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Rapid Note

X-ray scattering by monodomains of blue phases with smectic ordering

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Abstract. We report the first X-ray study on monodomains of the recently discovered blue phases with presumed smectic order. We have succeeded in growing large, well oriented monodomains of BP2. X-ray scattering performed on these monodomains clearly show that smectic order is present in these blue phases but with a smaller correlation length than in the neighbouring TGB phase. Moreover the smectic order possesses the symmetry of the blue phase lattice.

PACS. 61.10.-i X-ray diffraction and scattering – 61.30.Eb Experimental determinations of smectic, nematic, cholesteric, and other structures

Liquid crystals offer a wide variety of phases with long range orientational order but, as in the smectic phases, with additional quasi-long range translational order. When the molecular mesogens are chiral a spontaneous twist of the molecular orientation is generated. For instance, the classical nematic phase, which exhibits only a short range translational order, gives birth to the cholesteric phase [1] characterized by a one dimensional periodic orientational order with period or pitch much larger than the molecular sizes. At "higher" chirality, other phases called blue phases [2], appear in a temperature range situated between the cholesteric phase and the isotropic one. Two of these blue phases, BP1 and BP2, exhibit a 3-dimensional orientational order. They show a cubic crystalline structure with selective Bragg reflections in the range of visible light. The monodomains are facetted and theses phases appear with platelet textures under optical microscope. At "low chirality", the BP1 and BP2 structures can be interpreted in terms of a 3D periodic director field. The twist is not only in one direction like in the cholesteric phase but, around each director, tends to be in both directions perpendicularly to this director. One can thus build "double-twist" cylinders with a size determined by the tilt angle (θ) of the director at the surface compared to the cylinder axis. The "double twist" cylinder radius is thus of the order of magnitude of the cholesteric pitch. The cubic structures (Fig. 1) can then be described by cubic networks of double-twist cylinders (with a surface tilt angle θ equal to 45°) separated by defect lines (disclination lines). In the "high" chirality limit, this description is no longer valid and a biaxial order parameter has to be introduced [3].

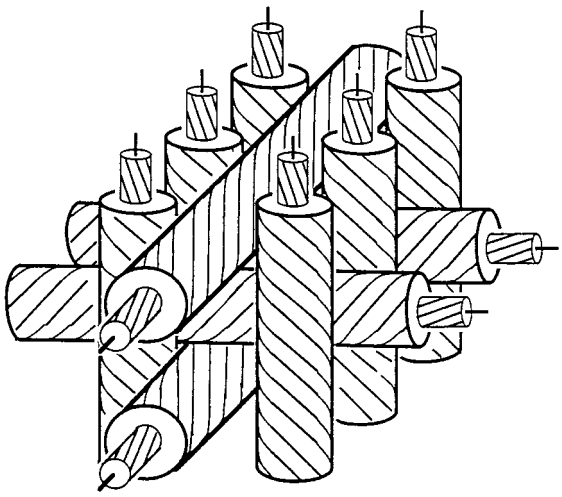

Fig. 1. Geometrical model of the BP2 phase built with double twist cylinders.

At lower temperatures smectic order may occur, but this translational order is not always compatible with

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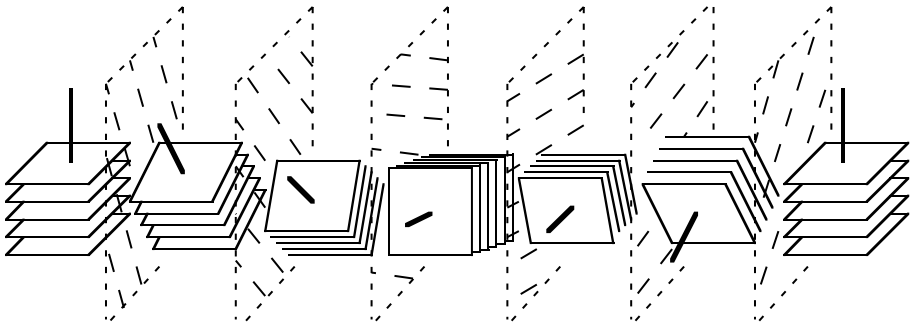

Fig. 2. The twist grain boundary phase model.

the twist due to the molecular chirality. For instance, the smectic layers in the SmA phase cannot be continuously twisted. Renn and Lubensky [4] predicted the existence of new phases called twist grain boundary phases, or TGB phases, which have been experimentally discovered in chiral thermotropic liquid crystals by Goodby *et al.* in 1989 [5]. Several TGB phases as TGB_A and TGB_C have already been identified [6–8]. These phases are usually observed when cooling the isotropic phase and an example of typical phase diagram is:

Isotropic - Blue phases - Cholesteric - TGB_A - TGB_C - SmC^*.

A twist-grain boundary phase is characterized by both smectic ordering and twist. In the SmC^*, the director is tilted compared to the layer normal and the twist axis is parallel to the normal to the smectic layers whereas, at least in the TGB_A phase, the twist axis is parallel to the smectic layers. A continuous twist of the director in this direction is not compatible with smectic ordering. Renn and Lubensky have proposed a model where twist occurs between blocks or grains, of size l_b in the twist direction, with perfect smectic ordering (Fig. 2). This implies the existence of walls between the grains and the presence of an array of parallel screw dislocations in each wall. If the screw dislocations within the grain boundary are separated by a distance l_d, then the rotation angle (for small angles) of adjacent blocks is given by $\Delta\theta = \frac{d}{l_d}$ where d is the smectic period. The size of the blocks l_b is also linked to $\Delta\theta$ through the relation: $\frac{\Delta\theta}{2\pi} = \frac{l_b}{\lambda}$ where λ is the twist period. Therefore the two lengths l_b, the size of the blocks, and l_d, the distance between the screw dislocations, are related to λ and p *via*: $l_d l_b = \frac{d\lambda}{2\pi}$. A reasonable estimation of the size of the blocks can be obtained by taking: $l_d = l_b = l \cong \sqrt{\frac{d\lambda}{2\pi}}$. Thus the size of the blocks is intermediate between the smectic period (typically a few tenth of Å) and the pitch (a few thousands of Å).

