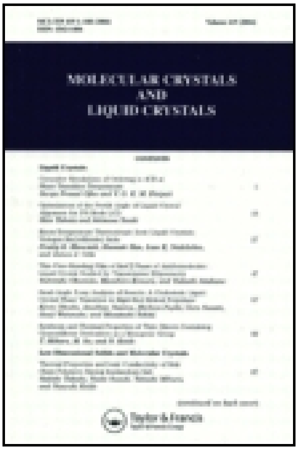

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Unusual Multiple Electron Scattering in Ultrathin Free-Standing Crystal-B Films

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Version of record first published: 18 Oct 2010

To cite this article: C. Y. Chao, T. C. Pan, C. F. Chou & J. T. Ho (2004): Unusual Multiple Electron Scattering in Ultrathin Free-Standing Crystal-B Films, Molecular Crystals and Liquid Crystals, 412:1, 1-8

To link to this article: http://dx.doi.org/10.1080/15421400490430698

Mol. Cryst. Liq. Cryst., Vol. 412, pp. 1/[1611]–8/[1618], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490430698

UNUSUAL MULTIPLE ELECTRON SCATTERING IN ULTRATHIN FREE-STANDING CRYSTAL-*B* FILMS

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Multiple coherent scattering may be observed in electron diffraction if the sample under investigation is very thick or its structure is perfectly ordered. Here we report surprising experimental results from ultrathin free-standing crystal-B films of 4-n-pentylbenzenethio-4′-n-tetradecyloxybenzoate (14S5) using electron diffraction. Multiple coherent scattering is observed down to two-layer films. Our result indicates that long-range crystalline order can be developed in a quasi-two-dimensional experimental system.

Keywords: electron diffraction; liquid-crystal thin films; multiple scattering

It is well known that a two-dimensional (2D) solid, unlike its three-dimensional counterpart, is not expected to exhibit true long-range positional order because of the logarithmic divergence of the mean-square fluctuations of the inter-atomic separation r as r diverges to infinity [1–3]. On the other hand, the positional correlations in a 2D solid, because of its resistance to shear, is expected to decay algebraically as $r^{-\eta}$, in contrast to the short-range exponential decay in a 2D liquid [4–6]. The exponent η is related to the compression and shear moduli. One possible indicator of the existence of this pseudo-long-range algebraic positional order in a 2D solid is the scattering line shape $S(\boldsymbol{Q})$ at the Bragg positions $\boldsymbol{G}$ as a function of the scattering wave vector $\boldsymbol{Q}$, which is expected to have the form

We are grateful to Y. H. Liu for participation in the early phase of this work, P. J. Wu for technical improvement in our image analysis and scanning system, and Prof. C. C. Huang for helpful discussions. This work was funded by the National Science Council, Taiwan, ROC.

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$|\boldsymbol{Q} - \boldsymbol{G}|^{-2+\eta}$ [5,7]. Perhaps the most promising system in which to study 2D crystalline order is the free-standing smectic liquid-crystal film, which is free from the influence of a substrate. The predicted scattering line shape has been verified in x-ray diffraction experiments on free-standing liquid-crystal thin films in the crystal-*B* (Cry-*B*) phase [8,9]. The value of η was found to be 0.13 in a two-layer film of 4-*n*-pentylbenzenethio-4′-*n*-tetradecyloxybenzoate (14S5) [8] and 0.15 in a four-layer film of *N*-(4-*n*-butyloxybenzylidene)-4′*n*-octylaniline (4O.8) [9]. A quantitative measurement of η as a function of thickness was done later in other liquid-crystal film [10]. Mechanical measurements have also indicated that these films exhibit solidlike shear response in the Cry-*B* phase, with the in-plane shear modulus being $2.0 \times 10^7\,\mathrm{erg/cm^3}$ in 14S5 and $1.5 \times 10^9\,\mathrm{erg/cm^3}$ in 4O.8 [11,12].

