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Chia-Fu Chou [a], John T. Ho [a], Sek-Wen Hui [b] & V. Surendranath [c]

[a] Department of Physics, State University of New York at Buffalo, Buffalo, New York, 14260, USA

[b] Department of Biophysics, Roswell Park Cancer Institute, Buffalo, New York, 14263, USA

[c] Liquid Crystal Institute, Kent State University, Kent, OH, 44242, USA

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SCALING OF BOND-ORIENTATIONAL ORDER PARAMETERS IN A 54COOBC TWO-DIMENSIONAL FILM

CHIA-FU CHOU[1], JOHN T. HO[1], SEK-WEN HUI[2], and V. SURENDRANATH[3]

[1]Department of Physics, State University of New York at Buffalo, Buffalo, New York 14260, USA
[2]Department of Biophysics, Roswell Park Cancer Institute, Buffalo, New York 14263, USA
[3]Liquid Crystal Institute, Kent State University, Kent, OH 44242, USA

Abstract Electron-diffraction measurements have been conducted on thin free-standing liquid crystal films of *n*-pentyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate (54COOBC). This compound undergoes the smectic-*A*-hexatic-*B*-crystal-*B* phase sequence, but its thin films exhibit power-law thermal anomalies at the smectic-*A*-hexatic-*B* transition which are not predicted in the theory of defect-mediated melting in two dimensions, despite the apparent absence of herringbone order. We have determined the $6n$-fold bond-orientational order (BOO) parameters C_{6n} and positional correlation length ξ in a two-layer film as a function of temperature in the hexatic-*B* phase. The results of C_{6n} are consistent with the scaling relation $C_{6n} = C_6^{\sigma(n)}$, where $\sigma(n) = n^2$, as expected in a two-dimensional *XY* system.

INTRODUCTION

Two-layer free-standing liquid-crystal thin film has long been realized as an ideal system to study two-dimensional (2D) physics[1]. Its feature of being centro-symmetric and substrate-free is especially suitable to test the defect-mediated melting theory in two dimensions introduced by Kosterlitz and Thouless (KT)[2], Halperin and Nelson[3], and Young[3]. The theory describes a process by which a 2D solid could melt via two KT-type transitions, through an intermediate *hexatic* phase, into the isotropic phase. The hexatic phase exhibits short-range positional order but quasi-long-range BOO and is characterized by a two-component order parameter $\psi_6(\mathbf{r}) = \exp[i6\theta(\mathbf{r})]$, where θ is the angle between the physical "bond" connecting neighboring molecules and a laboratory axis. This phase is therefore

expected to be described by the *XY* universality class in the modern theory of critical phenomena. Pioneering x-ray measurements revealed the first indication of a three-dimensional or "stacked" hexatic phase, called the hexatic-*B* (Hex-*B*) phase, in thick films of 65OBC (a member of the *n*-alkyl-4'-*n*-alkyloxybiphenyl-4-carboxylate, *nm*OBC, homologous series)[4]. In this novel phase of 65OBC, the x-ray work also revealed the existence of herringbone order but the range of this order was not determined. Detailed quantitative measurements on the BOO parameters were achieved later by x-ray in thick films[5] and electron diffraction in thin films[6,7]. Despite the success of structural measurements on hexatic ordering based on the scaling behavior among the BOO parameters[5-7], heat-capacity measurement from two-layer 3(10)OBC films revealed a diverging anomaly near the continuous smectic-*A* (Sm-*A*)-Hex-*B* transition that can be fitted by a power-law[8]. This is in disagreement with the predictions of 2D melting theory[9], according to which the heat capacity should involve only an essential singularity at T_c which is not expected to be observable, as well as a broad hump far above T_c due to the gradual dissociation of defect pairs. Electron-diffraction studies on a 3(10)OBC film revealed weak herringbone order in the Hex-*B* phase[10]. This is consistent with the fact that the *nm*OBC compounds transform from the Hex-*B* phase, not to the hexagonal crystal-*B* (Cry-*B*) phase, but to the orthorhombic crystal-*E* phase. Hence one may argue the discrepancy between the heat-capacity data and theoretical prediction is mainly due to the presence of herringbone order in addition to hexatic order in these compounds[11].

