

INVESTIGATION OF THE LAYER-BY-LAYER TRANSITION NEAR THE BULK SMECTIC-A-CRYSTAL-B TRANSITION IN THICK FREE-STANDING FILMS

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Employing high-sensitive optical reflectivity measurements, we have investigated the layer-by-layer transition in extremely thin and thick *N*-(4-*n*-hexyloxybenzylidene)-4-*n*-hexylaniline (6O.6) films. The simple power-law form, $N = N_0 t^{-1/3}$, for the penetration of the crystal-B order described the transitions near the surface only. The deviation from the power law was observed for the interior layers.

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There has been considerable experimental interest in finite-size effects and surface-induced ordering transitions in freely suspended liquid-crystal films [1-10]. Recently, the layer-by-layer transition associated with the Smectic-A-Crystal-B (Sm-A-Cry-B) transition of 40.8 has been observed by Jin, Stoebe, and Huang [11]. Identification of the Cry-B phase in the *n*O.m homologous series has been made in free standing films [12,13]. In this paper we will report optical reflectivity measurements near the Sm-A-Cry-B transition in free-standing films and investigations of bulk samples. Our experiments differ in several aspects from those in [11]. We have obtained optical reflectivity data both from extremely thin (2-layers) and from thick films. Previously it was thought that the sensitivity of the optical reflectivity experiment decreased rapidly as the film thickness was increased and so reflectivity measurements were used for the investigations of the layer transitions in thin films only. We have measured the temperature variation of optical reflectivity from thick films at the wavelength λ_m near the reflectivity minimum λ_0 ($\lambda_0 = 2Nnd$, where N is the number of layers of each film, $n = 1.5$ is the index of reflection, d is the smectic layer spacing). In this case the sensitivity of the optical reflectivity could even be increased in comparison with the data from thin samples. This has enabled us for the first time to investigate the layer-by-layer transition in thick films using optical reflectivity.

The experiments were performed on the liquid-crystal compound 6O.6 [*N*-(4-*n*-hexyloxybenzylidene)-4-*n*-hexylaniline]. The bulk samples possess the following phase sequence: Cry-B (62°C) Sm-A (76.4°C) Nematic (79.54°C) Isotropic. Calorimetric, X-ray, and optical (absorption and fluorescence) measurements were carried out for bulk samples. The Sm-A-Cry-B transition is weak first order with transition enthalpy $7J/g$. X-ray diffraction studies were made using a curved linear position sensitive multidetector and a curved quartz monochromator [14]. The layer spacing was constant in the Cry-B phase ($d = 27.9\text{\AA}$). The small discontinuity was observed at the phase transition ($d = 27.18\text{\AA}$ at $T = 63^\circ\text{C}$). The layer spacing decreased in

Sm-A temperature range ($d = 27.06 \text{ \AA}$ at 72°C). The orientational order parameter $\langle P_2 \rangle$ for bulk sample was calculated from the relative intensities of the polarised luminescence and absorption spectra as described in [15]. The luminescent additive was 4-diethylamino-4-nitrostilben. The values of $\langle P_2 \rangle$ found from the luminescence and absorption results were the same. In the Cry-B phase $\langle P_2 \rangle = 0.92$ was almost independent of the temperature. Drastic decreases in $\langle P_2 \rangle$ were observed at the phase transition ($\langle P_2 \rangle = 0.81$ at $T = 63^\circ\text{C}$) and in the Sm-A phase ($\langle P_2 \rangle = 0.69$ at 75°C). The 2-100 layer free-standing films were prepared by drawing a small amount of the liquid crystal in Sm-A state across a 6-mm-diameter hole in a 0.2mm thick steel plate. The temperature was controlled with an accuracy of $\pm 0.005^\circ\text{C}$. The film was illuminated with nearly normally incident light. The experimental set-up enabled simultaneous measurements of the reflection and transmission spectra. The thickness of the films were determined by the optical diffraction measurements as described in [5,7]. The reflectivity for light is given by [16]:

$$I(\lambda) = \frac{f \sin^2(2\pi D/\lambda)}{1 + f \sin^2(2\pi D/\lambda)}, \quad (1)$$

where

$$f = \frac{(n^2 - 1)^2}{4n^2}, \quad (2)$$

$D = Nnd$ is the optical thickness of the film. The values of D were determined by comparing the experimental curves with the results of calculations based on Eq.(1). For thick films the number of layers could be calculated using the layer spacing obtained from X-ray experiments.

