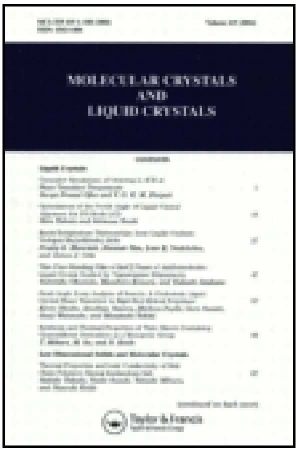

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Calorimetric, Optical Reflectivity and Electron-Diffraction Studies of 4O.8 Free-Standing Films

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To cite this article: A. J. Jin , J. T. Ho , T. Stoebe , M. Cheng & C. C. Huang (1995): Calorimetric, Optical Reflectivity and Electron-Diffraction Studies of 4O.8 Free-Standing Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 260:1, 469-476

To link to this article: http://dx.doi.org/10.1080/10587259508038720

*Mol. Cryst. Liq. Cryst.* 1995, Vol. 260, pp. 469–476
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# CALORIMETRIC, OPTICAL REFLECTIVITY AND ELECTRON-DIFFRACTION STUDIES OF 4O.8 FREE-STANDING FILMS

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Abstract Calorimetric, optical reflectivity and electron-diffraction measurements have been employed to investigate the nature of the smectic-A-crystal-B transition in thin free-standing 4O.8 (N-4-n-butyloxybenzylidene)-4-n-octylaniline) films. The results from thin films shed an important light on previous results obtained from mechanical response investigations. Moreover, while the smectic-A-crystal-B transition of bulk 4O.8 samples shows a strongly first order transition, the corresponding transition at the outermost layers exhibits pronounced fluctuations, indicating the remarkable effects of reduced dimensionality.

## INTRODUCTION

Upon cooling below the smectic-A (SmA) phase, detailed x-ray investigations [1,2] have revealed two distinct orthogonal liquid-crystal phases, namely, the hexatic-B (HexB) and crystal-B (CryB) phases. The SmA-HexB transition is found in several members of the *nm*OBC homologous series (n-*alkyl*-4'-n-*alkyl*oxybiphenyl-4-carboxylate) [1]. On the other hand, the transition near 49 °C of the bulk 4O.8 (N-(4-*n*-butyloxybenzylidene)-4-*n*-octylaniline) sample is demonstrated to be the SmA-CryB transition [2,3]. From the standpoint of molecular ordering, the major difference is that, while the CryB phase possesses three-dimensional long-range positional order, the HexB phase does not. Furthermore, according to the symmetry of the order parameter associated with the transition, the SmA-CryB transition is definitely first order in bulk samples, while the SmA-HexB transition can be continuous [4]. High-resolution x-ray diffraction studies [2,3] of thick 4O.8 free-standing films revealed long-range positional order in the CryB phase. The phase is uniaxial as the molecules can freely rotate around their long axis which on average is parallel to the layer normal. Calorimetric investigations of bulk samples yielded a hysteretic and broad heat-capacity peak, indicative of the first order SmA-CryB transition [4,5].

Theoretical advances of the phase transition in two dimensions (2D) predict that at 2D melting transition (from a liquid to "solid" at $T_m$) the shear modulus ($\mu$) of a 2D system undergoes a discontinuous jump ($\mu_D \geq 4\pi k_B T_m/a_0^2$) [6]. Here $a_0$ is the lattice spacing. Thin and uniform free-standing films of 4O.8 can be easily prepared in its SmA phase. Thus thin 4O.8 films became a prime candidate to test this important theoretical prediction. Pindak et al. [7] constructed an extremely high sensitivity torsional oscillator (operated at frequency f = 524 Hz and torsional constant k = $5 \times 10^6$ ergs) to measure the in-plane shear modulus of various film thicknesses as a function of temperature. The data enable them to identify a separate surface transition (around 55 °C) from the interior one (around 48 °C). However, no evidence for a discontinuous jump in $\mu$ at either of the transitions was found. Tarczon and Miyano [8] argued that the restoring force of the film should be very small and a much "softer" torsional oscillator is required to test the prediction of the 2D melting theory. They built another torsional oscillator system with k ≈ 5 ergs and f ≈ 5 Hz. Even reducing the operating frequency down to 0.25 Hz, they failed to reach an asymptotic region and found that $\mu$ was always smaller than $\mu_D$. Furthermore, no clear onset temperature for solid-like response was observed and any evidence of surface ordering was definitely below 60 °C. In addition to obtaining many new physical insight into the nature of thin 4O.8 films, our simultaneous measurements of heat capacity and optical reflectivity from thin 4O.8 films provide important insight into this puzzling issue.