We report here the novel use of electron diffraction to examine 2D crystalline order in ultra-thin Cry-*B* films. Unlike x-ray, electrons interact strongly with matter, leading to the possibility of secondary or even tertiary scattering if the diffracting medium is essentially a perfect crystal [13,14]. Thus multiple electron diffraction could be used as an alternative indicator of the degree of crystalline order in the 2D limit. We have studied both 14S5 and 4O.8, whose Cry-*B* thin films were found previously to give similar x-ray diffraction line shapes consistent with quasi-long-range algebraic positional correlations [8,9]. We find that 14S5, but not 4O.8, shows strong multiple electron diffraction in thin films suggestive of a high degree of crystalline order. We speculate that the different diffraction patterns in the Cry-*B* phase of these two materials might be related to the different layer-by-layer transitions that occur as they undergo freezing from the smectic-*A* (Sm-*A*) to the Cry-*B* film [15,16]. Our experimental result in a 2-layer 14S5 Cry-*B* film indicates that secondary diffraction can nevertheless occur in a crystal with only pseudo-long-range positional order.

Our experimental technique for making electron-diffraction measurements of free-standing liquid-crystal thin films using a transmission electron microscope equipped with a pressurized, temperature-controlled sample chamber has been reported elsewhere [17]. We studied free-standing smectic films from 2 to 20 molecular layers in thickness suspended across an aperture 1 mm in diameter. At high temperatures, 14S5 and 4O.8 exhibit the Sm-*A* phase, composed of liquidlike layers with the long axis of the molecules normal to them. In the bulk, both materials freeze directly from the Sm-*A* to the orthogonal Cry-*B* phase, at 66.5°C for 14S5 [12] and 49°C for 4O.8 [8]. In thin films, previous studies have shown that 14S5 undergoes direct Sm-*A*-Cry-*B* layer-by-layer surface-freezing transitions [15], while 4O.8 transforms from the Sm-*A* to the Cry-*B* phase via layer-by-layer transitions involving the intermediate hexatic-*B* (Hex-*B*) phase [16]. We concentrated our effort in this study to electron diffraction in films of both materials that were entirely in the Cry-*B* phase.

We first present the data on 14S5. The electron diffraction pattern shown in Figure 1(a) for a 6-layer film represents a typical result obtained in 14S5 films of more than 2 molecular layers in the Cry-*B* phase below 66.5°C. While the diffraction pattern is unusually complex, several clear features are immediately apparent. The first is the occurrence of 6 strong spots arranged at 60° interval along a circle surrounding the incident beam, indicative of the lowest-order diffraction of the primary beam by a single hexagonal crystalline domain. The second is the existence of 3 weaker but still prominent spots arranged in an arc of about 10° along the circle on one side of each of the six strong diffraction spots. These represent primary diffraction by smaller domains present within the illuminated area whose crystalline axes deviate from one another by about 3°–10°. The indexing of the primary diffraction spots from the multi-crystalline film is also shown in Figure 1(a). The third feature is the presence of other even weaker spots surrounding each strong diffraction spot, in groups of 3 along arcs in 5 different directions. Figure 1(b) shows details of these extra diffraction spots surrounding the $\bar{1}$ 10 primary spots in groups. The spots along the 5 arcs can be separated into two categories. Those along the 2 arcs closest to the $\bar{1}$ 10 primary spots are the result of secondary diffraction, by an interior layer of the film, of electrons which have been diffracted once by the surface layer. However, the spots along the remaining 3 arcs are the result of tertiary diffraction, by an even deeper layer of the film, of electrons that have already undergone both primary and secondary diffraction. The unusual observance of tertiary electron diffraction is unambiguously identified here only because of the fortuitous presence of the slightly disorientated domains in the illuminated region. Since the probing electron beam has a diameter of 50 μm, we estimate that the illuminated region typically contains a main crystalline domain of 30 to 40 μm in size and several smaller, slightly disorientated, domains of 3 to 10 μm. More importantly, the existence of tertiary electron diffraction suggests a very high degree of positional order both within and among the molecular layers in the 6-layer 14S5 Cry-*B* film.

