PHYSICAL REVIEW E, VOLUME 64, 050702(R)

Orientational ordering in the chiral smectic-C^*_{FI2} liquid crystal phase determined by resonant polarized x-ray diffraction

A. Cady,[1] J. A. Pitney,[2] R. Pindak,[2] L. S. Matkin,[3] S. J. Watson,[3] H. F. Gleeson,[3] P. Cluzeau,[4] P. Barois,[5] A.-M. Levelut,[6] W. Caliebe,[7] J. W. Goodby,[8] M. Hird,[8] and C. C. Huang[1]
[1]*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455*
[2]*Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974*
[3]*Department of Physics and Astronomy, University of Manchester, Manchester M13 9PL, United Kingdom*
[4]*Laboratoire de Dynamique et de Structure des Matériaux Moléculaires, ESA CNRS 8024, Université de Lille I, 59655 Villeneuve d'Ascq Cedex, France*
[5]*Centre de Recherche Paul Pascal, CNRS, Université Bordeaux I, Avenue A. Schweitzer, F-33600 Pessac, France*
[6]*Laboratoire de Physique des Solides, Unversité Paris–Sud, F-91405 Orsay, France*
[7]*NSLS, Brookhaven National Laboratory, Upton, New York 11973*
[8]*School of Chemistry, The University, Hull HU6 7RX, United Kingdom*

(Received 13 July 2001; published 18 October 2001)

High-resolution resonant polarized x-ray diffraction experiments near the sulfur *K* edge have been performed on free-standing liquid crystal films exhibiting the chiral smectic-C^*_{FI2} phase. It is widely accepted that this phase has a four-layer repeat unit, but the internal structure of the repeat unit remains controversial. We report different resolved features of the resonant x-ray diffraction peaks associated with the smectic-C^*_{FI2} phase that unambiguously demonstrate that the four-layer repeat unit is locally biaxial about the layer normal and that the measured angle, describing the biaxiality, is in good agreement with optical measurements.

DOI: 10.1103/PhysRevE.64.050702 PACS number(s): 61.30.Eb, 77.84.Nh, 78.70.Ck, 83.80.Xz

Significant research in the field of liquid crystals has been directed at characterizing the structure of the recently discovered chiral smectic phases [1]. These phases have proven to be of theoretical importance because they provide instances of ferroelectric (smectic-C*), antiferroelectric (smectic-C^*_A), and ferrielectric behavior in samples without long-range positional order. The chiral smectic phases also have technological importance in fast electro-optic switching devices [2]. In these phases, the molecules form layers and show a finite tilt to the layer normal. As illustrated in Fig. 1(a), the azimuthal orientation of the molecules in the ith layer is described by the angle ϕ_i, or equivalently, by the vector $\mathbf{c}_i$, which is the projection of the molecular long axes onto the layer plane. The layer-to-layer progression of ϕ_i distinguishes the various chiral smectic phases.

Despite successes in determining the structures of the smectic-C* and smectic-C^*_A phases [3–5], the interlayer ordering of the other chiral smectic phases has proven to be difficult to characterize. Although it is now generally accepted that the smectic-C^*_{FI1} and smectic-C^*_{FI2} phases [6], intermediate in temperature between the smectic-C^*_A and smectic-C* phases, exhibit three and four layer superstructures respectively, with a uniform tilt [7,8], the molecular arrangements within their 3 and 4 layer repeat units are still being debated [2,7]. Traditional optical experiments fail to give clear-cut information about the molecular arrangements within the repeat units while conventional x-ray diffraction is insensitive to the molecular orientations in the layers. Resonant polarized x-ray diffraction (RPXRD) provides a means to probe ordering that is orientational, rather than positional, in nature, because the diffracted intensity depends on the orientation of the generally asymmetric local bonding environment of the resonant atoms relative to the polarization of the incident x-ray beam. Here we report high-resolution RPXRD results from one liquid crystal compound exhibiting the smectic-C^*_{FI2} phase that enable us to determine unambiguously the detailed structure within its four-layer repeat unit.

