Pis'ma v ZhETF, vol.61, iss.11, pp.951 - 956 © 1995 June 10

DIMENSIONAL CROSSOVER OF THE PHASE DIAGRAM IN FERROELECTRIC SMECTIC FREE STANDING FILMS

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Submitted 28 April 1995

Qualitatively new for liquid crystals phase diagram of surface melting type has been observed in free standing films: the SmC* - Sm C_{ferri} and Sm C_{ferri} - SmC_A phase transitions are shifted to lower temperatures by decreasing the number of layers. This phenomenon is explained by the influence of the depolarizing fields.

The phenomenon of surface reconstruction is well-known in liquid-crystalline systems. Quantized layer growth was found in high resolution synchrotron measurements on the free surface of the isotropic liquid of dodecylcyanobiphenyl (12CB) in [1], where the first smectic layer has been registered at approximatelly 10° C above the isotropic–smectic A phase transition. Analogous behaviour 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 [5]. Layer-by-layer phase transitions in free standing films has been studied calorimetrically and optically in [6, 7]. All situations mentioned above correspond to the surface freezing in liquid crystalline phases where the boundary regions are more ordered than the bulk.

Qualitatively different behaviour 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 results from taking into account the electrostatic interaction of the dipoles with depolarizing fields. In this case the phase transition to the ferroelectric phase should be shifted to lower temperatures by decreasing the film thickness. From this point of view it is extremely interesting to find out what kind of surface ordering is relevant to the ferroelectric films with 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 by lowering the number of layers in the SmC* [10–14]. The stripe state is stable in thick highly polar films. The anisotropic state is spontaneously formed in thin films and corresponds to the predictions of Pelcovits–Halperin–Pikin theory [15, 16]. To explain the stripe texture a model was proposed [13] where it was considered to be a flexoelectric instability in an electric field produced by the film. Thus, both the phase diagram and films textures can depend on the depolarizing electric fields.

In this work it is shown that the phase diagram of compound 14P1M7 possessing the SmC* – SmC_{ferri} – SmC_{anti} phase sequence has the surface melting character. The textural transition stripe state - schlieren has been observed in ferro-, ferri- and antiferroelectric phases by decreasing the number of layers. The features of this transition are discussed using the structural models of dipolar phases and the model of the stripe state [13, 14].

A high spontaneous polarization material 14P1M7 reported in [17] has been studied in this work. It possesses the following phase transitions in the bulk ($T(\infty)$) [18]: I (94.5) Sm A* (90.5) Sm C* (57.7) Sm C_{ferri} (47.7) Sm C_{anti} (40) Cry.
The spontaneous polarization of this material has been measured in [17] and lies between 30 and 100 nC/cm^2 in the SmC*.

The films has been produced in the smectic C* phase and sealed 20–30 minutes to obtain a homogeneous thickness. The number of layers has been determined at $T = 87°\mathrm{C}$ by the light diffraction measurements as described in [19, 20]. The interlayer spacing was taken 4.2 nm and $n = 1.6$ from [17]. The films textures has been studied at temperatures lower 88° C and $N = 2 - 1000$.

Fig.1 shows the phase diagram of 14P1M7. In thick smectic C* films the stripe texture has been observed. Properties of this texture are similar to that of C7 [10]. This structure corresponds to the in-plane rotation of the projection of the director onto the smectic layers (c – vector). The interstripe distance increases with decreasing the temperature. 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 14P1M7 films. The textural difference between ferroelectric and ferrielectric phases is very small. The stripe state of the ferroelectric phase is transformed into the stripe state of the ferrielectric phase (fig.2) without change

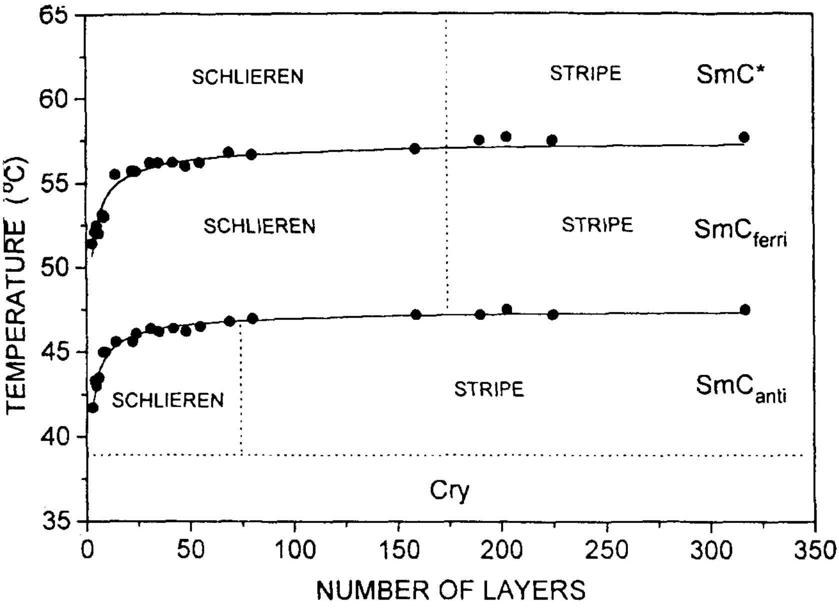

Fig.1. Phase diagram of 14P1M7

of 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* – SmC$_{ferri}$ transition temperature is shifted to lower temperatures by decreasing the number of layers.