Recently, we have established a state-of-the-art high-resolution differential ac calorimetric system which enables us to carry out simultaneous measurements of heat capacity and optical reflectivity from liquid-crystal free-standing films as thin as two molecular layers in thickness [9,10]. The relative resolution in both heat capacity and optical reflectivity is better than a few parts in $10^5$. Under several reasonable assumptions, the in-plane molecular density can be obtained from the optical reflectivity data [10,11]. Due to the intrinsic limitation of the quasi-adiabatic ac calorimeter, the information obtained from the heat-capacity data near a first order transition is somewhat limited. Under this circumstance, it has been found that the high-resolution differential optical reflectivity measurement is an extremely handy and important experimental probe complementary to our calorimeter [11]. Here we will use the results from an 8-layer film to highlight our experimental finding.

Figure 1 shows the temperature variation of heat capacity and optical reflectivity obtained from a cooling run of an 8-layer 4O.8 film. In the bulk sample, the compound 4O.8 displays the following transition sequence [5]:

isotropic(I) (78°C) nematic(N) (64°C) SmA (49°C) CryB

Thus in the temperature range of the bulk SmA phase, Fig. 1 displays three heat-capacity anomalies and four "step-wise" changes in optical reflectivity which manifest layer-by-layer transitions. From our experimental results of 3-, 4-, and 5-layer films (see Fig. 2), we conclude that similar to many other phase transitions found in liquid crystals, surface-enhanced ordering plays an important role. As a result, the layer-by-layer transition starts from two outermost layers and progresses to the inner ones as the temperature decreases.

In Fig. 1, the transition ($AB_S$) at the highest temperature ($T_{CS}$ = 63 °C) exhibits the largest heat-capacity anomaly with a significant amount of pretransitional critical-fluctuation contribution. The reflectivity data obtained concurrently exhibit a much smoother change. Combining with the data shown in Fig. 2, we conclude that the heat-capacity anomalies near 63 °C signal the crystalline order of the two outermost layers. The previously observed "solid"-like mechanical response started at much low temperature (< 60 °C). Thus our experimental results point to the fact that the surface "crystalline" order of 4O.8 films is extremely "soft". It would

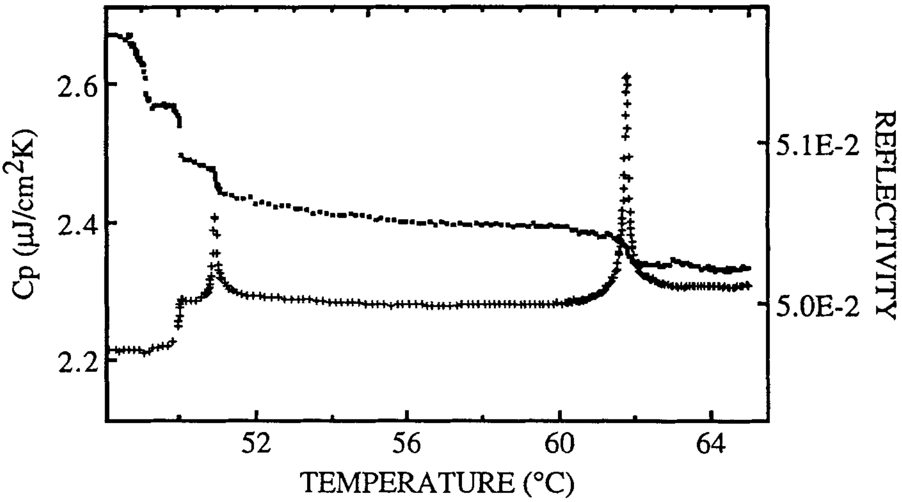

Figure 1. Temperature variation of heat capacity (crosses) and optical reflectivity (solid squares) simultaneously obtained from an 8-layer 40.8 film near the SmA-CryB transition. The transition associated with the innermost two layers is clearly discernible in the optical reflectivity data but not in the heat capacity data.

