Structural Study of a Commensurate TGB$_A$ Phase and of a Presumed Chiral Line Liquid Phase

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We report the first experimental observation of a commensurate twist-grain-boundary smectic-*A* phase (TGB$_A$). The number of blocks per pitch is found to vary with temperature but is independent of the thickness of the well aligned sample. For the first time the variations with temperature of the distance between the screw dislocations l_d and the grain boundaries l_b have been determined in the TGB$_A$ phase. The ratio l_b/l_d is found to be very close to the one predicted by Renn and Lubensky. We also report the first structural study of the phase presumed to be the chiral line liquid phase, the liquid-crystal analog of the vortex liquid phase in type-II superconductors. [S0031-9007(98)07559-0]

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Liquid crystals are intermediate states of condensed matter which combine long range positional or orientational order along some directions of space and liquid like disorder along other directions. A striking similarity between the liquid crystals and superconductors was pointed by de Gennes in 1972 [1] but only the pioneering work of Renn and Lubensky in 1988 [2] permitted the identification of the liquid crystal analog to the Abrikosov flux phase appearing in type-II superconductors. The result is the strongly dislocated structure of the twist grain boundary (TGB) smectic phases, shown in Fig. 1. Twist penetrates the TGB structure via a twisted lattice of screw dislocations analogous to magnetic vortices. Smectic slabs of constant thickness, l_b are regularly stacked along the pitch direction. The presence of a grain boundary allows the rotation of the layer normal by a finite angle Δ, which depends on the density of screw dislocations: $d/2l_d = \sin(\Delta/2)$ and $l_b/P = \Delta/2\pi = \alpha$, where l_d is the distance between the screw dislocation lines in the grain boundaries, P the cholesteric pitch, and d the smectic period. Depending on the character of the smectic blocks (SmA = smectic A, SmC = smectic C, SmC^* = smectic C^*), TGB$_A$, TGB$_C$, and TGB$_{C^*}$ phases are predicted [3].

The reciprocal space structure of the TGB phase depends on the value of the ratio α. If α is irrational, the structure exhibits no periodicity (incommensurate TGB). In the reciprocal space, the intensity is located in an uniform ring of radius $q = 2\pi/d$ in the plane (q_y, q_z) perpendicular to the pitch taken along the x direction. The profile along q_x is Gaussian proportional to $\exp(-q_x^2\xi^2)$ with ξ being the coherence length. If on the other hand α is rational ($\alpha = n/m$), the TGB structure is periodic with a period $nP = ml_b$ along x with m fold rotational symmetry (commensurate TGB). In the reciprocal space, the intensity is located in equispaced Bragg spots distributed along a ring of radius $q = 2\pi/d$ in the plane (q_y, q_z). The number of spots is just $n \times m$, if this number is even or $2n \times m$ if it is odd. The number of spots is therefore always even. The intensity of these spots varies with q_x with a Gaussian envelope $\exp(-q_x^2\xi^2)$.

The TGB phase can presumably melt to a chiral line liquid just as the Abrikosov phase melts to a directed line liquid. Significant short-range TGB structure in the cholesteric phase (N^*), corresponding to a liquid of screw dislocations (called a chiral line liquid and denoted as N_L^*), has been introduced by Kamien and Lubensky [4]. N_L^* and N^* are not thermodynamically distinct phases (i.e., they share the same phase symmetry), but they differ appreciably in the extent of short range smectic layer formation.

