Orientational and Positional Order in a Tilted Hexatic Liquid-Crystal Phase

J. D. Brock, A. Aharony,[a] R. J. Birgeneau, K. W. Evans-Lutterodt, and J. D. Litster
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

P. M. Horn and G. B. Stephenson
I.B.M. Thomas J. Watson Research Center, Yorktown Heights, New York 10598

and

A. R. Tajbakhsh
Department of Chemistry, The University, Hull HU6 7RX, England
(Received 17 April 1986)

We present a synchrotron-x-ray study of smectic-C (S_C) and smectic I (S_I) phases in a *single-domain* freely suspended film. Weak bond-orientational order in the S_C phase evolves continuously into the S_I phase so that the two phases are not thermodynamically distinct. From a Fourier analysis we obtain the hexatic order parameter C_6, the coefficient of $\cos 6\chi$. The higher harmonics behave as $C_{6n} = C_6^{\sigma_n}$, with $\sigma_n \simeq n + 0.3n(n-1)$, in agreement with a scaling theory.

PACS numbers: 64.70.Md, 61.30.Gd

It has been known for many decades that condensed-matter systems may be described by independent positional and bond-orientational (BO) order parameters.[1] Further, there is no symmetry reason why the positional and BO order must vanish at the same temperature. Thus it is possible to have a phase of matter in which the positional order is short range as in a liquid or glass but the BO order is long range as in a crystalline solid. Indeed, by generalizing concepts developed in the context of theories of two-dimensional dislocation-mediated melting it has been suggested that such an unusual phase could occur in certain smectic-liquid-crystal materials.[2] This phase has been labeled "stacked hexatic" for hexagonal-symmetry systems. Pindak and co-workers[3] first observed this novel phase in freely suspended liquid-crystal films. However, in the materials studied by that group it was not possible to produce single-domain samples so that the BO order could not be studied quantitatively.

Very interesting theoretical predictions have been made for the smectic-C (S_C), smectic-F (S_F), and smectic-I (S_I) phases, in which the molecules are tilted with respect to the layer normal.[4] The S_F and S_I are hexatic phases with molecules tilted between and towards near neighbors, respectively. However, coupling to the molecular tilt should induce long-range hexatic order even in the fluid S_C phase. This prediction by itself presents an interesting problem for study. An equally attractive feature of the tilted hexatics is that the coupling between the tilt and BO order provides a possible avenue for the growth of *single-domain* samples. This would, in turn, make possible direct measurements of the BO order, an essential aspect of BO-ordered phases which has not yet been studied in substrate-free systems.

In this paper we report a study of the $S_C \rightarrow S_I$ transition in the liquid-crystal material racemic 4-(2-methylbutyl)phenyl 4'-(octyloxy)-(1,1')-biphenyl-4-carboxylate (8OSI). 8OSI has a rich phase diagram[5]:

$$I \xrightarrow{174.5^\circ} N \xrightarrow{170.0^\circ} S_A \xrightarrow{133.4^\circ} S_C \xrightarrow{79.9^\circ} S_I \xrightarrow{75.1^\circ} S_J \xrightarrow{61.9^\circ} S_K.$$

The phase sequence $S_A \rightarrow S_C \rightarrow S_I$ on cooling was an essential factor in choosing this material. S_J and S_K are crystalline phases without and with herringbone order, respectively. The smectic layers were aligned by pulling a freely suspended S_A film across an 8-mm hole in a 0.64-mm-thick piece of polished stainless steel. This yielded a film of approximate thickness 10 μm. The sample was maintained at 1 Torr of nitrogen in a two-stage oven which controlled the temperature to better than 5 mK. The tilt field, $\phi(\mathbf{r})$, of the sample was aligned as the film cooled from the S_A phase into the S_C phase by two $SmCo_5$ magnets ($H \sim 0.1$ T) which held the tilt field in place thereafter. Samples consisting of a single tilt domain could be routinely produced and maintained for weeks. Optical measurements show that the tilt mosaic is $< 1.5^\circ$. Over the course of the experiment (~ 3 weeks) the $S_C \rightarrow S_I$ transition temperature drifted $< 1^\circ$C. These measurements were the first done on beam line X-20C at the National Synchrotron Light Source (NSLS). Running in an unfocused configuration, the monochromator consisted of a pair of Si(111) crystals set to the Cu-K edge ($\lambda = 1.3796$ Å). The analyzer was a Ge(111) single crystal. [$\Delta Q_{\parallel} = 2 \times 10^{-4}$ Å^{-1}, $\Delta\chi < 0.05^\circ$ (the χ axis is normal to the smectic plane)]. The illuminated spot size was set by a 1.6-mm-diam hole in a tantalum plate directly in front of the sample. A Huber six-circle diffractometer provided the neces-