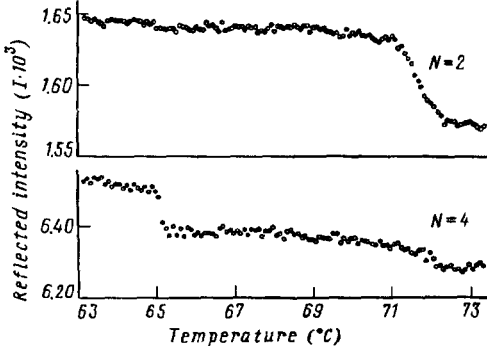


Fig.1. Temperature variation of reflectivity from two-layer and four-layer films. The temperature was decreased with the rate 2mK/s

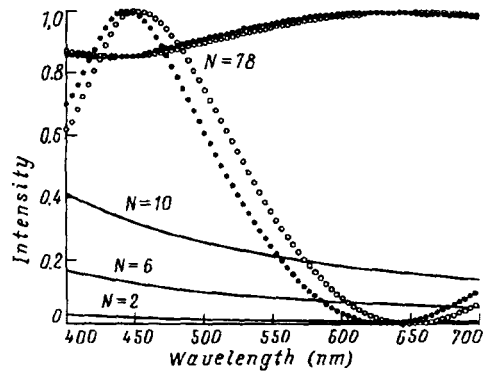


Fig.2. An example of transmission (two upper curves) and reflection spectra for the films consisting of 78 layers (\bullet, \circ), 2, 6, 10 layers (solid lines). The measurements were made in the Sm-A phase (\bullet , solid lines) at 74°C and in Cry-B phase (\circ) at 61°C . The reflection spectra are shown in arbitrary units

Fig.1 displays the temperature dependence of the measured reflectivity from 2- and 4-layer films. The layer transitions appear as one anomaly for 2-layer film and as two anomalies for 4-layer film. Upon cooling, the first anomalies at about

72°C correspond to the phase transitions of the two outside layers. In the case of the 4-layer film, the interior two layers remain Sm-A from about 72°C to 65°C. The second transition related to the interior layers appears as an abrupt jump at about 65°C. It is interesting to note that in thin films the transitions of the outside layers were continuous.

An example of the reflection and transmission spectra from thick film in the Sm-A (74°C) and Cry-B (61°C) phases is shown in Fig.2. Relative increase of the optical thickness $\Delta D/D$ over a range of temperature from 74°C to 61°C is about 3%. The variation of D can be related to the change of the layer spacing d and the index of reflection n ($\Delta D/D = \Delta d/d + \Delta n/n$). The increase of d obtained from X-ray measurements is also about 3%. Thus we conclude that the change of the optical thickness when passing through the phase transition takes place mainly because of the increase in d . The contribution of the change of n to ΔD is small. Upon cooling, the reflected intensity increases when passing through the phase transition if the measurements in thick film are made at $\lambda_m < \lambda_0$, (λ_0 is the wavelength of the reflectivity minimum). In this case the sensitivity of the optical reflectivity is higher in thick film over a range of λ from λ_0 to the point λ_i of intersection of the spectra from thick and thin films (Fig.2). For example, the sensitivity of the measurements in 78-layer film is higher than that in 2-layer film over a range of $\Delta\lambda = (\lambda_0 - \lambda_m) < 15\text{ nm}$ ($\Delta\lambda < 87\text{ nm}$ for 78- and 10-layer films).

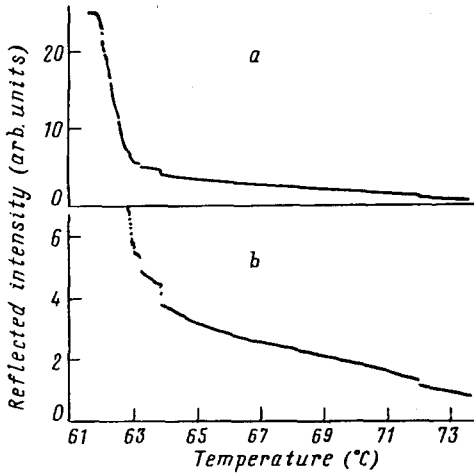


Fig.3. Temperature dependence of optical reflectivity near Sm-A-Cry-B transition of a 71-layer thick film. The vertical scale for figure 3(b) has been enlarged

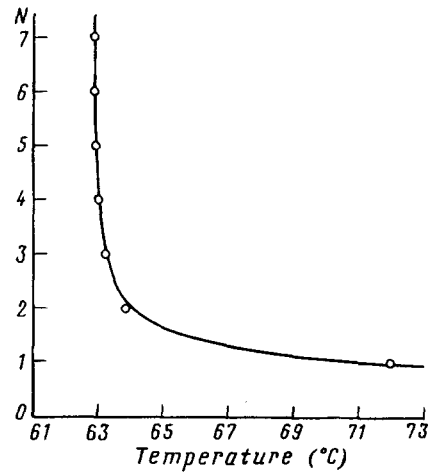


Fig.4. Number of frozen surface layers versus temperature. The solid line is the best fitting result to the simple power law [Eq. (3)]