Electron diffraction patterns similar to Figure 1(a), whose schematic is shown in Figure 2 for clarity, were obtained in other 14S5 Cry-*B* films of at least 3 molecular layers. On the other hand, the electron diffraction pattern in a 2-layer 14S5 Cry-*B* film is distinctly different, as shown in Figure 3. Each of the 6 strongest diffraction spots forming a hexagonal pattern is accompanied by 6 weaker spots on either side of it spread over a mosaic arc of about 20° along the main circle. These spots are indicative of primary diffraction in a multi-crystalline film. In addition, surrounding each strong spot are even weaker spots lying along arcs in two other directions. These are identified as originating from secondary diffraction by the lower layer of the film of electrons that have undergone primary diffraction by the upper

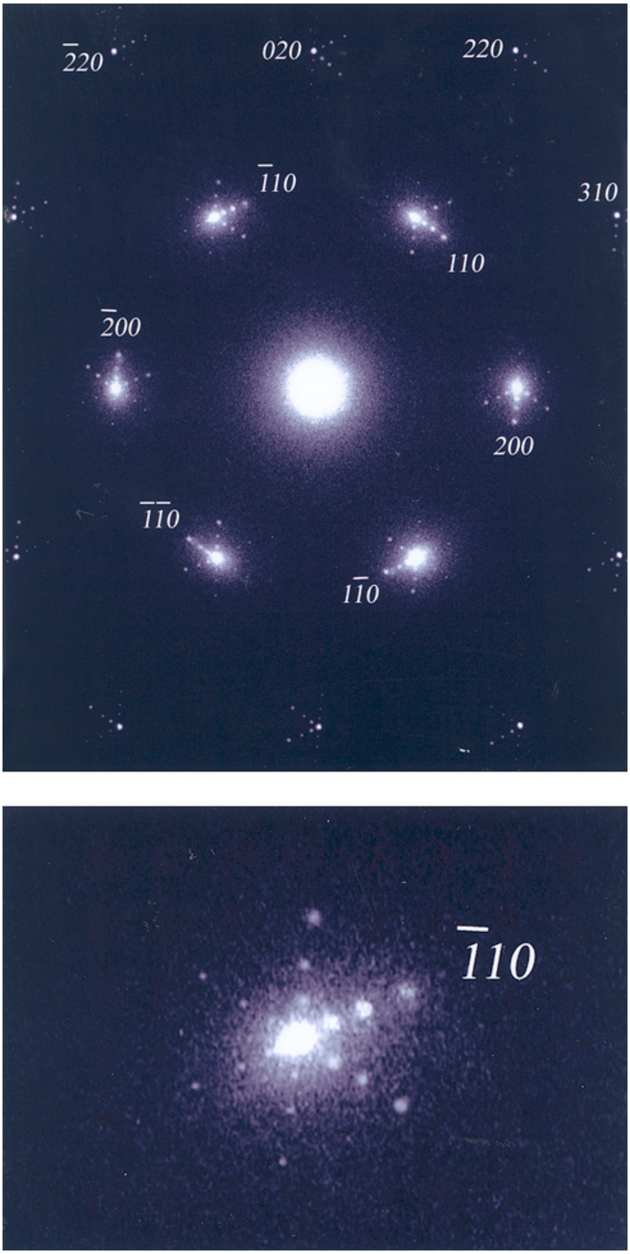

FIGURE 1 (a) Upper: electron diffraction pattern of a 6-layer 14S5 film at 64.5°C and indexing of some diffraction spots. (b) Bottom: Enlargement of a cluster of multiple diffraction spots surrounding the $\bar{1}$ 10 primary spots in (a). (See COLOR PLATE I)

