X-Ray Measurement of the Twist Grain Boundary Angle in the Liquid Crystal Analog of the Abrikosov Phase

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We report the first experimental observation of the commensurate state of the recently discovered helical smectic-C phase. The projection of the reciprocal lattice on the plane perpendicular to the pitch axis consists of a ring of equispaced Bragg spots, as predicted by Renn and Lubensky for the "twist grain boundary" phase. On cooling, the number of spots q jumps from 16 to 18 and 18 to 20. A noticeable thermal hysteresis is observed on heating. The corresponding symmetries are quasicrystalline since the q-fold screw axes are not crystallographically allowed. These observations allow an accurate determination of all the parameters of the twisted lattice of screw dislocations.

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Introduced by de Gennes in 1972 [1], the analogy between the nematic (N) to smectic-A (Sm-A) transition in liquid crystals and the normal to superconductor transition in metals was beautifully illustrated in 1989 by the discovery of a helicoidal smectic-A phase in a chiral compound by Goodby *et al.* [2]. The highly dislocated structure of this new phase, called the twist grain boundary smectic-A phase (TGBA), had been proposed shortly before by Renn and Lubensky (RL) [3] as a liquid crystal analog of the Abrikosov phase in type II superconductors [4]: Slabs of smectic-A material (i.e., superconducting phase in the analogy) of thickness l_b are regularly stacked in a helical fashion along an axis $\hat{\mathbf{x}}$ parallel to the smectic layers. Adjacent slabs are continuously connected via a grain boundary constituted of a grid of parallel equispaced screw dislocation lines analogous to magnetic vortices. The finite twist angle of each grain boundary is $\Delta\theta = 2\tan^{-1}(d/2l_d) \approx d/l_d$, where d is the smectic period and l_d the distance between parallel dislocation lines. As a result, twist penetrates the smectic structure just as magnetic field penetrates the type II superconducting phase via the Abrikosov flux lattice.

The same authors argued that the type II condition (i.e., Ginzburg parameter $\kappa > 1/\sqrt{2}$) was certainly met near the cholesteric (N^*)-smectic-A-chiral smectic-C (Sm-C^*) point [2,5]. Furthermore, the existence of two new twist grain boundary phases was predicted in between the N^* and Sm-C^* phases, namely, TGBC and TGBC*, in which the smectic slabs are, respectively, smectic C and smectic C^* [6,7]. This distinction between three different Abrikosov phases is particular to liquid crystals and does not exist in superconductors.

On the experimental side, the new TGBA phase was first characterized by measurements of both a helical pitch $\lambda_0 = 2\pi/k_0$ in the optical range and a smectic layer spacing d by x-ray scattering [2] since, unlike its superconductor analog, the smectic order parameter is associated with a mass density wave of period d (about a few nanometers) and therefore easily probed by x-ray scattering. The x-ray structure factor was then shown by Srajer *et al.* [8] to have a Gaussian profile along the pitch direction $\hat{\mathbf{x}}$ as expected from the RL model [3]. The TGBC phase was discovered by Nguyen *et al.* [9] in a new series of tolane derivatives which reproduces remarkably well the theoretical phase diagram of Renn [7].

The basic features of the RL structure, i.e., the lattice of screw dislocations and the rotation of infinite angle $\Delta\theta$ between adjacent smectic slabs, were recently observed on freeze fracture electron micrographs by Ihn *et al.* [10]. Neither their existence at thermal equilibrium nor their long range organization could, however, be demonstrated from x-ray experiments on aligned samples. A plausible explanation is that $\Delta\theta$ was an irrational multiple of 2π in the reported experiments. If so, the scattering is intense on a cylinder of radius $q_0 = 2\pi/d$ and the Gaussian profile in q_x is the only visible signature of the TGBA structure [3]. If on the contrary $\Delta\theta = 2\pi\alpha$ with $\alpha = p/q$ (p,q mutually prime integers), q (or $2q$ if q is odd) Bragg peaks are equally spaced on rings of radius q_0 in the q_y-q_z plane and of coordinate $q_x = Jk_0/p$ along the pitch axis [3]. Since k_0 (of order a few μm^{-1}) is much smaller than q_0 (≈ 0.15–0.20 Å^{-1}) only wave vectors of the reciprocal lattice in the q_y-q_z plane are easily accessible to x-ray diffraction.