On the basis of symmetry considerations and thermodynamic arguments, Lorman proposed that there are only two possible structures for the four-layer repeat unit of the smectic-C^*_{FI2} phase that both maintain a uniform magnitude of the layer tilt angle and can be described by a single order

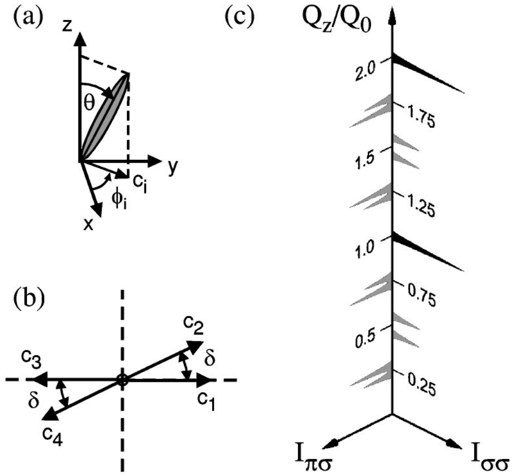
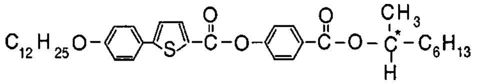


FIG. 1. (a) The azimuthal orientation of the molecules in the *i*th layer is described by the angle ϕ_i or by the vector $\mathbf{c}_i$. (b) The biaxial model of the repeat unit as proposed by Lorman [9]. (c) The $I_{\sigma\sigma}$ and $I_{\pi\sigma}$ diffracted intensities for the biaxial structure shown in (b). The black peaks correspond to ordinary diffraction peaks. The gray peaks are the resonant satellite peaks.

1063-651X/2001/64(5)/050702(4)/$20.00

parameter in a transition from the untilted smectic-A phase [9]. The first structure involves a constant interlayer change in ϕ_i of 90° resulting in a structure that is *uniaxial* about the layer normal. The second structure consists of ϕ_i changing by alternating angles of δ and $180° - \delta$, as shown in Fig. 1(b). The second structure is *biaxial* about the layer normal. In both structures there is an additional constant interlayer rotation of $\phi_0 = 2\pi d/P_0$, where d is the layer spacing and P_0 is the optical pitch (typically $\sim 1\ \mu$m). Previous RPXRD results were consistent with the *uniaxial* structure [7,8], whereas recent null-transmission ellipsometry data [10] provide strong evidence supporting the *biaxial* structure. To resolve these conflicting results, we repeated RPXRD measurements with higher resolution.

The high degree of polarization and the energy tunability demanded by RPXRD require a synchroton x-ray source. The RPXRD experiment described here was conducted at beamline X19A at the National Synchrotron Light Source (NSLS). The compound studied was MHDDOPTCOB with a chemical structure shown below:



This compound was chosen because the thiophene ring within its core has a sulfur atom with a resonant edge at a convenient x-ray energy. The phase sequence for the compound is isotropic (98 °C) smectic-A (93 °C) smectic-C* (83 °C) smectic-C^*_{FI2} (80 °C) smectic-C^*_A (64 °C) crystal. The resonant edge energy was determined by measuring the total fluorescence signal of a powder sample of MHDDOPTCOB while the incident energy is tuned through the sulfur K edge. The fluorescence signal is proportional to the absorption coefficient. The incident x-ray energy was then set to the maximum of the white line at $E_0 = 2475$ eV. The diffraction experiment was carried out in the Bragg geometry on free-standing liquid crystal films. Films of smectic liquid crystals, which always consist of an integer number of well-aligned layers, were prepared by drawing material in the smectic-A phase between two steel knife edges. By this method, films a few thousand layers thick and an area of 5x25 mm were prepared inside a two-stage oven with temperature stability better than 5 mK. The diffraction was done along the Q_z reciprocal space direction where z denotes the layer normal direction. Films were cooled from the smectic-A phase to the smectic-C^*_{FI2} phase, and scans through Q_z were carried out. The sample chamber and adjacent x-ray flightpaths were purged with helium to reduce attenuation of the low-energy x rays used in the experiment.

In the case of non resonant x-ray diffraction, only the scalar component of the x-ray structure factor (XSF) is important and the periodic modulation of the electron density due to the smectic layers can be readily observed as a series of Bragg peaks at $Q_z/Q_0 = n$, where $Q_0 = 2\pi/d$ and n is an integer. In the case of RPXRD, a resonant atom in the core of the molecule scatters in a way that is dependent on the orientation of the molecule relative to the direction and polarization of the incident x-ray beam so the off-diagonal terms in the XSF are significant. The tensor XSF can be represented in the molecular reference frame as [11]:

$$\mathbf{S}_M = f \begin{pmatrix} -1/3 - \Delta/f & 0 & 0 \\ 0 & -1/3 + \Delta/f & 0 \\ 0 & 0 & 2/3 \end{pmatrix}.$$

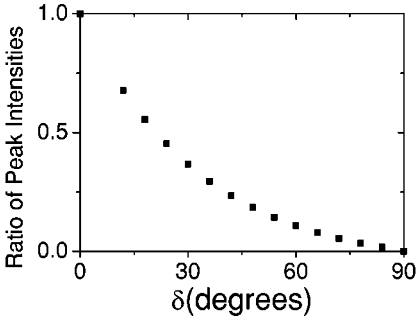


FIG. 2. The intensity ratio of the two peaks at each quarter-order position versus δ is shown. $\delta = 90°$ corresponds to the uniaxial structure, which yields no splitting of the first-order satellite peaks.

