10). This structure corresponds to the in-plane rotation of the projection of the director onto the smectic layers (the **c** vector). The interstripe distance increases with decreasing tem-

FIG. 2. Stripe state of the ferrielectric phase (C_{ferri}) at $T = 47.8$ °C, $N = 317$.

perature. The textural transition occurs at $N_{c1} = 175 \pm 15$ layers, where the stripe state disappears and the schlieren texture occurs. The spontaneous anisotropic texture with discontinuous walls (the weak anisotropic state)[10] has not been observed in the 14P1M7 films. The textural difference between the ferroelectric phase and the ferrielectric phase is very small. The stripe state of the ferroelectric phase is transformed into the stripe state of the ferrielectric phase (Fig. 2) without any change in their shape and periodicity. The ferrielectric phase texture shows no change with decreasing temperature. The stripes in the ferrielectric phase disappear in films with $N \leq 175$ and the schlieren texture is formed. The SmC^*–$\mathrm{SmC}_{\mathrm{ferri}}$ transition temperature can be shifted to lower temperatures by decreasing the number of layers.

The film texture changes drastically during the phase transition $\mathrm{SmC}_{\mathrm{ferri}}$–$\mathrm{SmC}_A$. The stripe state has been detected in the antiferroelectric phase (Fig. 3). The stripe state

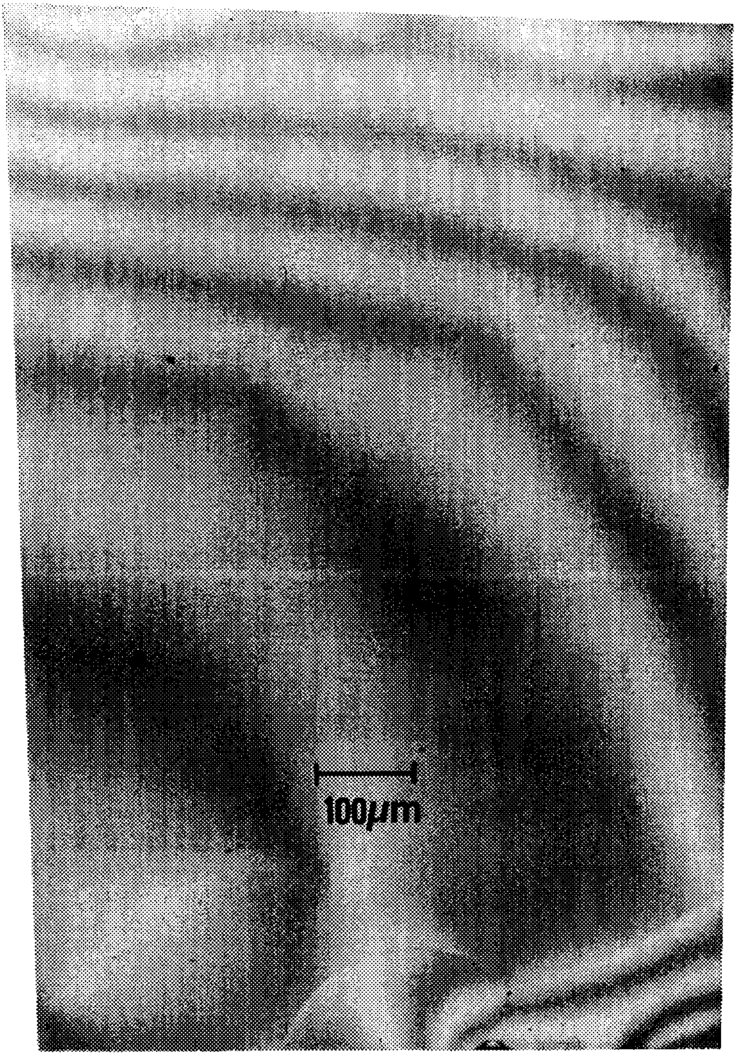

FIG. 3. Stripe state of the antiferroelectric phase (SmC_A), $T=45.68$ °C, $N=317$.

periodicity in the antiferroelectric phase is smaller than in the ferro- and ferri-electric phases. The textural transition has been observed with $N_{c2}=75\pm10$ layers. A schlieren texture was found in thin films. Typical for the anitferroelectric phase is a formation of the domain texture during the SmC_{ferri}–SmC_A phase transition which disappears as a function of time. The SmC_{ferri}–SmC_A transition can be shifted to lower temperatures by decreasing the number of layers.

To compare the surface melting phase diagram of 14P1M7 with the predictions of Refs. 8 and 9, we will show that in the case of thin films the variation in the direction of the polarization vector can be ignored. A simple consideration shows that the conical helix is suppressed in all films studied here. The stripe state recorded in thick films corresponds to the in-plane rotation of the two-dimensional **c** director.[10] The stripe state of 14P1M7 disappears in films thinner than $D=735$ nm ($N_{c1}=175$ layers). Because the helical pitch in the smectic C* is about 500 nm, the stripe state will not be observable in the films with $N \geqslant N_{c1}$ since the azimuth angle rotates as a function of the coordinate perpendicular to the smectic planes, which contradicts the experimental results. We can therefore ignore the conical helix in the films with $N \leqslant N_{c1}$. The image of the schlieren texture reveals a smooth variation of the tilt plane direction in thin films, which in a first approximation can also be ignored. Therefore, our experimental conditions correspond to the assumptions of Refs. 8 and 9.