In this Letter, we report the first experimental observation of such a ring of Bragg spots on a well-aligned sample of the TGBC phase. The spots are equally spaced and their number q is found to vary with temperature. The corresponding TGB structure is therefore commensurate along the pitch direction with quasicrystalline rather than crystalline symmetry since the q-fold screw axis is not crystallographically allowed ($q \neq 2,3,4,6$) [3]. These observations together with previous measurements of the layer spacing d and of the pitch of the helix λ_0 [9] allow an independent determination of the distances between screw dislocations l_d and grain boundaries l_b and of their variation with temperature throughout the TGBC phase.

The liquid crystal compound was the R enantiomer of

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the $n=12$ homolog of the series studied by Nguyen *et al.* [9], 3-fluoro-4-[(*R*) or (*S*)-1-methylheptyloxy]-4′-(4″-alkoxy-2″,3″-difluorobenzoyloxy) tolane ($n\mathrm{F_2BTFO_1M_7}$ for short). Upon heating, the phase sequence is as follows: crystal (36.6) Sm-C^* (102.8) TGBC (103) N^* (110.5) blue phases (111.7) isotropic. The transition temperatures (in °C) were determined by differential scanning calorimetry (Perkin Elmer DSC7). The TGBC is more easily found on cooling since its temperature range is then about 1 °C. The pitch of the TGBC phase increases strongly on cooling from 1.05 μm at the N^*-TGBC transition to about 2 μm at the TGBC-Sm-C^* transition [9]. The layer spacing measured by x-ray diffraction is about 37.5 Å [9]. The tilt angle of the nematic director relative to the layers normal is 18° in the Sm-C^* phase at the TGBC-Sm-C^* transition [9]. It is certainly comparable in the TGBC phase since the layer spacing is continuous at the TGBC-Sm-C^* transition.

Well aligned samples were classically prepared between thin ($\sim 50\,\mu$m) flat pieces of polymer coated and unidirectionally buffed glass [8,11]. The thickness of the cells was fixed by a calibrated spacer (two 25 μm parallel gold wires about 1.5 mm apart). The cells were filled by capillarity in the isotropic phase. The alignment was achieved in the cholesteric phase and controlled under a microscope: The helicity was characterized by selective reflection of white light and observation of Grandjean-Cano steps. Moreover, the bright reflected colors did not change upon rotating the cell between crossed polarizers which showed that the helical axis lay perpendicular to the cell walls. The texture looked exactly the same in the TGBC phase. The N^*-TGBC transition only manifested itself by a sudden change in color and in position of the Grandjean-Cano lines, indicating a significant change of the pitch value λ_0. These observations were used to measure the variation of the pitch with temperature in a previous paper [9]. On the other hand, the Grandjean-Cano lines disappeared and the texture exhibited domains of different colors and strong in plane birefringence in the Sm-C^* phase. Total extinction could be achieved in all the domains separately when rotating the cell between crossed polarizers which suggested a classical bookshelf geometry (i.e., smectic layers perpendicular to the walls). The cells were then introduced in a two-stage oven which allowed a temperature control within a 10 mK accuracy.

X-ray scattering experiments were performed using Cu $K\alpha$ radiation of an 18 kW rotating anode x-ray generator. A flat pyrolytic graphite (002) monochromator delivered a 0.6×0.6 mm^2 beam onto the sample. The scattered radiation was collected on a two dimensional detector purchased from Mar Research (Hamburg). The detector system was an imaging plate (Fuji Photo Film Co. Ltd) read out by scanning with a He-Ne laser. The diameter of the circular plate is 180 mm, and the pixel size 150 μm$\times$150 μm. The intensity map was stored as a 1200 pixel$\times$1200 pixel numerical image on a VAX station. The sample to detector distance was 1100 mm through