Recent experimental progress has been made to remove one possible explanation for the disagreement[12], using the compound 54COOBC (a member of the *n*-alkyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate, *n*4COOBC, homologous series), which undergoes the following bulk transition sequence[13]:

isotropic (70°C) Sm-*A* (55°C) Hex-*B* (53°C) Cry-*B*.

Detailed electron-diffraction investigations showed that the Hex-*B* phase of 54COOBC possesses BOO but does not exhibit discernible herringbone order[14]. However, the heat-capacity data from two-layer 54COOBC films nevertheless revealed a single sharp symmetric peak[12]. The pronounced pretransitional heat capacity and divergent character are in sharp contrast to the theoretical prediction. In light of the puzzle posed by the heat-capacity results, it is important to examine the nature and dimensionality of the hexatic order in thin 54COOBC films and its temperature behavior in relations to that of the heat capacity. We have conducted a direct measurement of the BOO parameters using electron diffraction in two-layer free-standing 54COOBC films[15], and performed the analysis of the in-plane

positional correlation.

The diffraction patterns from a two-layer 54COOBC film suggest the following temperature sequence:

Sm-A (66°C) Hex-B_1 (63°C) Hex-B_2 (60°C) Cry-B.

The labels Hex-B_1 and Hex-B_2 do not necessarily imply two distinct phases but rather refer to the appearance of different features of Hex-B-like diffraction as described below. Above 66°C, the film was in the Sm-A phase. Its diffraction pattern shows a diffuse ring of constant intensity, signifying the liquid nature of this phase. The positional correlation length ξ derived from the radial linewidth (Q_l-scan) is of the order of 14 Å. When the film was cooled down to about 66°C, a temperature which coincides with the location of the heat-capacity anomaly reported in a two-layer 54COOBC film[12], a diffraction pattern labeled as Hex-B_1 was observed, as shown in Fig. 1(a). This transition was characterized by the

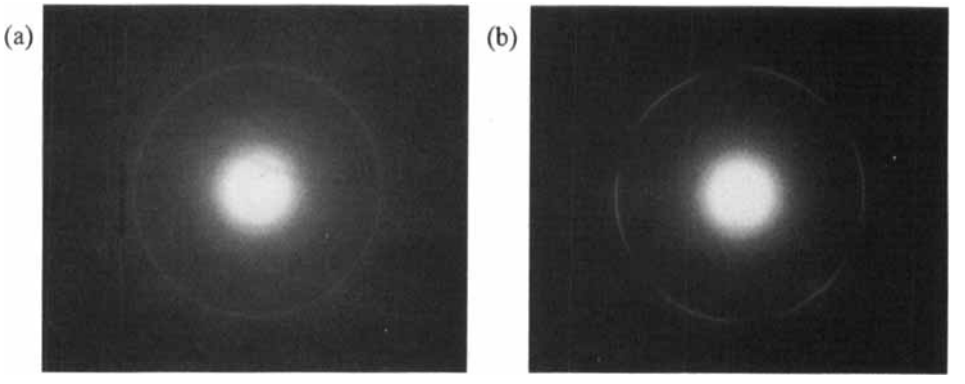

FIGURE 1 Electron-diffraction patterns from a two-layer free-standing film of 54COOBC. (a) Hex-B_1, T=66.3°C. (b) Hex-B_2, T=61.8°C.

enhancement of the in-plane positional correlation within the film as the diffuse ring sharpened in the radial direction[16], which is typical of that in a hexatic phase[4,17] as shown in Fig. 2(a). However, the measured scattering intensity around the ring (a χ-scan) was uniform and did not exhibit any six-fold modulation as expected from a single-domain Hex-B sample, probably due to the spatial-averaging of the diffraction from multiple domains within the beam diameter of 50μm. Over a 3°C temperature window in the Hex-B_1 region, ξ increases slowly. At around 63°C, the Hex-B_2 diffraction pattern appeared, as shown in Fig. 1(b), consisting of six identical arcs that are indicative of a sample with long-range

BOO. In the subsequent temperature range, ξ increases more drastically. The sample made another transition at about 60°C to the hexagonal Cry-*B* phase. This Hex-*B*-Cry-*B* transition was not resolved previously in the heat-capacity measurement for films thinner than seven layers[12]. The analysis of the Q_l-scan shown in Fig. 2(b) was done by fitting to a Lorentzian line shape in the Sm-*A* phase and by to a square-root Lorentzian, $I(Q_l) = A\xi[1+\xi^2(Q_l-Q_0)^2]^{-1/2}$, in the Hex-*B* phase, where Q_0 is the peak position and equals to 1.410 $Å^{-1}$. The analysis of the in-plane positional correlation performed in Fig. 2 was not convoluted with the instrumental resolution function. Figure 2(a) nevertheless shows three distinct regions corresponding to Sm-*A*, Hex-B_1, and Hex-B_2.