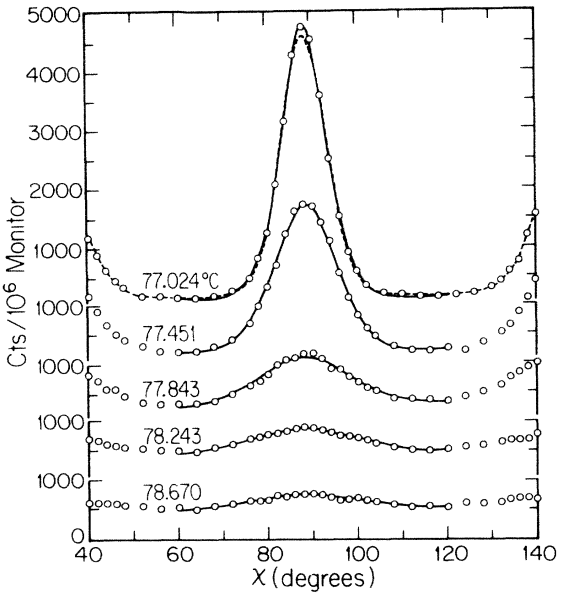

FIG. 1. Angular scans in χ along the peak of the form factor and structure factor as a function of temperature in 8OSI. The solid lines are the results of fits to Eq. (1) with $C_{6n} = C_6^{2.6(n-1)}$ while the dashed line for $T = 77.024\,^{\circ}\mathrm{C}$ is the result of a fit to Eq. (2).

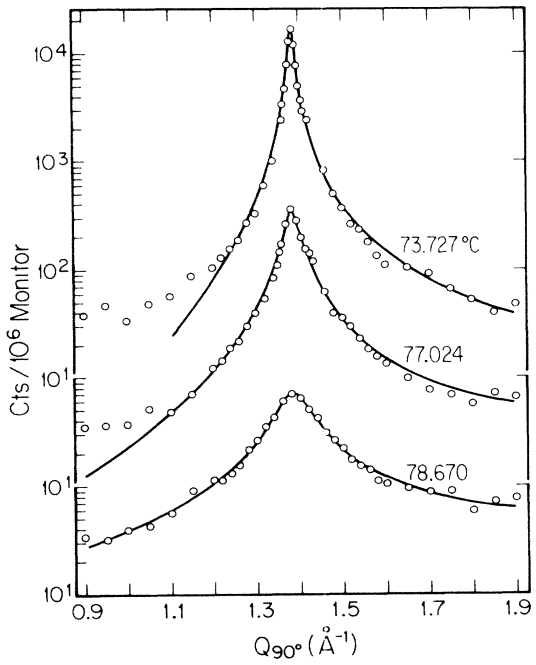

FIG. 2. Longitudinal scans through the $\chi = 90°$ peak. The solid lines are the results of fits to Eq. (2).

sary sample and analyzer motions.

The in-plane x-ray-scattering profile of the S_A phase is a diffuse ring characteristic of the fluid order in the smectic layers. As hexatic ordering develops in a single-domain sample, one expects the ring to develop a sixfold modulation, eventually breaking up into six symmetrically placed diffuse spots. In the case of the S_C phase, the shape of the diffuse ring is more complex. As a result of the tilt of the molecules, the molecular form factor is tilted with respect to the plane of the smectic layers, effectively tilting the diffuse ring. Accordingly, it is necessary that χ scans be done in the tilted plane which contains the maximum of the molecular form factor.[3] Further, because of the tilt, the BO order will have overall twofold symmetry although the sixfold aspect should dominate.