The experimental discovery of the first TGB phase is due to J. Goodby and co-workers in 1989 [5]. The optical properties of this phase are similar to these of the cholesteric phase. X-ray diffraction experiments on oriented samples have revealed the existence of a continuous ring whose profile is consistent with the Renn-Lubensky model [6]. Estimation of different lengths ($l_b = l_d =$ 18 nm and $\Delta = 13°$) and the existence of a lattice of screw dislocations was confirmed by freeze fracture experiments [7]. A new chiral liquid crystal series combining strong chirality with nematic-SmA-SmC (NAC)

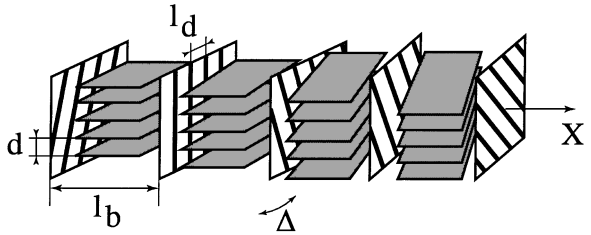

FIG. 1. Schematic representation of the TGB$_A$ phase (twist grain boundary). The pitch axis is along the x direction. Blocks of SmA layers of spacing d are separated by regularly spaced twist grain boundaries separated by a distance l_b. The distance between screw dislocations within a grain boundary is l_d.

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polymorphism [8] was synthesized by Nguyen. The experimental phase diagram involves two TGB phases with different smectic order: TGB_A and TGB_C. TGB_A exhibits the classical uniform (i.e., incommensurate) diffraction ring, whereas the TGB_C ring is commensurate [9] with a m-fold symmetry (with $m = 16$, 18, or 20). Finally, high resolution calorimetry has been used by Chan and coworkers [10] to study a homologous series which exhibits SmA, TGB_A, and N^* phases. An unexpected phase transition was observed between the TGB_A and N^* phases. A large rounded heat capacity peak in the N^* phase is consistent with the evolution of short range chiral line liquid (N_L^*) character but does not represent a thermodynamic transition. The same result was obtained on the $n = 10$ homolog of the Bordeaux series [11].

The x-ray scattering experiments presented in this Letter are consistent with previous high resolution calorimetry [11] studies since all expected phase transitions (SmC^*-TGB_A, TGB_A-N_L^*, and N_L^*-N^*) have been observed. Moreover, we report the first experimental observation of a commensurate TGB_A phase. The number of blocks per pitch is found to vary with temperature but is independent of the thickness of the well-aligned sample. These observations allow an independent determination of the distance between screw dislocations l_d and grain boundaries l_b. Thus, for the first time the values and variation of the ratio l_b/l_d with temperature can be determined in the TGB_A phase. A ratio of $l_b/l_d \approx 1$ is observed as predicted by Renn and Lubensky [2]. We also report the first structural study of the phase presumed to be the chiral line liquid phase (N_L^*).

X-ray scattering experiments were performed on the D43 beam line at LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Orsay, France) using synchrotron radiation. The beam was monochromatized with a curved Ge monochromator ($\lambda = 1.44$ Å) and then focused on the detector (imaging plate) which was located at about 400 mm from the sample. The final beam size at the sample position was defined by a 500 μm collimator. The sample was placed in a Mettler hot stage with metallized Kapton windows and mounted inside a cage made of copper to avoid possible temperature gradients. This was then mounted on a θ-X-Z stage. The temperature of the sample was manually set with the temperature controller (± 0.1 °C).

We have used the $n = 10$ homolog of the series 3-fluoro-4[(S)-1-methylheptyloxy]-4′-(4″-alkoxy-2″,3″-difluorobenzoyloxy) tolane (nF2BTF01M7 for short). This compound has been previously studied [8] by calorimetry (DSC), optical microscopy, and x-ray method, and more recently by high resolution calorimetry [11]. The phase sequence appears to be

$$\mathrm{Sm}C^*(99.7\,^\circ\mathrm{C})\mathrm{TGB}_A(102.85\,^\circ\mathrm{C})N_L^*(106.71\,^\circ\mathrm{C})N^*.$$