$2f/3$ is the scalar structure factor along the long axes of the molecules and Δ represents the anisotropy perpendicular to the molecular long axes from the bonding environment of the sulfur atom. The XSF in the layer reference frame, $\mathbf{S}_L$, is then found by rotating $\mathbf{S}_M$ through appropriate angles. Finally, the XSF for the composite structure, $\mathbf{S}$, is calculated by summing $\mathbf{S}_L$ multiplied by the appropriate phase factor over all the layers in the film. For a σ-polarized incident beam, the diffracted intensity takes the form $I_{\sigma\sigma} = \sigma_f \mathbf{S} \sigma_i$ and $I_{\pi\sigma} = \pi_f \mathbf{S} \sigma_i$ for the σ-polarized and π-polarized components of the diffracted beam, respectively. Carrying out this procedure for the *uniaxial* four-layer repeat unit proposed for the structure of the smectic-C^*_{FI2} phase, Levelut and Pansu showed [11] that, in addition to the σ-polarized, integer-order, layer peaks, there are resonant satellite peaks at $Q_z/Q_o = l + m(0.25 + \epsilon)$, where $\epsilon = d/P_0$, l is an integer, and $m = \pm 1, \pm 2$. The second-order $(m = \pm 2)$ resonant satellite peaks are σ-polarized, centered around half-integer values of Q_z/Q_0 and are separed by 4ϵ. A measurement of their spacing is a direct determination of P_0. There are also *single* first-order $(m = \pm 1)$ resonant satellite peaks near the quarter-integer values of Q_z/Q_0 that are π-polarized. Extending the calculation of Levelut and Pansu to the *biaxial* 4-layer repeat structure, shown in Fig. 1(b), additional π-polarized peaks appear at $Q_z/Q_0 = l \pm (0.25 - \epsilon)$. The $I_{\sigma\sigma}$ and $I_{\pi\sigma}$ diffracted intensities for the *biaxial* structure are summarized schematically in Fig. 1(c). The two first-order resonant peaks are symmetrically displaced about quarter-integer values of Q_z/Q_0 with a separation of 2ϵ, but are asymmetric in intensity with their intensity ratio a function of the angle δ defined in Fig. 1(b). A plot of the intensity ratio versus δ is shown in Fig. 2. $\delta = 90°$ corresponds to the uniaxial structure, which yields no splitting of the first-order satellite peaks. Although previous RPXRD measurements confirmed both the existence of first- and second-order resonant satellite peaks and their predicted polarization states, the

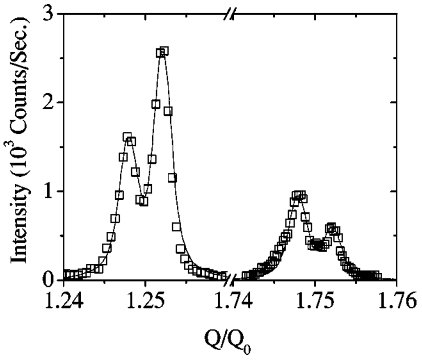


FIG. 3. The first-order resonant satellite peaks (squares) found in the experiment along with simulations (solid lines) are shown. For both simulations $\Delta/f = 0.2$, $P_0 = 1.65$ μm, and $\delta = 15°$ The simulated peaks are convoluted with an experimental resolution function that is described in the text. The simulations have been normalized to match the measured intensities.

splitting of the first-order resonant peak was not resolved, and hence, the uniaxial structure was favored.

In the RPXRD experiment reported here, entrance and exit slit dimensions were chosen to define the instrumental resolution to 4×10^{-4} Å^{-1}. This resolution represented a significant improvement over the 1×10^{-3} Å^{-1} instrumental resolution of the previous RPXRD measurements on MHDDOPTCOB, so finer diffraction features could be resolved. Polarization analysis was achieved by reflection from pyrolitic graphite analyzer crystals. Representative scans through regions of quarter-integer Q_z/Q_0 values are shown in Fig. 3. The incident x-ray intensity was reduced by factors of 13 and 7 for scans through the $1.25Q_0$ and $1.75Q_0$ positions, respectively. The positions of the peaks are scaled according to the relative $1.00Q_0$ and $2.00Q_0$ peak positions [12]. As the data show, *two peaks* were clearly resolved in scans through both $1.25Q_0$ and $1.75Q_0$. The smaller peak near $1.25Q_0$ lies on the lower-Q, side whereas the smaller peak near $1.75Q_0$ lies on the higher-Q side. The relative peak intensities would have been inverted if the rotation within the four-layer repeat unit had a different sense than that of the optical pitch. Scans through the half-integer peaks yielded split peaks of equal intensities with separation being twice those found in the first-order satellite peaks as expected. These results are qualitatively consistent with the calculated XSF for the biaxial structure. Furthermore, our simulation uses the (C_1,C_2,C_3,C_4) shown in Fig. 1(b). Other sequences, e.g., (C_1,C_3,C_4,C_2), yield very different results from the data shown in Fig. 3. Scans through the integer-order peaks provided a measure of the layer spacing, $d = 34.7\pm0.2$ Å.