Figure 1 shows χ scans along the peak of the molecular form factor at several temperatures near the previously reported S_C to S_I phase transition. At high temperatures the ring is uniform to within our counting statistics. As the sample is cooled, a measurable sinusoidal modulation of the ring develops. At $T \sim 77.5\,^{\circ}\mathrm{C}$ the χ scan shows definite peaks every 60° indicating substantial amounts of hexatic BO ordering. The magnetic field direction is $\chi = 0°$ so that the BO-order peaks indeed come at the angles expected for a S_I phase.[3] Figure 2 shows longitudinal scans through the same peak. At high temperatures we see a broad diffuse scattering profile indicative of short-range positional order. As the sample is cooled, the width of the peak narrows simultaneously with the development of the BO order, suggesting that the enhanced positional correlations are due to a coupling to the BO order. At no point do we approach the resolution of our spectrometer; the positional order is always of short range.

In order to characterize the BO order quantitatively, we performed a nonlinear least-squares fit of the χ scans between 60° and 120° to the Fourier cosine series

$$S(\chi) = I_0\left[\tfrac{1}{2} + \sum_{n=1}^{\infty} C_{6n}\cos 6n(90° - \chi)\right] + I_{\mathrm{BG}}, \quad (1)$$

where χ is the angle between the in-plane component of **Q** and **H**. The coefficients C_{6n} measure the amount of $6n$-fold ordering in the sample. These fits neglect the residual twofold effects arising from the molecular tilt which breaks the hexagonal symmetry; this approximation does not affect our principal conclusions. With the constant term chosen as $\frac{1}{2}$ in Eq. (1), the C_{6n} approach 1 for perfect BO and positional order. From the scans deep in the S_I phase we find a background, I_{BG}, of 20 counts per 10^6 monitor counts. The fits show explicitly that the system smoothly develops first sixfold order, then twelvefold order, then eighteenfold order, etc. There is no abrupt transition; rather the evolution is smooth and continuous. This behavior confirms the prediction that coupling between the tilt and hexatic fields induces hexatic ordering in the S_C phase, destroying the $S_C \rightarrow S_I$ phase boundary.[4] The situation is similar to that of a fer-

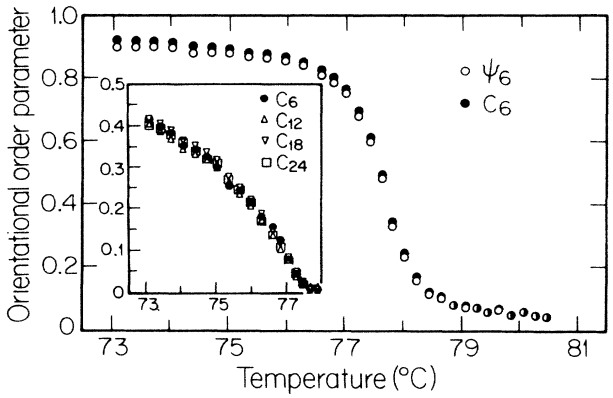

FIG. 3. Orientational order parameters C_6 [Eq. (1) unrestricted] and ψ_6 [$\sigma_n = 2.6(n-1)$] vs temperature. Inset: the first four Fourier coefficients plotted as $C_{6n}^{\sigma_4/\sigma_n}$.

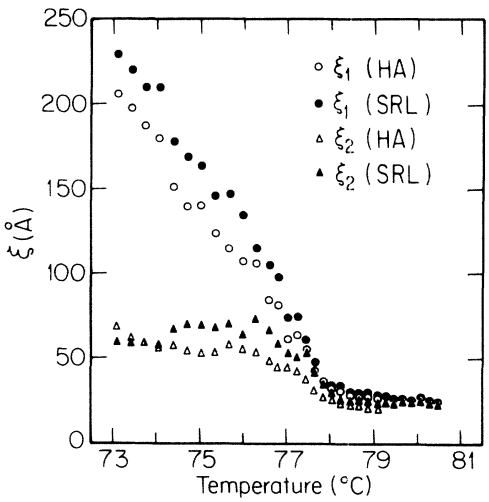

FIG. 4. Longitudinal correlation lengths for the 90° (ξ_1) and 30° (ξ_2) peaks. ξ(SRL) is the value obtained from the SRL line shape while ξ(HA) is the value obtained from the harmonic approximation Eq. (2).

