

## SURFACE ORDERING NEAR THE SMECTIC-A-SMECTIC-C TRANSITION IN THIN, FREE-STANDING, LIQUID-CRYSTAL FILMS

V. K. Dolganov\*, E. I. Demikhov\*\*, R. Fournier\*\*\*, C. Gors\*\*\*

\* Institute of Solid State Physics, Russian Academy of Sciences  
142432, Chernogolovka, Moscow Region, Russia

\*\* Institute of Physical Chemistry, University of Paderborn  
33095 Paderborn, Germany

\*\*\* Laboratoire de Dynamique et Structures des Matériaux Moléculaires, Université de Lille I  
59655, Villeneuve d'Ascq Cedex, France

Submitted 7 August 1996

Optical reflectivity measurements have been conducted near the smectic-A-smectic-C phase transition in free-standing films with thickness between two and eleven molecular layers. The temperature dependence of the reflectivity in thin film differs significantly from that in thick films. The optical thickness per layer increases in films with two to five layers as a result of cooling, in contrast with thick films. The average layer spacing was found to decrease with decreasing film thickness.

Phase transitions in thin, liquid-crystal, free-standing films have recently been studied extensively [1–10]. Free-standing films reveal rich variety of properties unknown for the bulk samples. The discrete layer-by-layer surface freezing has been observed near the Sm-A-Sm-I, Sm-A-Hex-B, Sm-A-Cry-B bulk transitions [4, 5, 10, 11]. In contrast, ellipsometric measurements of the molecular tilt angle have demonstrated that the order parameter for the Sm-A-Sm-C transition is a continuous function of temperature in thin films [12, 13]. The surface ordering phenomena near the Sm-A-Sm-C transition are very unusual. Boundary layers in free-standing films are tilted in the temperature interval of Sm-A phase [12, 13]. This tilt causes an increase in the transition temperature on decreasing the number of layers [12–15]. The optical reflectivity measurements are an informative tool for studies of phase transitions in free-standing films. Until now, however, detailed optical reflectivity measurements have not been conducted in extremely thin films near the Sm-A-Sm-C transition.

In this paper we report the results of high-precision, optical-reflectivity measurements near Sm-A-Sm-C transition for free-standing films varying from two to eleven molecular layers. We have observed an anomalous temperature dependence of the optical thickness in ultrathin layers. We present the thickness dependence of the average interlayer spacing on the film thickness. The penetration length of the Sm-C surface ordering was found to be significantly larger than in the case of the layer-by-layer transitions.

The experiments were performed on free-standing films of *p*-decyloxybenzoic acid-*p*-*n*-hexyloxyphenyl ester. The bulk samples possess the following phase sequence: Sm-C (77°C) Sm-A (83°C) Nematic (89°C) Isotropic. Using the polarizing microscope we did not observe discontinuities of the optical properties at the bulk transition temperature ( $T_{AC}$ ). These observations indicate that the Sm-A-Sm-C transition is a second-order or weakly first-order transition. Our experimental setup enabled simultaneous optical observations and measurements of the reflection and transmission intensities to be made. The films were illuminated with nearly normally incident light. The temperature was controlled with an

accuracy of  $\pm 0.01^\circ\text{C}$ . *X*-ray-diffraction studies of the bulk samples were carried out using a curved linear position-sensitive multidetector and a curved quartz monochromator. The layer spacing was  $d_A = 3.02$  nm at  $82^\circ\text{C}$  and increased slightly in Sm-*A* temperature range with decreasing temperature (about  $10^{-3}$  nm/ $^\circ\text{C}$ ). In the Sm-*C* phase  $d_C$  decreased significantly with decreasing temperature ( $d_C = 2.92$  nm at  $71^\circ\text{C}$ ).