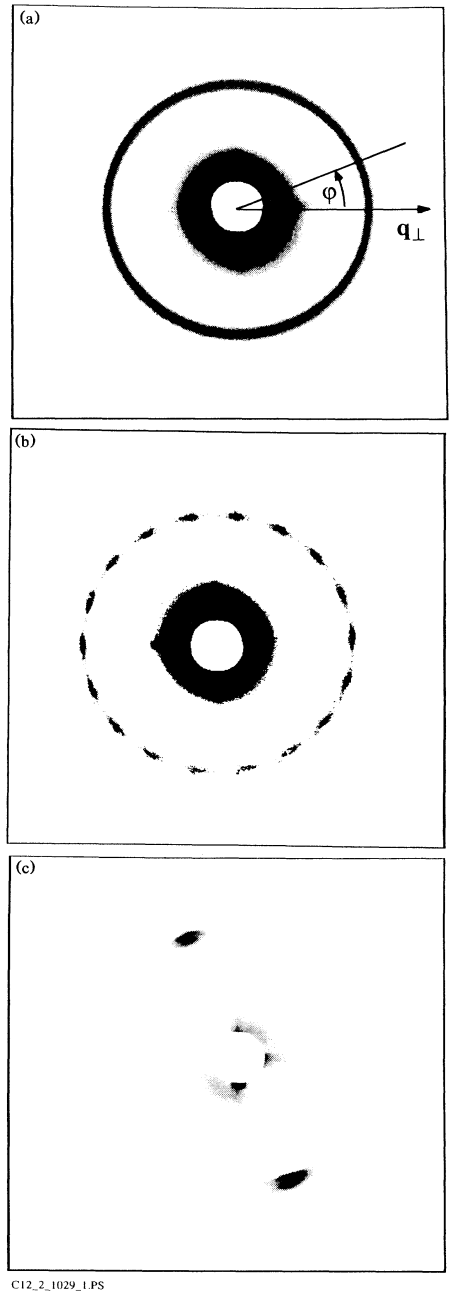

FIG. 1. Two dimensional intensity maps $(q_\perp,\varphi)$ recorded in the plane perpendicular to the pitch axis. The direction of rubbing of the polymer coating is almost vertical ($\varphi=\pi/2$). (a) Cholesteric phase at 103.00 °C. The intensity scale is expanded between two thresholds: white (<500 counts) and black (>800 counts). The radius of the ring is 0.168 Å^{-1}. Its width (0.016 Å^{-1} FWHM) is equal to the resolution. (b) Twist grain boundary smectic-*C* phase (TGBC) at 102.15 °C. Thresholds are 550 counts (white) and 630 counts (black). The ring is split into 18 spots. (c) Unwound smectic-C^* phase at 101.80 °C. Thresholds are 400 counts (white) and 3000 counts (black). The layers are perpendicular to the cell walls (bookshelf geometry). The two spots make an angle $\theta\approx 20°$ with the direction of rubbing.

helium in order to lower absorption and diffusion. The instrumental resolution in reciprocal space was about 1.6×10^{-2} Å^{-1} FWHM in both vertical and horizontal directions.

The samples were mounted with their flat walls perpendicular to the beam. The scattered intensity was thus recorded in the plane (q_y,q_z) [or $(q_\perp,\varphi)$ in cylindrical coordinates] perpendicular to the pitch axis $\hat{\mathbf{x}}$. Typical exposure times were about 8 h.

At 103.00 °C in the cholesteric phase just above the N^*-TGBC transition, the diffraction pattern (Fig. 1) displays a continuous ring of radius $q_0=0.168$ Å^{-1} corresponding to a layer spacing of 37.5 Å, consistent with earlier studies [9]. The intensity is uniform over the ring (i.e., no coherent dependence on φ is observed). Although the smectic order is expected to be short ranged in the cholesteric phase, no significant broadening of the peak is measured close to the N^*-TGBC transition. This is due to the limited resolution of our spectrometer (1.6×10^{-2} Å^{-1} FWHM) well above the intrinsic width of the peak (about 5×10^{-3} Å^{-1} at 103.00 °C [9]).

Below 102.80 °C, in the TGBC phase, a continuous but strongly modulated ring is now observed. If the intensity scale is expanded to visualize the modulation (Fig. 1), the ring at 102.15 °C for instance appears split into 18 equispaced spots revealing a commensurate (along $\hat{\mathbf{x}}$) TGB structure. The intensity profile on the ring ($q_\perp=q_0$) versus azimuthal angle φ is almost sinusoidal (Fig. 2). The radial width of the spots is resolution limited ($\Delta q_\perp=1.6\times10^{-2}$ Å^{-1} FWHM) whereas their angular width looks clearly larger ($q_\perp\Delta\varphi=2.4\times10^{-2}$ Å^{-1} FWHM). Upon cooling from the cholesteric phase, the number N of spots is successively 16, 18, and 20 (Fig. 3). Heating up again from the Sm-C^* phase reveals a clear hysteresis of about 0.25 ± 0.05 °C for the $N=18$ to $N=20$ transition whereas the $N=16$ state is not observed on heating. No incommensurate state was found.