romagnet in an applied magnetic field or a triangular, incommensurate, hexatic phase on a hexagonal substrate such as xenon on graphite.[6]

The hexatic order parameter C_6 is shown in Fig. 3; as noted above, C_6 evolves continuously. In analyzing the results of the fits we discovered a simple scaling relation $C_{6n} = C_6^{\sigma_n}$. As average values we find $\sigma_2 = 2.57 \pm 0.05$, $\sigma_3 = 4.80 \pm 0.14$, $\sigma_4 = 7.59 \pm 0.27$, $\sigma_5 = 10.96 \pm 0.44$, $\sigma_6 = 14.85 \pm 0.70$, and $\sigma_7 = 19.2 \pm 1.4$. With this scaling, all C_{6n} out to $n = 7$ fall on the same curve to within the fitting error over the complete temperature range with no adjustment in the amplitude. This is illustrated for the first four harmonics in the inset of Fig. 3. We note that the successive σ_n are increasingly determined by the large-C_6 data.

In an attempt to understand this novel scaling behavior, we first noted empirically that to a good approximation $\sigma_n = 2.6(n-1)$ for $1 < n < 6$; this form allows one to sum Eq. (1) exactly. The solid lines in Fig. 1 are, in fact, calculated with this approximation and the order parameter so obtained is plotted as ψ_6 in Fig. 3. Clearly ψ_6 and C_6 obtained from the unrestricted fits agree well. More recently, stimulated by these experiments, a multicritical scaling theory for this transition has been developed.[7] The theory predicts that the effective exponents should have the form $\sigma_n = n + \lambda(T) n(n-1)$. Indeed, the values quoted above fit this prediction excellently with $\lambda(T) = 0.295$. Plots using this form are indistinguishable from those in Fig. 1 although the goodness-of-fit parameter χ^2 improves by a factor ~ 4 deep in the S_I phase. The order parameter obtained in these latter fits agrees within the errors with C_6 and ψ_6 in Fig. 3.

To characterize quantitatively the positional order, it is necessary to use a simple model. For a hexatic with perfect BO order but only short-range positional order, a reasonable *Ansatz* is a sixfold symmetric pattern of circular Lorentzian spots.[6] Inclusion of BO fluctuations produces an effective mosaic averaging of these circular Lorentzian spots. In the harmonic approximation the consequent line shape is[8]

$$S(\mathbf{Q}) \propto \int_{-\pi/6}^{\pi/6} d\psi \, \frac{\exp[-\frac{1}{2}\psi^2/\langle|\delta\psi|^2\rangle]}{\kappa^2 + Q^2 + G^2 - 2QG\cos(\theta-\psi)}, \tag{2}$$

where θ is the angle between the in-plane component of $\mathbf{Q}$ and $\mathbf{G}$.

For $|\mathbf{Q}-\mathbf{G}| < G|\delta\psi|$, the BO fluctuations distort the longitudinal line shape so that they are well approximated by the square root of a Lorentzian. In previous studies it has been found that the square root of a Lorentzian (SRL) line shape fits smectic-phase in-plane longitudinal scans quite well.[3,9] The ratio of the longitudinal to the transverse linewidths is 1:5 at $\chi = 90°$. Interestingly, this same aspect ratio was found for monolayer xenon on graphite.[6] Therefore, we fit the 90° longitudinal scans in the region $G \pm 5\kappa$ to a SRL line shape. The SRL line shape works well for this range of Q over the entire temperature range. The out-of-plane component of the line shape is due to the molecular form factor and is well described by a Lorentzian of width κ_z. Including this form factor in Eq. (2), we can simultaneously fit the longitudinal and χ scans. This fit should hold over a larger range of Q. The solid lines in Fig. 4 are results of fits to Eq. (2); the SRL results are indistinguishable. As expected, Eq. (2) holds over a much larger range of $\mathbf{Q}$. It should be noted that Eq. (2) has been multiplied by a linear scale factor $1 + B(Q-G)$ to account for the overall asymmetry[9] of the profile about G.