The films texture is drastically changed during the phase transition SmC$_{ferri}$ – SmC$_A$. The stripe state has been registered in the antiferrolectric phase (fig.3) The stripe state periodicity in the antiferroelectric phase is smaller than in ferro- and ferrielectric phases. The textural transition has been observed at $N_{c2} = 75 \pm 10$ layers. In thin films a schlieren texture was found. Typical for the antiferrolectric 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 is shifted to lower temperatures by decreasing the number of layers.

To compare the surface melting phase diagram of 14P1M7 with predictions of [8, 9] let us show that in the case of thin films the variations of polarization vector direction can be neglected. A simple consideration shows that the conical helix is suppressed in all films studied here. The stripe state registered 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 D = 735 nm (N_{c1}=175 layers). Because the helical pitch in the smectic C* is about 500 nm the stripe state would not be observable in the films with $N \geq N_{c1}$ due to the azimuth angle rotation as a function of the coordinate perpendicular to the smectic planes, which contradicts to the experiment. Thus, we can neglect the conical helix in the films with N$\leq N_{c1}$. The image of schlieren texture reveals a smooth variation of the tilt plane direction in thin films which in the first approximation can also

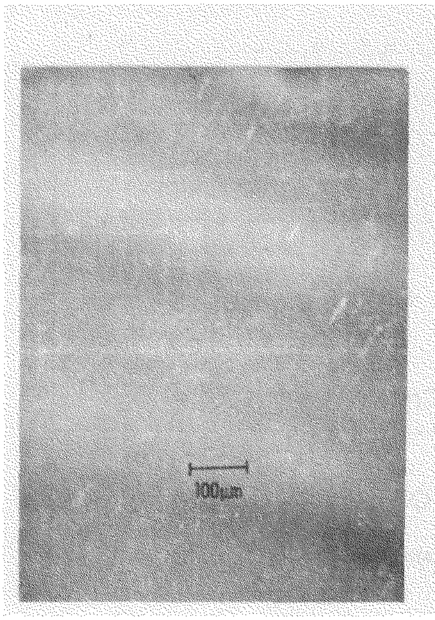

Fig.2

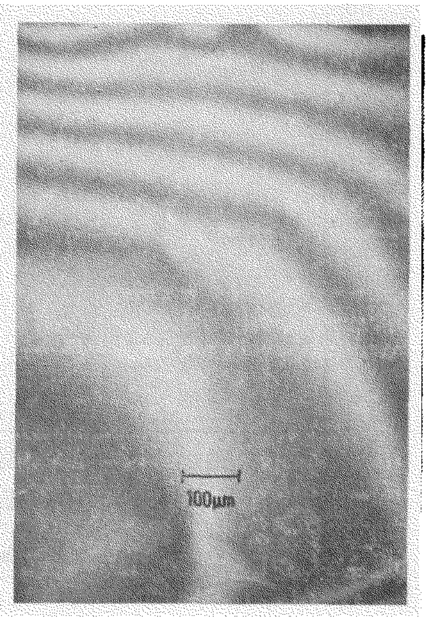

Fig.3

Fig.2. Stripe state of the ferrielectric phase (C_{ferri}) at $T = 47.8°$ C, $N = 317$
Fig.3. Stripe state of the antiferroelectric phase (SmC_A), $T = 45.68°$ C, $N = 317$

be neglected. Therefore our experimental conditions correspond to the assumptions of [8, 9].

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

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

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

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

where B is a constant.

The solid lines on fig.1 show the fitting of the phase diagram with the function: $T_c(N) = T(\infty) - C/N^{\alpha}$. Both transition temperatures show appoximatelly the same dependence on the number of layers with $\alpha \approx 0.59 \pm 0.01$. The results of this work indicate the deviation from exp.2 and show that the depolarizing field really influence the type of the phase diagram, because exp. 2 does not depend on the phase structure. The relation of the experimental phase diagram to the exp.1 has to be stuied separatelly 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 is opposite to the previouis findings of [20–24], where it was evidenced that the boundary layers in the smectic C* phase are more ordered than film interior.

The stripe state formation was treated in [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 the evidence for 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 is 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 dipoles because in the opposite case no stripes will be observed in the antiferroelectric phase. In the first approximation the induced field should be proportional to the number of layers. The textural transition occurs by 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 for the stripe state disappearance in the antiferroelectric phase is essentially less than for the ferro- and ferrielectric phases. In the framework of the model [14] following relation can be written:

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

where Θ is the tilt angle of the molecule with respect to the layers normal 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 phase transition $\mathrm{SmC}_{ferri}-\mathrm{Sm\ C}_A$. To demonstrate that this can be relevant to our case let us use a qualitative microscopic model of [26] which calculated the flexoelectric coefficient for the asymmetric banana shape molecules. According to it 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 $\Theta << \epsilon$ the flexoelecrtic 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 regard that the SmC_A effectively consists of longer broken molecules with a bend angle $\epsilon = 2\Theta$ going from one layer to the next one. As a result of the $\mathrm{SmC}_{ferri}-\mathrm{SmC}_A$ phase transition the molecular bend angle is effectively changed from $\epsilon \sim \Theta$ to $\epsilon \sim 2\Theta$, which produced the increase of the flexoelectric coefficient.

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

Acknowledgements. The author is grateful to Professor H. Stegemeyer for the cooperation; Dr. U. Hoffmann for the development of the computer program; the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (Germany) for the financial support.

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