Well-aligned samples were prepared between two flat pieces of polymer coated and unidirectional buffed glass [8,12]. Two cells of different thickness were prepared. In cell 1, we used two calibrated 25 μm gold wire spacers. Cell 2 was prepared without spacer and its thickness can be reasonably estimated to be 5–10 μm. The cells were filled by capillarity in the isotropic phase and the alignment was achieved in the cholesteric phase and controlled under a polarizing microscope. This procedure promotes an alignment of the molecular director parallel to the glass plates, which means that the helical pitch axis is oriented perpendicularly to the boundaries. The helicity has been characterized by selective reflection of white light and observation of Grandjean-Cano (GC) steps [13]. Each cell has been introduced in the Mettler hot stage and mounted with its flat walls perpendicular to the beam. The scattered intensity was recorded in the plane (q_y, q_z) perpendicular to the pitch axis x. The alignment procedure involved the following steps: first, the temperature of the oven was set such that the sample was in the isotropic phase ($T \approx 120$ °C during 3 min). Second, we decreased the temperature quickly (10 °C/min) and left the sample for several hours at $T \approx 103$ °C inside the cholesteric phase. Care was taken to avoid radiation damage to the sample due to the synchrotron beam by keeping the exposure times around 20 min.

Experimental results.—We have in a first stage performed x-ray scattering on the TGB_A phase. Figure 2 shows the x-ray scattering pattern obtained at $T = 101.4$ °C (upon heating), in cell 2, right in the middle of the TGB_A temperature domain deduced from the calorimetry experiments [11]. Surprisingly enough, this pattern exhibits 46 equispaced spots along the ring. This visible regular distribution of the spots is confirmed by taking the Fourier transform of the intensity along the

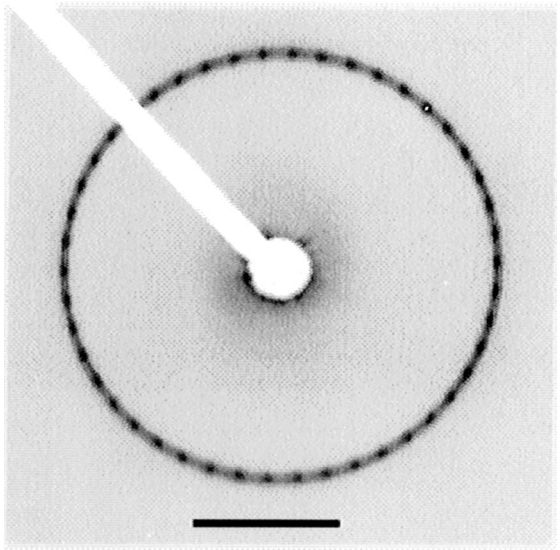

FIG. 2. X-ray diffraction pattern of the TGB_A phase upon heating at $T = 101.4$ °C. This pattern exhibits 46 spots equispaced along a ring and is the signature of a commensurate TGB_A phase. The line indicates the buffing direction.

ring (only one mode appears). This clearly indicates that the TGB phase producing this pattern is commensurate. If we assume that two neighboring blocks give two neighboring spots, the twist angle between adjacent blocks is therefore

$$\Delta = 2\pi/46 \approx 7.8°.$$

This angle is about twice as small as those observed in the commensurate TGB_C phases. The pitch value P at this temperature has been measured using optical experiments [13]: $P = 0.95\ \mu$m. The smectic period is $d = 3.8$ nm [8]. This value leads to a block size l_b equal to $P/46 = 20.6$ nm and to a distance l_d between dislocation lines equal to $l_d = d/\Delta = 27.8$ nm. Therefore the ratio l_b/l_d is close to 1, as first predicted by Renn and Lubensky [2].