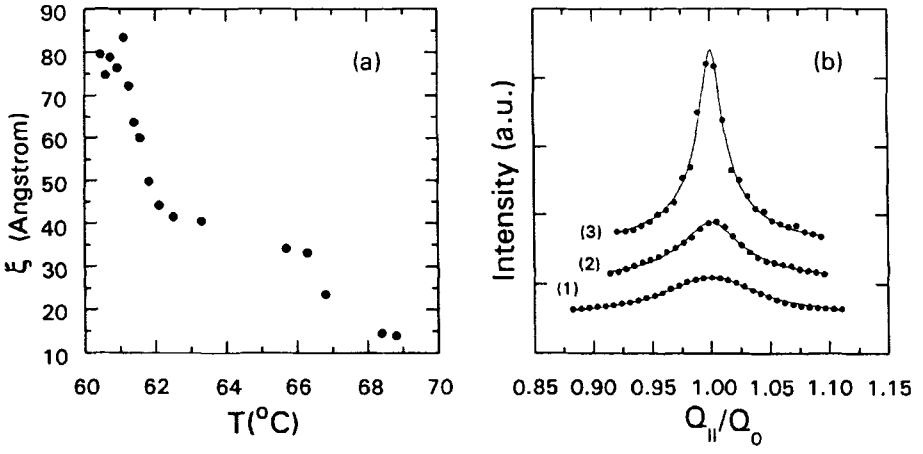

FIGURE 2 (a) Temperature dependence of in-plane positional correlation length ξ. (b) Radial Q_l scans at (1) Sm-*A*, *T*=68.4°C, (2) Hex-B_1, *T*=66.3°C, and (3) Hex-B_2 phase, *T*=60.7°C. The dots are data and the solid lines are fits.

Between 60°C and 63°C, the higher-harmonic 6*n*-fold BOO parameters, $C_{6n} = \mathrm{Re}\langle\exp(i6n\theta)\rangle$, in the Hex-$B_2$ phase were determined from diffraction intensity $I(\chi)$ along an arc over an angular range χ of 60° by fitting with the following expression

$$I(\chi) = I_0\{1/2 + \sum_{n=1}^{\infty} C_{6n}\cos[6n(\chi - 30°)]\} + I_{BG}, \quad (1)$$

where I_{BG} is a fitting parameter representing the background intensity. Aharony *et al.*[18] showed that these order parameters C_{6n}, at least in the critical region, should follow the scaling relation

$$C_{6n} = C_6^{\sigma(n)}, \tag{2}$$

where the exponents $\sigma(n)$ are related to the crossover exponents from the XY to other universality classes. In three dimensions, they can be expressed as

$$\sigma(n) = n + \lambda n\,(n\text{-}1), \tag{3}$$

with $\lambda \cong 0.3$. Detailed x-ray measurement has confirmed this behavior quantitatively in thick smectic-I films[5]. It has been further pointed out that Eq. (3) is expected to hold also in two dimensions, but with $\lambda = 1$ (or $\sigma(n) = n^2$)[19]. This has also been confirmed by electron-diffraction experiments on thin films[7], despite the occurrence of herringbone order in the compound being used.

From the experimentally-determined BOO parameters C_{6n}, the scaling exponents $\sigma(n)$ were calculated using Eq. (2). The values of $\sigma(n)$ were then compared with Eq. (3) to obtain the value of λ that best described the data. The results of our analysis are summarized in Fig. 3. The fact that the data are generally consistent with $\lambda = 1$ indicates

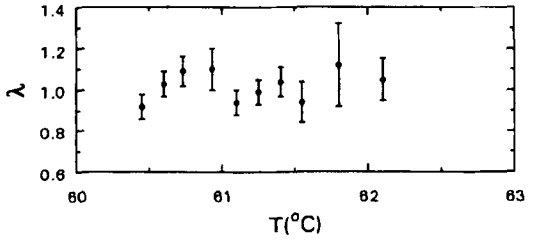

FIGURE 3 Temperature dependence of the scaling parameter λ.

that the scaling relation $\sigma(n) = n^2$ expected in a 2D XY system is obeyed in our two-layer 54COOBC film in the temperature range in which long-range BOO was observed.