As noted previously, the molecular tilt breaks the

hexagonal symmetry so that the peaks $\pm 90°$ differ from those at $\pm 30°$ and $\pm 150°$; specifically, the in-plane lattice constants differ by about 10%. We have fitted the two types of peaks separately to Eq. (2); the results for the 30° and 150° peaks are less reliable because the beam was blocked by the $SmCo_5$ magnets for $\chi < 32°$ and $\chi > 155°$. With this caveat, the transverse angular spread $\langle |\delta\psi^2| \rangle^{1/2}$ is identical for the two peaks while as shown in Fig. 4, $\xi(30°) = \xi(90°) = \xi_1$ in the S_I phase.[10] In general, the simplified SRL line shape gives results quite similar to those obtained from the full theory, Eq. (2).

These experiments have enabled us to obtain rather complete information about the BO and positional correlations in the S_C and S_I phases of 8OSI. The BO order is locked to the tilt and grows continuously as one cools from the S_C to S_I phase so that the two phases are not, in fact, thermodynamically distinct. Successive Fourier components of the hexatic order grow progressively with the simple law, $C_{6n} = C_6^{\sigma n}$. The positional correlations grow anisotropically in the S_I phase with $\xi(90°)$ reaching ~ 250 Å before the transition into the crystalline S_J phase.

We are especially grateful to the members of both the Massachusetts Institute of Technology and IBM groups, who have contributed greatly to the development of the IBM-MIT beam lines at NSLS. We thank R. Pindak for advice on the oven design. We have enjoyed stimulating discussions of this work with G. Aeppli, S. G. J. Mochrie, and P. S. Pershan. Two of us (J.D.B. and J.D.L.) acknowledge support from the National Science Foundation under Grant No. DMR83-19985. The MIT contributions to the operation and construction of the beam lines at the NSLS are supported by the National Science Foundation, Materials Research Laboratory program under Grant No. DMR84-18718 and by the Joint Services Electronics Program under Contract No. DAAL03-86-K-0002. Two of us (R.J.B. and K.W.E.-L.) also acknowledge the support of this latter grant. The National Synchrotron Light Source, Brookhaven National Laboratory is supported by the U. S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences.

Note added.— An elegant experiment demonstrating BO order in a S_I phase via the defect structures was recently reported by Dierker, Pindak, and Meyer.[11]

---

[a]On leave from Tel Aviv University, Tel Aviv, Israel.

[1]R. E. Peierls, private communication; L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, MA, 1969), p. 466.

[2]R. J. Birgeneau and J. D. Litster, J. Phys. (Paris), Lett. **39**, 1399 (1978); B. I. Halperin and D. R. Nelson, Phys. Rev. Lett. **41**, 121 (1978).

[3]R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, Phys. Rev. Lett. **46**, 1135 (1981); J. Budai, R. Pindak, S. C. Davey, and J. W. Goodby, J. Phys. (Paris), Lett. **45**, L1053 (1984).

[4]D. R. Nelson and B. I. Halperin, Phys. Rev. B **21**, 5312 (1980); R. Bruinsma and D. R. Nelson, Phys. Rev. B **23**, 402 (1981).

[5]P. A. C. Gane, A. J. Leadbetter, and P. G. Wrighton, Mol. Cryst. Liq. Cryst. **66**, 247 (1981).

[6]See, for example, S. E. Nagler, P. M. Horn, T. F. Rosenbaum, R. J. Birgeneau, M. Sutton, S. G. J. Mochrie, D. E. Moncton, and R. Clarke, Phys. Rev. B **32**, 7373 (1985).

[7]A. Aharony, R. J. Birgeneau, J. D. Brock, and J. D. Litster, to be published.

[8]G. Aeppli and R. Bruinsma, Phys. Rev. Lett. **53**, 2133 (1984).

[9]B. M. Ocko, A. R. Kortan, R. J. Birgeneau, and J. W. Goodby, J. Phys. (Paris) **45**, 113 (1984).

[10]Similar behavior has been seen previously in thin film S_F and S_I phases; E. B. Sirota, P. S. Pershan, L. B. Sorensen, and J. Collett, Phys. Rev. Lett. **55**, 2039 (1985).

[11]S. B. Dierker, R. Pindak, and R. B. Meyer, Phys. Rev. Lett. **56**, 1819 (1986).