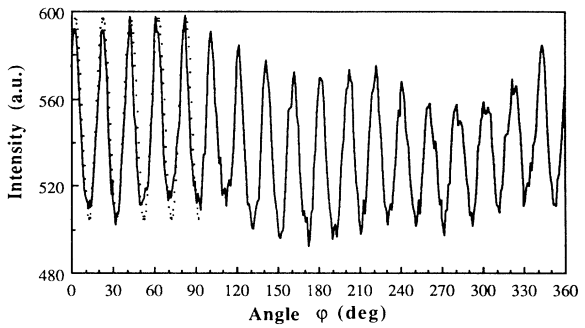

FIG. 2. Angular variation of the intensity over the ring of scattering in the TGBC phase at 102.15 °C [Fig. 1(b)]. The intensity is integrated over a ring of width $\Delta q_\perp=0.016$ Å^{-1} (i.e., resolution width) centered around $q_\perp=0.168$ Å^{-1} and plotted as a function of the angular coordinate φ. The solid line is experimental and clearly shows 18 maxima. The dotted line is calculated as the sum of 18 equispaced Gaussian functions of width $\Delta\varphi=11°$ ($q_\perp\Delta\varphi$ about 0.032 Å^{-1}, i.e., twice the resolution) superimposed on the diffuse background of about 350 counts/pixel. The relative intensities of the maxima and of the minima are well reproduced for this particular value of $\Delta\varphi$. The apparent width of the calculated peaks does not depend on $\Delta\varphi$ provided it is larger than the resolution.

One may argue that the observed spots may be due to sample mosaicity rather than to a regular precession about the helical axis. We rule out this possibility for at least two reasons: The helical structure was unambiguously established optically on all samples as explained above and the regular distribution of 16, 18, or 20 spots on a ring (which would be quite unlikely reproducible if due to 16, 18, or 20 grains in a mosaic) was consistently recorded on five different samples.

The estimation of the angular width of the Bragg spots deserves further comments: The recorded intensity map of the ring $I(q_\perp,\varphi)$ is reasonably well reproduced (Fig. 2) by a set of Gaussian peaks of radial width $\Delta q_\perp=1.6\times10^{-2}$ Å^{-1} FWHM (i.e., resolution limited) and of angular width $\Delta\varphi=11°$ or $q_\perp\Delta\varphi=3.2\times10^{-2}$ Å^{-1} FWHM (i.e., twice the resolution). In such case of overlapping Gaussian functions of φ, the actual width of the individual peaks turns out to affect strongly the ratio I_{max} (intensity of the maxima) to I_{min} (intensity of the minima) but *not* the apparent width of the peaks. We consider Gaussian profiles since they approximate well our resolution function. We do not claim, however, that the broad profile in φ is truly Gaussian: A Lorentzian angular broadening for instance would fit our data as well and give comparable angular width.

All the transition temperatures were found to shift slowly towards lower temperatures with time (a few mK per day). This effect can be classically attributed to a slow chemical degradation of the liquid crystal. It is, however, interesting to notice that the N^*-TGBC and TGBC-Sm-C^* transitions shift at slightly higher rates than the 16 to 18 and 18 to 20 transitions. As a result

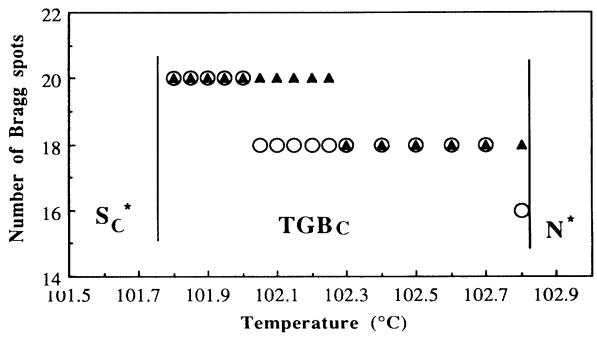

FIG. 3. Variation with temperature of the number q of Bragg spots on the ring of scattering in the twist grain boundary smectic-C phase (TGBC). Data recorded on cooling (open circles) and heating (black triangles) show a noticeable hysteresis (0.25 ± 0.05 °C) at the 18 to 20 transition. $q=16$ is not observed on heating. Vertical lines represent the temperatures of the N^*-TGBC and TGBC-Sm-C^* transitions on cooling.