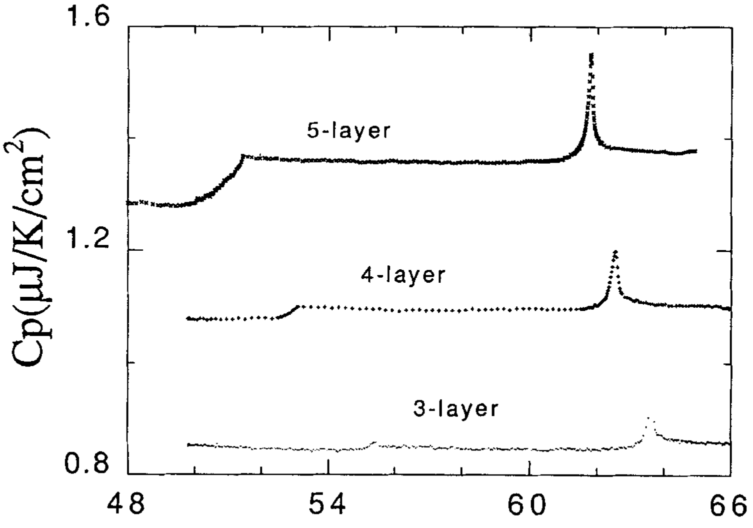

Figure 2. Temperature dependence of heat capacity obtained from 3-, 4- and 5- layer films of 40.8 near the SmA-CryB transition.

requires a much softer torsional oscillator with higher sensitivity to detect the existence of the surface crystalline order.

Furthermore, the data in Figs. 1 and 2 clearly indicate that the liquid-"solid" ordering of the two outermost mono-layers on the SmA interior layer(s) exhibits pronounced critical-fluctuation contribution to the heat-capacity anomalies. This unique feature is very different not only from that of bulk 4O.8 samples but also from the successive SmA-CryB transitions of the interior layers. We believe that the effects of reduced dimensionality in two outermost mono-layers are the major source of the observed critical fluctuations.

The magnitude of the second heat-capacity peak (near 51 °C) from the the SmA-CryB transition ($AB_{as}$) of two adjacent-to-surface layers is more than a factor of two smaller than that of the surface one. The corresponding reflectivity jump is also somewhat smaller and without any sign of pretransitional anomaly. Actually, the heat-capacity peaks associated with the $AB_{as}$ transition exhibit a systematic variation with the film thickness. In the case of 4- and 5-layer films, only very small heat-capacity anomalies can be resolved. For much thicker films (say 25-layer film), a large and delta-function-like heat-capacity peak is obtained [12]. Currently, we do not have any good explanation for the variation.

The third heat-capacity peak (at about 50 °C) is very small and is accompanied by a sharp drop in the heat capacity. The overall feature is very similar to the $AB_{as}$ transition found in 4- and 5-layer films (see Fig. 2). Again, the corresponding optical reflectivity data exhibit a step-like increase. Finally at the last step-like increase in the optical reflectivity, no heat-capacity peak or jump can be resolved. Experimentally, this is the first case in which the optical reflectivity exhibits a change, but the corresponding heat capacity fails to display any signature of the transition.

To further strengthen our interpretation of the layer-by-layer transition, we have conducted a series of electron-diffraction studies of thin 4O.8 films. Details of experimental set-up has been reported [13]. A slightly overexposed electron-diffraction pattern from an 8-layer 4O.8 film taken around 50 °C is shown in Fig. 3. Both a diffuse constant-intensity ring and six bright diffraction spots are obvious. In conjunction with the experimental results reported in Figs. 1 and

2, we conclude that the bright spots are from the outer CryB layer(s) and the diffuse ring is due to the interior SmA layer(s). Similar diffraction pattern was obtained from a 4-layer film with a much weaker diffuse ring.

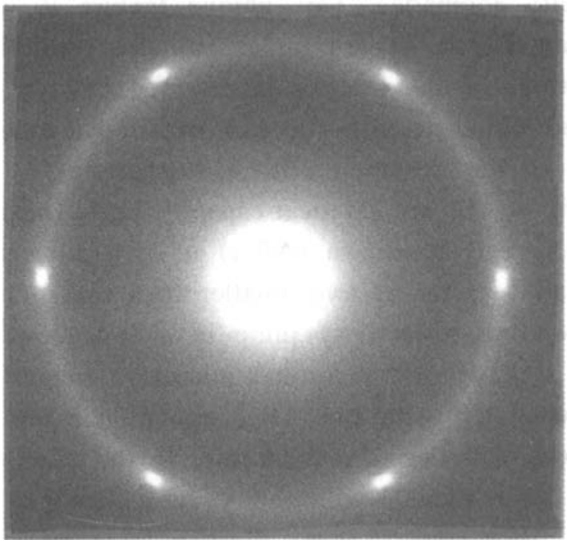

Figure 3. Electron diffraction pattern obtained from an 8-layer 4O.8 film at about 50 °C. The diffraction consists of a diffuse constant-intensity ring and six sharp diffraction spots.