The two-layer 54COOBC film, by exhibiting the Sm-A-Hex-B-Cry-B transition sequence without the presence of herringbone order, has been expected to be an ideal prototype in which to examine the predictions of the melting behavior of a 2D XY system. The experimental results to date[12,15] imply that a complete understanding of the true nature of this laboratory system still represents a challenge. Interestingly, our electron-diffraction measurements suggest that the heat-capacity peak corresponds to a transition from the Sm-A phase to a phase that initially shows hexatic-like enhanced positional correlations but no equilibrium bond-orientational order. Further study of this phase may shed some light on the interpretation of the heat-capacity results.

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REFERENCES

1. For recent reviews, see C.C. Huang and T. Stoebe, Adv. Phys., 42, 343 (1993).
2. J.M. Kosterlitz and D.J. Thouless, J. Phys. C, 6, 1181 (1973).
3. B.I. Halperin and D.R. Nelson, Phys. Rev. Lett., 41, 121 (1978); D.R. Nelson and B.I. Halperin, Phys. Rev. B, 19, 2457 (1979); A.P. Young, *ibid.*, 19, 1855 (1979).
4. R. Pindak, D.E. Moncton, S.C. Davey, and J.W. Goodby, Phys. Rev. Lett., 46, 1135 (1981).
5. J.D. Brock, A. Aharony, R.J. Birgeneau, K.W. Evans-Lutterodt, J.D. Litster, P.M. Horn, G.B. Stephenson, and A.R. Tajbakhsh, Phys. Rev. Lett., 57, 98 (1986).
6. M. Cheng, J.T. Ho, S.W. Hui, and R. Pindak, Phys. Rev. Lett., 59, 1112 (1987).
7. M. Cheng, J.T. Ho, S.W. Hui, and R. Pindak, Phys. Rev. Lett., 61, 550 (1988).
8. T. Stoebe, C.C. Huang, and J.W. Goodby, Phys. Rev. Lett., 68, 2944 (1992).
9. A.N. Berker and D.R. Nelson, Phys. Rev. B, 19, 2488 (1979); S.A. Solla and E.K. Reidel, *ibid.*, 23, 6008 (1981).
10. T. Stoebe, J.T. Ho, and C.C. Huang, Int. J. Thermophys., 15, 1189 (1994).
11. I.M. Jiang, S.N. Huang, J.Y. Ko, T. Stoebe, A.J. Jin, and C.C. Huang, Phys. Rev. E, 48, R3240 (1993).
12. A.J. Jin, M. Veum, T. Stoebe, C.F. Chou, J.T. Ho, S.W. Hui, V. Surendranath, and C.C. Huang, Phys. Rev. Lett., 74, 4863 (1995).
13. V. Surendranath, D. Fishel, A. de Vries, R. Mahmood, and D.L. Johnson, Mol. Cryst. Liq. Cryst., 131, 1 (1985).
14. A.J. Jin, M. Veum, T. Stoebe, C.F. Chou, J.T. Ho, S.W. Hui, V. Surendranath, and C.C. Huang, Phys. Rev. E, 53, 3639 (1996).
15. C.F. Chou, J.T. Ho, S.W. Hui, and V.Surendranath, Phy. Rev. Lett., 76, 4556 (1996).
16. The positional correlation length reported in Ref. 15 should read 35Å.
17. S.C. Davey, J. Budai, J.W. Goodby, R. Pindak, and D.E. Moncton, Phys. Rev. Lett., 53, 2129, (1984).
18. A. Aharony, R.J. Birgeneau, J.D. Brock, and J.D. Litster, Phys. Rev. Lett., 57, 1012 (1986).
19. M. Paczuski and M. Kardar, Phys. Rev. Lett., 60, 861 (1988).