Similar patterns exhibiting regular discrete spots have been observed in cell 1 for temperatures ranging from 98.6 to 101.8 °C (upon cooling). Although the transition temperatures are slightly different from those measured for the TGB_A phase by calorimetry [11], the temperature range extent (about 3.2 °C) is the same. Although a slight shift in TGB_A temperature range has been observed, the same patterns have been obtained in both cells and the number of spots present in the diffraction patterns of both cells is of the same order. For instance, upon cooling, we have observed 42 spots at $T = 101.9$ °C with cell 1 and 40 spots at $T = 101.8$ °C with cell 2. This indicates that *commensurability* does not depend on the cell thickness, but that it is an *intrinsic* feature of this phase and is not due to surface constraints.

In this temperature range, all the patterns are not so regular. In some patterns the intensity along the diffraction ring is still obviously modulated but not along the whole ring. Perpendicular to the buffing direction, we still observe regular spots, but this is not the case along the buffing direction where the ring appears to be more continuous. This result reveals a competition between the surface anchoring of the molecules and the volumic phase structure. As a matter of fact, the volumic commensurate structure and the surface anchoring can easily fit together if the number of half pitch in the cell is close to an integer. Otherwise, competition occurs in the vicinity of the walls and, in that case, the ring cannot be perfectly modulated. A possible interpretation of these observations is that the material is always commensurate and exhibits discontinuous jumps between commensurate phases.

Although the ring modulation is not always perfect, the number of spots present on the diffraction patterns clearly decreases as temperature increases. For temperatures ranging from 99.6 to 101.8 °C, the number of spots varies, respectively, from 60 to 40 (Fig. 3), decreasing by two spots steps. This implies that the number of spots along the whole ring really corresponds to the number N of blocks per pitch and that the Δ angle between adjacent blocks is given by $2\pi/N$. This variation of the number of spots and therefore of the twist angle Δ is linked to the

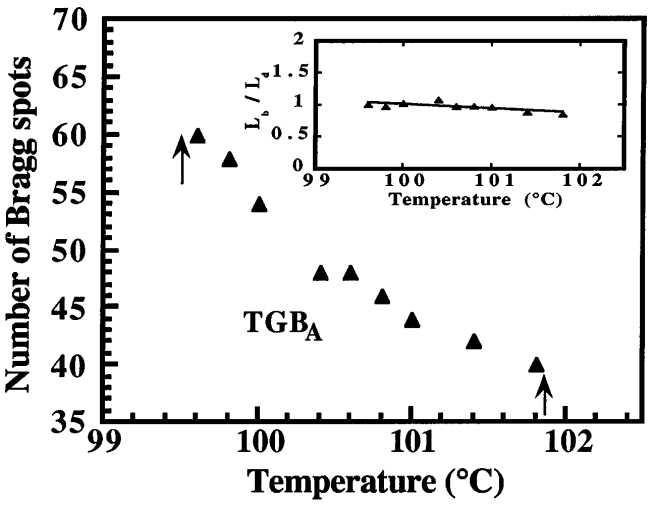

FIG. 3. Variation of the number of Bragg spots and of the ratio l_b/l_d as a function of temperature. This ratio l_b/l_d remains constant, close to 1, as first predicted by Renn and Lubensky (inset).

variation of the pitch. The block size l_b and the distance l_d between dislocation lines also vary. But, according to the previously measured values of the pitch P [13], the *ratio l_b/l_d remains constant, close to 1,* within this temperature range (inset in Fig. 3). It must be noted that this result provides the first experimental verification of Renn and Lubensky's prediction concerning this ratio for the TGB_A phase.