For thicker films, we have detected up to six separate heat-capacity peaks [12]. Thus the SmA-CryB transition in 4O.8 free-standing films proceeds in a layer-by-layer fashion. Even with our very high resolution in both calorimetric and optical reflectivity probes, we do not have enough resolution to address if the first-order SmA-CryB transition of 4O.8 possesses a complete or an incomplete wetting transition [14]. Nevertheless, the sequence of layer-by-layer transition temperature can be well-characterized by a simple power-law expression with an exponent consistent with a wetting theory based on the van der Waals-like interlayer interaction [15]. Thus even though the SmA-HexB transition of *nm*OBC and the SmA-CryB transition of 4O.8 develop very different in-plane positional order, the layer-by-layer transitions found in both types of transitions are characterized by the same exponent [12,16], indicative of the van der Waals-like interlayer interaction

At least twenty attempts have been made to measure the heat capacity from 2-layer 4O.8 films. So far we have failed to achieve an experimental run with sufficiently high quality without the film breaking spontaneously right below the SmA-CryB transition.

In summary, we have conducted detailed calorimetric, optical reflectivity and electron-diffraction measurements on thin 4O.8 free-standing films near the bulk SmA-CryB transition temperature. This transition proceeds in a layer-by-layer fashion, with the two outermost layers undergoing the transition at about 63 °C, which is much higher than the one (< 60 °C) observed by the torsional oscillator experiments. This strongly suggests that the CryB phase in 4O.8 is extremely soft. Pronounced pretransitional fluctuation contribution to the heat-capacity anomalies has been observed near the SmA-CryB transition of the two outermost mono-layers.

This work was supported by the National Science Foundation, Solid State Chemistry Program, Grants No. DMR93-00781 (CCH) and 91-03921 (JTH).

## References

1. R. Pindak, D.E. Moncton, S.C. Davey, and J.W. Goodby, Phys. Rev. Lett. 46, 1135 (1981).
2. D. E. Moncton and R. Pindak, Phys. Rev. Lett. 43, 701 (1979).
3. P.S. Pershan, G. Aeppli, J. D. Litster, and R.J. Birgeneau, Mol. Cryst. Liq. Cryst. 67, 205 (1981).
4. C.C. Huang, J.M. Viner, R. Pindak, and J.W. Goodby, Phys. Rev. Lett. 46, 1289 (1981).
5. K.J. Lushington, G.B. Kasting, and C.W. Garland, J. Phys. Lett. (Paris) 41, L-419 (1980).
6. B.I. Halperin and D.R. Nelson, Phys. Rev. Lett. 41, 121 (1978); D.R. Nelson and B.I. Halperin, Phys. Rev. B 19, 1855 (1979).
7. R. Pindak, D. J. Bishop, and W. O. Sprenger, Phys. Rev. Lett. 44, 1461 (1980).
8. J.C. Tarczon and K. Miyano, Phys. Rev. Lett. 46, 119 (1981).
9. R. Geer, T. Stoebe, T. Pitchford, and C.C. Huang, Rev. Sci. Instrum. 62, 415 (1991).
10. T. Stoebe, C.C. Huang, and J.W. Goodby, Phys. Rev. Lett. 68, 2944 (1992).

11. T. Stoebe and C.C. Huang, Phys. Rev. E 49, 5238 (1994).
12. A.J. Jin, T. Stoebe, and C.C. Huang, Phys. Rev. E 49, R4791 (1994).
13. M. Cheng, J. T. Ho, S. W. Hui, and R. Pindak, Phys. Rev. Lett. 61, 550 (1988).
14. A number of excellent review articles on wetting have been presented, including M. Schick, in *Liquids at Interfaces*, edited by J. Charvolin, J.F Joanny, and J. Zinn-Justin, (Elsevier Science Publishers B.V., 1990), and P.G. de Gennes, Rev. Mod. Phys. 57, 827 (1985).
15. J.G. Dash, Contemporary Physics 30, 89 (1989).
16. T. Stoebe, R. Geer, C.C. Huang, and J.W. Goodby, Phys. Rev. Lett. 69, 2090 (1992).