The 2 to 11-layer films were spread over a 6-mm-diam hole in a 0.2-mm-thick steel plate. Two methods of films preparation were used. Thin films could be spread by a movement of a mobile steel slip across the hole. As a rule, it took many attempts to obtain a film of the required thickness. The second method was based on the step-by-step thinning of free-standing films above the bulk Sm-*A*-Isotropic [16] or Sm-*A*-Nematic [17, 18] phase transitions. The film thickness decreased in a stepwise manner on increasing the temperature. After preparing a film of a required thickness, the heating was stopped and the film was cooled in the temperature interval of the bulky Sm-*A*. Combining these two methods, we prepared films ranging from 2 and 11 layers. The film thickness and interlayer spacings were determined by optical-reflectivity measurements using the equation [19]:

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

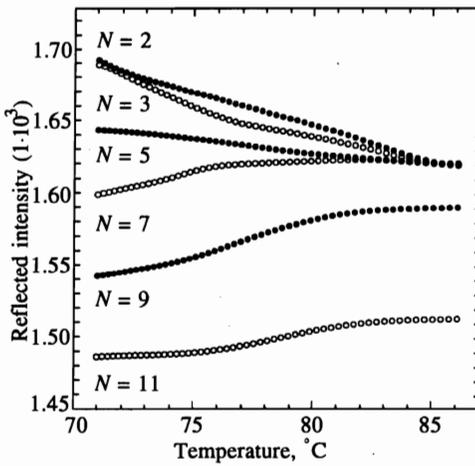
where  $N$  is the number of layers,  $n=1.48$  is the refractive index, and  $d$  is the interlayer spacing. For thin films Eq. (1) can be simplified [20]:

$$I(\lambda) = \frac{N^2 \pi^2 d^2 (n^2 - 1)^2}{\lambda^2}. \quad (2)$$

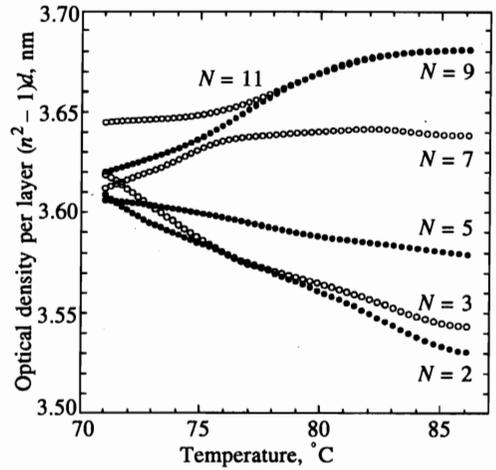
Equation (2) allows the determination of the optical thickness per layer  $(n^2 - 1)d$ . In our case this equation gives the optical thickness with acceptable accuracy only for very thin film. For thicker films, it was necessary to use the exact equation [Eq. (1)]. The thickness of very thick films, together with the refractive index, can be obtained from the fitting of the reflectivity spectra  $I(\lambda)$  with Eq. (1) [14]. However, this does not work properly for thin films ( $N < 15$ ), because the  $\lambda$ -dependence of the reflectivity is very smooth. In this case, we used the bulk value for the refraction index and reduced the number of fitting parameters. The numerical estimates show that this procedure allows us to find optical thickness without significant error (no more than 0.3%).

Figure 1 shows the temperature dependences of the reflectivities from 2- and 11-layer films ( $\lambda = 550$  nm) multiplied by  $4/N^2$  to compare results from films of different thicknesses. As expected for the second-order transition, we observed the continuous variation in the reflected intensities. Unexpected result is a drastic change in the temperature dependences with decreasing the number of layers. The variation in the slope of the curves was found to occur for the number of layers ranging from 7 to 5.

Using the reflectivity data in Fig. 1, the temperature dependences of the optical thickness per layer  $(n^2 - 1)d$  were calculated. These dependences are shown in Fig. 2. The change of the thickness is continuous, which corresponds to the second-order Sm-*A*-Sm-*C* transition. For the 7 to 11 layer films the optical thickness decreases on cooling. Qualitatively similar decrease in the optical thickness at the Sm-*A*-Sm-*C* transition was observed previously for very thick films [14]. The interlayer spacing was estimated using the optical thickness per layer and the refractive index. In thick films (9 to 11 layers) at  $82^\circ\text{C}$  (Sm-*A* phase)  $d_A$  coincided with the value obtained from *X*-ray measurements with accuracy of 2%. Since the value of the



**Fig. 1.** Temperature dependence of the reflectivity in various free-standing films. The data from 3-, 5-, 7-, and 11-layer films were multiplied by  $4/N^2$ . The temperature was decreased at the rate  $2\text{mK/s}$



**Fig. 2.** Temperature dependence of the optical density per layer  $(n^2 - 1)d$  for 2-, 3-, 5-, 7-, 9-, and 11-layer films

optical reflectivity was measured with an uncertainty of about 1% and  $n$  with accuracy of 0.02, there was a good agreement between optical and  $X$ -ray data in the Sm- $A$  phase. However, the relative decrease of the layer spacing  $(d_A - d_C)/d_A \approx 0.03$  ( $X$ -ray measurements) in the range of temperatures from 82 to  $71^\circ\text{C}$  was more than the decrease of the optical thickness in thick films. In our opinion this difference stems from the change of the refractive index.