An anomalous feature of the phase diagram in Fig. 1 is the decrease of SmC*–$\mathrm{SmC_{ferri}}$ and $\mathrm{SmC_{ferri}}$–SmC_A transition temperatures with decreasing number of layers. This result shows that in all the phases the boundary layers are less ordered than the inner parts. In the smectic C* phase this statement corresponds to the predictions of Refs. 8 and 9 for the order-parameter profiles in ferroelectric films with the positive extrapolation length. According to Ref. 8, the depolarizing fields manifest themselves in the low-temperature shift of the Curie point (T_c) in accordance with

$$T_c(N)-T(\infty)=-\frac{A\cos\theta}{\lambda N}, \tag{1}$$

where A is a constant, θ is the angle between the surface normal and the polarization vector ($\theta\neq 0$), and λ is the extrapolation length. If the depolarizing field plays no role, the other finite-size effect should be expected to occur:

$$T_c(N)-T(\infty)=-\frac{B}{N^2}, \tag{2}$$

where B is a constant.

The solid lines in Fig. 1 show the fitting of the phase diagram to the function: $T_c(N)=T(\infty)-C/N^{\alpha}$. Both transition temperatures show approximately the same dependence on the number of layers with $\alpha\approx 0.59\pm 0.01$. The results of this study indicate the deviation from expression (2) and show that the depolarizing field expression influences the type of the phase diagram, because expression (2) does not depend on the phase structure. The relation of the experimental phase diagram to expression (1) must be studied separately because the dependence of the extrapolation length and Θ on the number of layers is not known. The author would like to emphasize that this result contradicts the previous results of Refs. 20–24, where it was shown that the boundary layers in the smectic C* phase are more ordered than the film interior.

The formation of the stripe state was treated in Ref. 13 as a flexoelectric instability in a field produced by the film. We can regard the low-temperature shift of the phase transitions between the dipolar phases as evidence of the presence of such depolarizing fields. The electric fields can originate from the up-down symmetry breaking due to the elastic stress produced by the gravity field. The value and direction of the electric field are determined by the orientation of dipoles with respect to the molecular long axis. In our case the main contribution is combined with the longitudinal component of the dipoles, because otherwise no stripes will be observed in the antiferroelectric phase. In a first approximation the induced field should be proportional to the number of layers. The textural transition, which occurs as a result of decreasing the number of layers, occurs because the inherent electric field in thin films is not strong enough to produce the flexoelectric stripe instability.[13,14] The dipolar interaction in the smectic films of 14P1M7 is not sufficiently strong to give rise to the weak anisotropic state, and the schlieren texture is observed in thin films. The critical number of layers required for the stripe state to disappear in the antiferroelectric phase is essentially smaller than that for the ferroelectric and ferrielectric phases. In the framework of the model[14] we can write the relation

$$N_c \sim \frac{1}{\beta^2 \Theta^2}, \tag{3}$$

where Θ is the tilt angle of the molecule with respect to the normal of the layers, and β is the flexoelectric coefficient.

The lower value of N_{c2} with respect to N_{c1} can be combined with an increase of β during the $\mathrm{SmC_{ferri}}$–SmC_A phase transition. To demonstrate that this factor can be relevant in our case, we will use a qualitative microscopic model of Ref. 26, which was used to calculate the flexoelectric coefficient of the asymmetric banana-shaped molecules. According to this model, the flexoelectric coefficient depends on the molecular bend angle ϵ and the tilt angle Θ:

$$\beta \sim \epsilon \frac{[1+(\Theta/\epsilon)^2]^2}{[1+(\Theta L/D)^2]^{7/2}}, \tag{4}$$

where L is the effective molecular length, and D is the molecular diameter. For $\Theta \ll \epsilon$ the flexoelectric coefficient is proportional to ϵ. The same is true for the case $\Theta \sim \epsilon \sim D/L$.

The elementary structure unit of the antiferroelectric phase is a bilayer with opposite directions of the tilt in the sublayers. We can assume that SmC_A effectively consists of longer broken molecules with a bend angle $\epsilon = 2\Theta$ going from one layer to the next. As a result of the $\mathrm{SmC_{ferri}}$–SmC_A phase transition, the molecular bend angle effectively changes from $\epsilon \sim \Theta$ to $\epsilon \sim 2\Theta$, which causes the flexoelectric coefficient to increase.

In conclusion, the author would like to note that the effects of the depolarizing fields produced by the free-standing ferroelectric films are seen in i) the low-temperature shift of the phase transitions and ii) the formation of the stripe instability in thick films. The change of the phase diagram can be qualitatively explained by using the results of Refs. 8 and 9. The properties of the stripe state in the ferrielectric phase and the antiferroelectric phase qualitatively correspond to the predictions of Refs. 13 and 14. The results of this study show that it is important to develop a complete theory of finite-size effects in the smectic ferroelectric films by taking into account the depolarizing fields.

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