The observed layer-by-layer transitions in thick film are shown in Fig.3 ($\Delta\lambda = (\lambda_0 - \lambda_m) = 4\text{ nm}$ at 74°C). The reflectivity data display very sharp anomalies. The runs with the jumps in the reflectivity were reproducible. Upon cooling, we see an increase in the reflected intensity $I(T)$ over the intervals between the reflectivity jumps. These variations in $I(T)$ have to be related to the increases in d and $\langle P_2 \rangle$ in bulk samples. In the case of the 71-layer film, we were able to resolve seven individual layer transitions. Fig.4 displays the depth of the surface

Cry-B phase (in layers, N) versus temperature. The first seven-layer transitions are described by a power-law form:

$$N(T) = N_0 \left(\frac{T_0}{T - T_0} \right)^\nu, \quad (3)$$

where N_0 , T_0 , ν are fitting parameters. The critical exponent $\nu = 0.35$ and $N_0 = 0.27$ are similar to those found in the 40.8 free standing films ($\nu = 0.36$, $L_0 = 0.32$) [11]. These values are in good agreement with the predictions for simple Van der Waals forces ($\nu = 1/3$) [17,18]. It is important to note that $T_0 = 62.85^\circ\text{C}$ differs noticeably from the bulk transition temperature. This suggests that for the interior layers the transition temperatures deviate essentially from the power-law form and the mechanism of transition is more complicated than the model. The deviation from the pure power-law divergence also have been observed near the Sm-A–Sm-I transition [19]. We believe that those phenomena are intrinsic to the layer-by-layer transition.

In conclusion, we investigated the Sm-A–Cry-B transition in extremely thin and thick free-standing films and in bulk samples. The reflectivity measurements were shown to yield information on the effects of the layer-by-layer transitions in thick films. We were able to observe seven layer-by-layer surface transitions in thick films of 60.6. The change of the reflectivity and optical thickness at the transition were related to the change of the layer spacing. The dependence of the number of surface transitions versus temperature deviated from the power-law form in the vicinity of the bulk transition temperature.

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1. S.Heinekamp, R.Pelkovits, E.Fontes et al., Phys. Rev. Lett. **52**, 1017 (1984).
 2. E.B.Sirota, P.S.Pershan, L.B.Sorensen, and J.Collett, Phys. Rev. A **36**, 2890 (1987).
 3. T.Stoebe, R.Geer, C.C.Huang, and J.W.Goodby, Phys. Rev. Lett. **69**, 2090 (1992).
 4. T.Stoebe, C.C.Huang, and J.W.Goodby, Phys. Rev. Lett. **68**, 2944 (1992).
 5. P.Pieranski et al., Physica A **194**, 364 (1993).
 6. T.Stoebe, C.C.Huang, and J.W.Goodby, Phys. Rev. E **48**, 404 (1993).
 7. I.Kraus, P.Pieranski, E.I.Demikhov, and H.Stegemeyer, Phys. Rev. E **48**, 1916 (1993).
 8. C.Bahr, D.Fiegner, C.J.Booth, and J.W.Goodby, Europhys. Lett. **26**, 539 (1994).
 9. T.Stoebe and C.C.Huang, Phys. Rev. E **49**, 5238 (1994).
 10. E.I.Demikhov, V.K.Dolganov, and K.P.Meletov, Phys. Rev. E **52**, 1285, (1995).
 11. A.J.Jin, T.Stoebe, and C.C.Huang, Phys. Rev. E **49**, 4791 (1994).
 12. D.E.Moncton and R.Pindak, Phys. Rev. Lett. **43**, 701 (1979).
 13. P.S.Pershan, G.Aeppli, J.D.Lister, and R.J.Birgeneau, Mol. Cryst. Liq. Cryst, **67**, 205 (1981).
 14. M.More et al., Liq. Cryst **18**, 337 (1995).
 15. E.V.Gordeev, V.K.Dolganov and S.P.Krylova, Fiz. Tverd. Tela **25**, 1109 (1983) [Sov. Phys. Solid State **25**, 637 (1983)].
 16. M.Born and E.Wolf, *Principes of Optics*, Pergamon, New York, 1980.
 17. R.Lipowsky, J. Appl. Phys. **55**, 2485 (1984).
 18. R.Lipowsky, Ferroelectrics **73**, 69 (1987).
 19. B.D.Swanson, H.Stragier, D.J.Tweet, and L.B.Sorensen, Phys. Rev. Lett. **62**, 909 (1989).