the extension of the $q=16$ TGBC domain was decreasing with time from 0.2 °C with fresh $12F_2BTFO_1M_7$ to less than 0.1 °C after several days (Fig. 3). A diffraction pattern with 24 spots was even observed on a very old sample (more than 20 days). We conclude that the lock-in number q is very sensitive to impurities.

Finally, at 101.70 °C a well aligned unwound Sm-C^* phase develops [Fig. 1(c)]. The ring is replaced by two intense Bragg spots along a direction that makes an angle $\theta \approx 20°$ with respect to the director at the surface, i.e., the direction of rubbing of the glass plates. Opposite tilt angles $-\theta$ and coexistence of both sets of spots (+ and $-\theta$) were also observed. The value of θ agrees well with optical measurements of the smectic-C tilt angle [9].

The rotation angle $\Delta\theta$ of the smectic slabs in the TGBC phase can be inferred from the reported observations. The number q of smectic slabs in the period $ql_b = p\lambda_0$ is N (or possibly $N/2$ if $N/2$ is odd). X-ray patterns with 18 spots may correspond to $q=9$ or 18 but 16 and 20 spots imply $q=16$ and 20, respectively, since $N/2$ is even. The simplest combination of numbers (p,q) is therefore $p=1$ and $q=16$, 18, and 20. With these numbers the average distance between screw dislocation lines within a grain boundary increases discontinuously upon cooling: $l_d = d/\Delta\theta = 94$ Å (16 spots), 106 Å (18 spots), and 118 Å (20 spots). These distances are almost constant on each step q since the layer period d does not vary significantly with temperature in the TGBC phase [9].

Helical pitch measurements reported in Ref. [9] show that the pitch λ_0 increases strongly upon cooling in the TGBC phase. The width l_b of the smectic slabs along the pitch axis varies as $\lambda_0(T)/q$, i.e., from 656 Å for $q=16$ at 102.80 °C up to about 1000 Å for $q=20$ at 101.80 °C. In between, the block size l_b must undergo a noticeable continuous variation with $\lambda_0(T)$ at constant q and discontinuities with temperature when q jumps from 16 to 18 and 20. At 102.50 °C, for instance, $q=18$ and l_b is about 720 Å.

The values and variations of the ratio l_b/l_d with temperature can thus be determined for the first time. We find 7 (102.80 °C, $q=16$) $\leq l_b/l_d \leq$ 8.5 (101.80 °C, $q=20$). These values are significantly higher than the theoretical values estimated by Renn and Lubensky of order unity in the TGBA phase [3]. Note that other possible values of the integers (p,q), i.e., $p>1$ or $q=9$ instead of 18, would lead to even higher values of the ratio l_b/l_d.

Our observations show that the lock-in interactions which favor commensurate structures are quite strong for the TGBC phase of $12F_2BTFO_1M_7$: No incommensurate state is observed and the variations of q are first order transitions with noticeable hysteresis. On the contrary, the TGBA phase studied in detail by Srajer *et al.* [8] was certainly incommensurate since no structure was found around the circumference of the Bragg cylinder. We know from Meyer *et al.* [12] that a smectic-C material made of chiral molecules ought to bear a nonzero electric polarization. This argument applies to the smectic-C slabs of the TGBC phase. The reported observations suggest that lock-in interactions may have this dipolar origin. Further experimental studies of the $nF_2BTFO_1M_7$ series are clearly needed to confirm this point since the polarization can be continuously monitored from zero with the $n=11$ homolog which exhibits a TGBC phase with vanishing tilt angle [9].

In summary, we have reported the first experimental observation of a three dimensional regular lattice in a twisted smectic phase made of chiral molecules. The lattice is periodic along the helical axis $\hat{\mathbf{x}}$ but quasicrystalline in the y-z plane. We believe that these observations definitely show the validity of the twist grain boundary model of Renn and Lubensky [3,5–7].

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