Data for the  $N < 5$  layer films display the anomalous increase of the optical thickness and seem to indicate that the Sm- $A$ -Sm- $C$  transition is not present in thin films. Extremely thin films exhibit similar variation of  $(n^2 - 1)d$  in the entire temperature range, in which these thicknesses are stable (up to  $104^\circ\text{C}$  for a two-layer film). These results can be explained if we assume that the surface field stabilizes the Sm- $C$  molecular ordering near the surface. The anomalous temperature dependence of the optical thickness in ultrathin films ( $N < 5$ ) can be interpreted in two ways: i) the increase of the refractive index as a result of cooling, ii) the change in the interlayer spacing. Our data are not sufficient to distinguish between these two cases. It should be noted that there cannot be a simple analogy with the behaviour of thick films. The increased packing efficiency and the quench of the layer fluctuations in thin films [21], as compared with thick films, can be the reason for the anomalous change of the optical thickness.

Recently,  $X$ -ray reflectivity studies of ultrathin Sm- $C^*$  films on substrates have shown an increase in the smectic layers spacing with decreasing number of smectic layers (about 20%) [22]. Figure 3 shows the plot of the optical thickness per layer versus the number of layers. Our results show that at low temperature ( $71^\circ\text{C}$ , Sm- $C$  phase) the change in the interlayer spacing is less than 1%. At high temperatures we observed significant differences in the optical interlayer spacings in thin and thick films (Fig. 3). The  $(n^2 - 1)d$  changes are continuous within the measurement error. From Fig. 3 it is clear that  $(n^2 - 1)d$  increases at different rates as the temperature changes. It should be noted that some surface ordering has been observed even below the bulk transition temperature ( $75^\circ\text{C}$ ; Fig. 3). The  $s$ -like shape

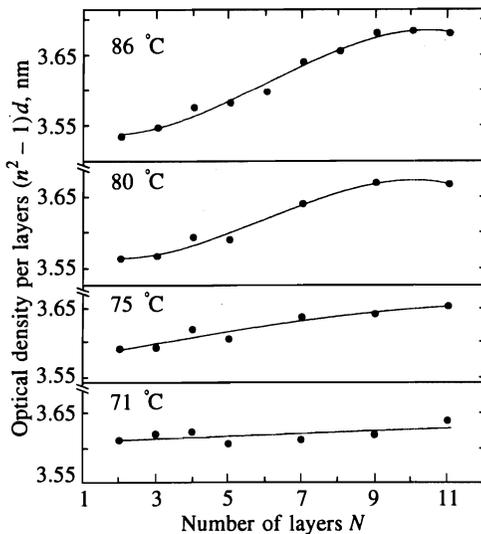


Fig. 3. Optical density per layer plotted as a function of the number of layers  $N$

of the thickness dependence (86°C) provides strong evidence of the transition from the Sm- $C$  surface to Sm- $A$  ordering. In the Sm- $C$  phase the thickness of the single smectic layer,  $d_C$ , may be assumed to be  $d_C = d_A \cos \theta$ , where  $\theta$  is the tilt angle. By assuming that the value of the refractive index does not depend on the film thickness and that the thickness of the eleven-layer film at 86°C is determined mainly by the Sm- $A$  ordering, we could estimate  $\theta$  at about 18° for a two-layer film. This value of  $\theta$  is slightly lower than that found in the DOBAMBC two-layer film (approximately 25°,  $T - T_{AC} \approx 10^\circ\text{C}$ ) [12]. For the layer-by-layer ordering [4, 5, 10, 11], only the surface layers exhibit transition at a temperature  $\approx 10^\circ\text{C}$  above the bulk transition. It is obvious that the penetration depth in our case is several times greater (Fig. 3). We estimate the surface order penetration depth to be about three layers. Another distinguishing feature of this transition is the behavior of the penetration depth near  $T_{AC}$ . For the layer-by-layer transition [4, 5, 10, 11] the penetration depth diverges near the bulk transition temperature, at which there is an abrupt transition in the whole sample. In contrast, the penetration depth remains finite in the temperature range of the bulk Sm- $C$  phase near the bulk transition temperature. These results can be attributed to the strong surface ordering and to the possibility of the continuous changes of the molecular tilt angle in the adjacent layers.