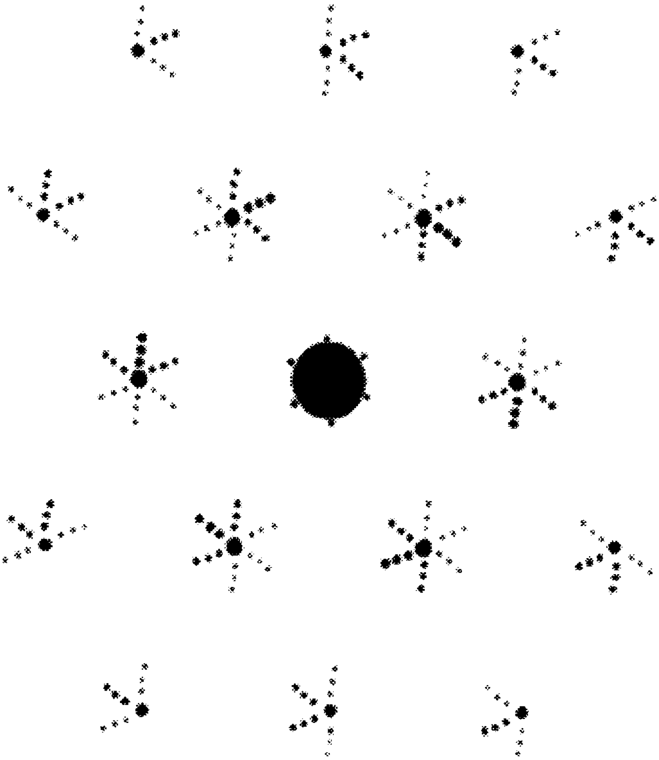

FIGURE 2 The schematic diagram of Figure 1(a). The biggest spots denote for the primary diffraction spots, the medium ones for the secondary diffraction spots, and the smallest ones for the tertiary diffraction spots (not including the central primary beam spot).

layer. It should be noted that there is no evidence of tertiary diffraction in the 2-layer film. The fact that tertiary diffraction is observed in films of 3 or more layers but not in the 2-layer film further reinforces our interpretation of the diffraction spots, and is also a good indication of the uniformity in thickness or the 2-layer film.

We now turn to the data on 4O.8. All the 4O.8 Cry-*B* films with two or more layers that we have examined gave electron diffraction patterns similar to the one shown in Figure 4. The dominant feature is a hexagonal array of 6 strong spots indicative of lower-order primary diffraction by a single crystal. There is no evidence of multi-crystalline domains, nor of higher-order primary diffraction, even in overexposed patterns. The lack of multi-crystalline diffraction makes it difficult to completely rule out the presence

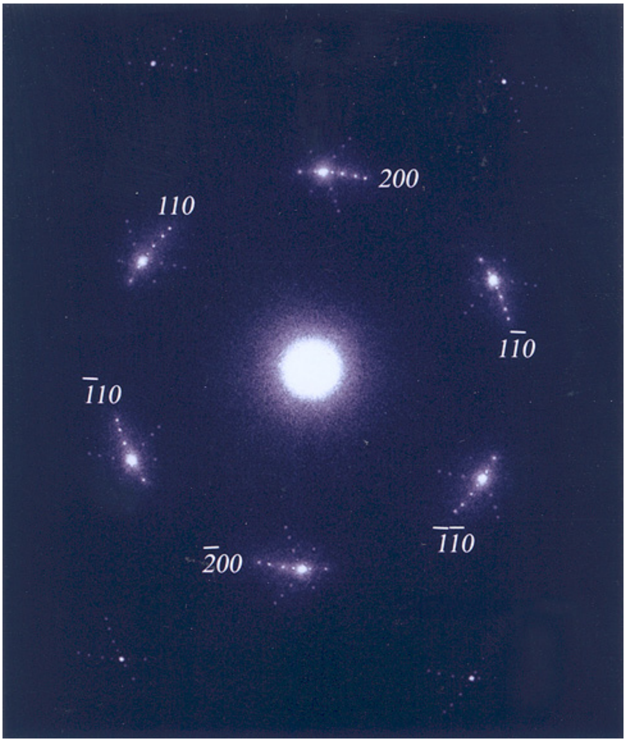

FIGURE 3 Electron diffraction pattern of a 2-layer 14S5 film at 71.5°C and indexing of the primary diffraction spots. (See COLOR PLATE II)

of multiple diffraction, but the absence of diffraction spots at the higher-order locations makes it highly unlikely.

Our observation of multi-crystalline samples and multiple electron diffraction in Cry-*B* films of 14S5 but not in 4O.8 suggests considerable difference in the detailed structures of the Cry-*B* phase in these two materials. The tendency to form multi-crystalline samples in 14S5 but not in 4O.8 may be related to the previous observation that the in-plane shear modulus in 14S5 is two orders of magnitude smaller than that in 4O.8 [11,12]. The unusual occurrence of tertiary electron diffraction in 14S5 films of 3 or more layers but not in 4O.8 films indicates that the interlayer positional order in 14S5 in the Cry-*B* phase may be much stronger than that in 4O.8. Our earlier experiments on these two materials showed different surface-induced layer-by-layer transitions from the Sm-*A* to the Cry-*B* phase [15,16]. The fact that the intermediate Hex-*B* phase, which is predicted to occur in two dimensions [18,19], is involved in the surface

FIGURE 4 Electron diffraction pattern of a 6-layer 4O.8 film at 47.0°C. (See COLOR PLATE III)

freezing in 4O.8 but not in 14S5 suggests that the smectic layers in 4O.8 are weakly coupled and more 2D-like, while 14S5 has stronger interlayer coupling. This is consistent with our current observation of the occurrence of multiple electron diffraction in 14S5 only.