The calculated XSF was convoluted with the resolution function determined by fitting the principal $1.00Q_0$ peak to a Gaussian function with a Lorentzian contribution. The convoluted XSFs for the measured peaks, shown as the solid curves in Fig. 3, are in good quantitative agreement with the data and yield $\delta = 15\pm2°$ and an optical pitch, P_0, of 1.65 ± 0.09 μm. The results are reproducible for different films. In this fitting, a value of 0.2 was used for Δ/f. The value of Δ/f sets the relative intensity ratio of the resonant to nonresonant peaks, but only weakly affects the amplitude ratio of the split quarter-integer resonant peaks. A value of 0.2 gave a good match to the measured resonant to nonresonant intensity ratios.

In order to gain further insight into the temperature dependence of the structure, we conducted Q_z scans at three temperatures in the smectic-C^*_{FI2} phase. The three scans were performed at 81.5 °C, 81.0° C, and 80.5° C, with corresponding fits to the convoluted XSF yielding $\delta = 16\pm2°$, $20\pm2°$, and $18\pm2°$, respectively, suggesting that there is no strong temperature dependence of this structure. These results compare well with the optical null-transmission ellipsometry results of Johnson *et al.* [10], which showed $\delta = 18\pm8°$.

In conclusion, we have applied the RPXRD technique to determine unambiguously the structure of the SmC^*_{FI2} phase of MHDDOPTCOB. Specifically, the four-layer repeat unit of this phase was established to be locally biaxial. This result demonstrates the effectiveness of RPXRD for investigating systems in which the ordering is orientational as well as positional in nature, opening up the possibility of determining the structures of a wide variety of different liquid crystal phases including the intriguing new phases formed by molecules with a bent core.

We thank D. A. Olson and P. M. Johnson for help with the simulation program and for detailed discussions of the results, V. L. Lorman for enlightening discussions of the proposed structures, and P. Siddons for help in developing the detectors and the polarization analyzer used. The research was supported in part by the National Science Foundation under Grant No. DMR-9703898, 9901739 and INT-9815859, and by CNRS (France) GDR606. The research was carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences, and Division of Chemical Sciences.

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[1] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, and H. Takezoe, J. Mater. Chem. **4**, 997 (1994).
[2] T. Matsumoto, A. Fukuda, M. Johno, Y. Motoyama, T. Yui, S. Seomun, and M. Yamashita, J. Mater. Chem. **9**, 2051 (1999).
[3] R.B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, J. Phys. (Paris) **36**, L-69 (1975).
[4] Y. Galerne and L. Liebert, Phys. Rev. Lett. **64**, 906 (1990); Y. Galerne and L. Liebert, *ibid.* **66**, 2891 (1991).
[5] Ch. Bahr and D. Fliegner, Phys. Rev. Lett. **70**, 1842 (1993).
[6] The SmC^*_{FI1} and SmC^*_{FI2} phases are also called the SmC^*_{γ} and the AF phases, respectively.
[7] P. Mach, R. Pindak, A.-M. Levelut, P. Barois, H.T. Nguyen, H. Baltes, M. Hird, K. Toyne, A. Seed, J.W. Goodby, C.C. Huang, and L. Furenlid, Phys. Rev. E **60**, 6793 (1999).

[8] P. Mach, R. Pindak, A.-M. Levelut, P. Barois, H.T. Nguyen, C.C. Huang, and L. Furenlid, Phys. Rev. Lett. **81**, 1015 (1998)
[9] V.L. Lorman, Liq. Cryst. **20**, 267 (1996)..
[10] P.M. Johnson, D.A. Olson, S. Pankratz, T. Nguyen, J. Goodby, M. Hird, and C.C. Huang, Phys. Rev. Lett. **84**, 4870 (2000).
[11] A.-M. Levelut and B. Pansu, Phys. Rev. E **60**, 6803 (1999).
[12] After rescaling, the center of the $1.75Q_0$ peaks occurs at $1.7501Q_0$. In the figure the peaks appear to occur at a slightly larger Q_0 value than the simulations. The shift is less than the accuracy of the Huber goniometer of about $1.2\times10^{-4}Q_0$.