In summary, we have presented the first study of the Sm- $A$ –Sm- $C$  transition in extremely thin films using optical reflectivity measurements. The temperature dependence of the layer spacing in thin films differs significantly from that in thick films near the bulk Sm- $A$ –Sm- $C$  transition. Our observations indicate that surface field stabilizes the Sm- $C$  phase in extremely thin films. In the high-temperature region, the layer spacing decreases with decreasing number of layers and remains approximately constant at lower temperatures. These observations indicate that the Sm- $C$ –Sm- $A$  transition takes place with increasing film thickness.

The research described in this publication was made possible, in part, by Grants INTAS 94-4078, the Russian Foundation for Fundamental Research 95-02-05343, program «Statistical physics and nonlinear dynamics» and from the French National Education Minister.

## References

1. S. P. Pershan, *Structure of Liquid Crystal Phases*, World Scientific, Sinrapore (1988), p. 1.
2. M. Cheng, J. T. Ho, S. W. Hui, and P. Pindak, *Phys. Rev. Lett.* **59**, 1112 (1987).
3. E. B. Sirota, S. P. Pershan, L. B. Sorensen, and J. Collett, *Phys. Rev. A* **36**, 2890 (1987).
4. B. D. Swanson, H. Stragier, D. J. Tweet, and L. B. Sorensen, *Phys. Rev. Lett.* **62**, 909 (1989).
5. T. Stoebe, R. Geer, C. C. Huang, and J. W. Goodby, *Phys. Rev. Lett.* **69**, 2090 (1992).
6. T. Stoebe, C. C. Huang, and J. W. Goodby, *Phys. Rev. Lett.* **68**, 2944 (1992).
7. P. Pieranski et al., *Physica A* **194**, 364 (1993).
8. T. Stoebe, C. C. Huang, and J. W. Goodby, *Phys. Rev. E* **48**, 404 (1993).
9. C. Bahr, D. Fliegner, C. J. Booth, and J. W. Goodby, *Europhys. Lett.* **26**, 539 (1994).
10. A. J. Jin, T. Stoebe, and C. C. Huang, *Phys. Rev. E* **49**, R4791 (1994).
11. V. K. Dolganov, R. Fouret, and C. Gors, *Pis'ma v ZhETF* **63**, 266 (1996) (*JETP Lett.* **63**, 285 (1996)).
12. S. Heinekamp, R. Pelkovits, E. Fontes, et al., *Phys. Rev. Lett.* **52**, 1017 (1984).
13. C. Bahr and D. Fliegner, *Phys. Rev. A* **46**, 7657 (1992).
14. I. Kraus, P. Pieranski, E. I. Demikhov, and H. Stegemeyer, *Phys. Rev. E* **48**, 1916 (1993).
15. E. I. Demikhov, U. Hoffmann, and H. Stegemeyer, *J. Phys. II France* **4**, 1865 (1994).
16. T. Stoebe, P. Mach, and C. C. Huang, *Phys. Rev. Lett.* **73**, 1384 (1994).
17. E. I. Demikhov, V. K. Dolganov, and K. P. Meletov, *Phys. Rev. E* **52**, R1285 (1995).
18. V. K. Dolganov, E. I. Demikhov, R. Fouret, and C. Gors, *Phys. Lett. A* **220**, 242 (1996).
19. M. Born and E. Wolf, *Principes of Optics*, Pergamon, New York (1980), p. 1.
20. T. Stoebe and C. C. Huang, *Phys. Rev. E* **49**, 5238 (1994).
21. R. Holyst, *Phys. Rev. A* **44**, 3692 (1991).
22. M. Tarabia, G. Cohen, J. Gersten, and D. Davidov, *Phys. Rev. E* **51**, 799 (1995).