According to the calorimetry experiments [11], a new state appears at higher temperature between the TGB_A and the cholesteric phase. This state has been interpreted as being a *chiral line liquid phase* (N_L^*). The purpose of this experiment was to verify the existence of this phase and to study the nature of the smectic order in this phase. At temperatures above the range of the commensurate TGB_A phase, that is above 101.9 °C when cooling and from 102.4 to 106 °C when heating, the diffraction patterns no longer exhibit spots but consist of a thin continuous ring. According to the results obtained by calorimetry, this temperature range corresponds to the phase identified as a chiral line liquid phase (N_L^*) [11]. We still observe a shift of the transition temperatures but the temperature range of the phase is preserved ($\Delta T \approx 4$ °C). We have systematically fitted the $I(q)$ profiles using a simple Gaussian function. We have thus obtained the numerical values of the full width at half maximum (FWHM) and the maximal intensity I_0. Within the concerned temperature range, no significant variation of the width is noticeable. The experimental resolution has been estimated by the width of the diffraction spot corresponding to the SmC^* phase (appearing at $T = 98$ °C) and is not a limiting factor. Therefore, within the presumed N_L^* phase, the width of the ring not only remains constant but its value is also identical to the one measured

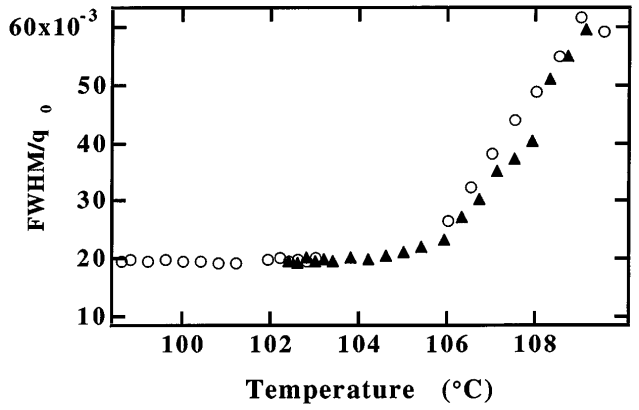

FIG. 4. Variation of the ratio FWHM/q_0 as a function of temperature (circles: upon cooling; full triangles: upon heating). FWHM is the width (full width at half maxima) of the homogeneous diffuse ring and q_0 the scattering vector at maximum intensity. The width remains constant in the presumed N_L^* phase and increases in the cholesteric phase.

in the TGB_A phase (FWHM = 0.0033 $Å^{-1}$) and is not resolution limited. While the ring width remains constant, the maximal intensity I_0 decreases linearly by a factor of 10 with increasing temperature. Since the scattered intensity depends on the square smectic order parameter, this can be interpreted as a decrease of the smectic order parameter with increasing temperature. Above $T = 106\,°C$ (when heating), the diffraction ring gets wider, which implies the loss of the quasi-long-range smectic ordering. This behavior indeed corresponds to the transition to a *cholesteric phase* which has been observed at $T = 106.71\,°C$ by calorimetry. The evolution of the FWHM of the $I(q)$ profiles as a function of temperature is shown in Fig. 4 where the transition from the N_L^* phase to the cholesteric phase is clearly seen.

The two main experimental results reported in this Letter are the first observation of an intrinsically commensurate TGB_A phase and the structural evidence of the existence of an intermediate state between this TGB_A and the cholesteric phase. The three main characteristic features of this intermediate state are the following: incommesurability, persistence of the quasi-long-range smectic ordering perpendicular to the twist direction, and decrease of the smectic order parameter. This intermediate phase has previously been assumed to be a chiral line liquid phase. Taking into account the x-ray results, it is thus surprising to observe a quasi-long-range TGB order. One might speculate a commensurate TGB_A (T6) incommensurate TGB_A (T5) cholesteric phase sequence. We could argue from calorimetry and x-ray studies that the T6 phase transition is of first order (large hysteresis and latent heat). We point out that the existence of such an incommensurate TGB phase above the commensurate phase strongly supports the intrinsic nature of the observed commensurability because arguments about boundary conditions are invalid with respect to the calorimetric results on quasi-infinitely thick samples. Our x-ray results suggest a second order T5 phase transition in contrast to the high resolution calorimetry results (the calorimetric peak is nonsingular and has no latent heat). However, more x-ray scattering experiments are needed to fully characterize this intermediate phase. In particular, the ring profile along the pitch direction may give useful information on the extent of smectic order in this direction.

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