Our results on the 2-layer films are of particular interest. Since earlier studies have shown that 2-layer smectic film is effectively 2D in nature [20,21], it is expected to exhibit only pseudo-long-range positional order in the crystalline phase. Previous x-ray results suggested that the positional correlations in thin films, as indicated by the exponent η, are similar in the Cry-*B* phase of 14S5 and 4O.8 [8,9]. Nevertheless, we have seen prominent secondary electron diffraction in a 2-layer Cry-*B* film of 14S5 but not of 4O.8, suggesting considerable difference in the detailed pseudo-long-range positional order in these two 2D crystals. However, more quantitative conclusions would require additional analysis of the diffraction intensities that takes into account dynamical scattering and multiple scattering.

REFERENCES

[1] Bloch, F. (1930). *Z. Phys.*, *61*, 206.

[2] Peierls, R. E. (1935). *Ann. Inst. Henri Poincare*, *5*, 177.

[3] Lyuksyutov, I., Naumovets, A. G., & Pokrovsky, V. (1992). *Two-dimensional crystals*, Academic: San Diego.

[4] Rice, T. M. (1965). *Phys. Rev. A 140*, 1889.

[5] Mermin, N. D. (1968). *Phys. Rev. A 176*, 250.

[6] Landau, L. D. & Lifshitz, E. M. (1969). *Statistical physics*, Addison-Wesley: London, 466.

[7] Jancovici, B. (1967). *Phys. Rev. Lett.*, *19*, 20.

[8] Moncton, D. E., Pindak, R., Davey, S. C., & Brown, G. S. (1982). *Phys. Rev. Lett.*, *49*, 1865.

[9] Moncton, D. E. & Pindak, R. (1979). *Phys. Rev. Lett.*, *43*, 701.

[10] Noh, D. Y., Brock, J. D., Fossum, J. O., Hill, J. P., Nuttall, W. J., Litster, J. D., & Birgeneau, R. J. (1991). *Phys. Rev. B 43*, 842.

[11] Pindak, R., Bishop, D. J., & Sprenger, W. O. (1980). *Phys. Rev. Lett.*, *44*, 1461.

[12] Bishop, D. J., Sprenger, W. O., Pindak, R., & Neubert, M. E. (1982). *Phys. Rev. Lett.*, *49*, 1861.

[13] Cowley, J. M., Rees, A. L. G., & Spink, J. A. (1951). *Proc. Phys. Soc.* (London) *A 64*, 609.

[14] Dorset, D. L. (1995). *Structural electron diffraction*, Plenum: New York, 149.

[15] Chao, C. Y., Liu, Y. H., Pan, T. C., Chang, B. N., & Ho, J. T. (2001). *Phys. Rev. E 64*, 050703 (**R**).

[16] Chao, C. Y., Chou, C. F., Ho, J. T., Hui, S. W., Jin, A. J., & Huang, C. C. (1996). *Phys. Rev. Lett.*, *77*, 2750.

[17] Cheng, M., Ho, J. T., Hui, S. W., & Pindak, R. (1987). *Phys. Rev. Lett.*, *59*, 1112.

[18] Nelson, D. R. & Halperin, B. I. (1979). *Phys. Rev. B 19*, 2457.

[19] Young, A. P. (1979). *Phys. Rev. B 19*, 1855.

[20] Chou, C. F., Ho, J. T., Hui, S. W., & Surendranath, V. (1996). *Phys. Rev. Lett.*, *76*, 4556.

[21] Chou, C. F., Ho, J. T., & Hui, S. W. (1997). *Phys. Rev. E 56*, 592.