Recently [9–11] a new sequence was discovered in a chiral material with the phase sequence (with decreasing temperature):

Isotropic - Blue phases - TGB phases - SmC^*.

Three blue phases have been observed in this compound: BP3 between 72.8 °C and 71.7 °C, BP2 between 71.7 °C and 71.3 °C, BP1 between 71.3 °C and 70.9 °C (upon cooling). The phase diagram has been established using calorimetric studies, optical microscopy. The pitch (0.2 μm) has been measured in the TGB_A phase using the Grandjean-Cano method. The textures of these blue phases are similar to those of classical blue phases and thus they have been labelled in the same way. However, in this phase diagram, there is no cholesteric phase between the blue phases and the TGB phases and thus, one can wonder whether the smectic order persists in the blue phases as it does in the TGB phases. If so, how can some translational smectic order be compatible with a three dimensional orientational order? Can twist grain boundaries build a three dimensional periodic phase? In other words, can a TGB blue phase exist? Such a question is not new: in [12], Onusseit and Stegemeyer observed a direct smectic to blue phase transition and in [13], Demikhov *et al.* have reported the observation of a new metastable blue phase called BP_S with smectic ordering. The latter blue phase is observed when the cholesteric range is small enough so that smectic ordering can persist. In our compound there is no cholesteric phase between the TGB phase and the blue phases are equilibrium phases.

In a previous paper [11], we reported X-ray scattering studies on one compound (called FH/FH/HH-18BTMHC). Such studies can give information only on the translational order. By analyzing the width of the diffusion ring obtained on a powder sample, we have shown that the smectic ordering persists in the blue phases, but with a correlation length smaller than in the TGB phase. The blocks are still present and their size remains constant. In these previous experiments, we used a Mettler hot stage, but the temperature control was not precise enough to clearly identify the three blue phases. In these new experiments, we have used a better controlled (up to 0.02 °C) hot stage. A X-ray capillary (1 mm diameter) has been filled with the same compound as the one used in [8] and placed inside this hot stage. X-ray scattering experiments have been done in LURE (Orsay, France) using synchrotron radiation. The wavelength ($\lambda_0 = 1.45$ Å) was selected using a Ge monochromator. The X-ray beam at the sample position probed a 0.5 mm^2 area and the beam was focused on the detector (imaging plate) situated at about 400 mm far from the sample. The resultant instrumental resolution measured on a parrafinic sample was HWMH $= 1.7 \times 10^{-3}$ $Å^{-1}$. To correlate the sample temperature (*i.e.* the temperature indicated by the hot stage controller) with the different phases observed by calorimetric studies, we have focused our attention

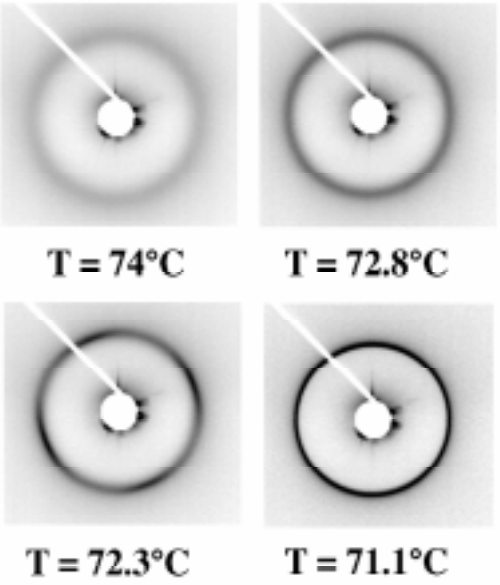

Fig. 3. X-ray patterns obtained on fixed samples obtained for different temperatures (exposure time: 15 min at 74 °C, 10 min at 72.8 °C and 72.3 °C, 5 min at 71.1 °C).

Table 1. BPII monodomain: dependence on temperature of the position Q_1(resp. Q_2) and the Full Width at Height Medium ΔQ_1 (resp. ΔQ_2) of the smectic peaks (resp. diffuse ring). The correlation length of the smectic order along the four-folf axes increases significantly with decreasing temperature.

T(°C)	Q_1 (Å^{-1})	ΔQ_1 (Å^{-1})	Q_2 (Å^{-1})	ΔQ_2 (Å^{-1})
72.5	0.1421	0.0090	0.1432	0.0110
72.4	0.1411	0.0063	0.1432	0.0110
72.3	0.1408	0.0063	0.1431	0.0105
72.1	0.1405	0.0055	0.1425	0.0105
71.9	0.1405	0.0053	0.1425	0.0105

on the TGB_A to TGB_C transition. At this transition, the smectic parameter decreases and the diameter of the diffuse ring therefore slightly increases. This variation has been detected at $T = 68.75$ °C in the X-ray scattering experiments whereas the $TGB_A - TGB_C$ transition is given at 68.5 °C by DSC measurements. Therefore a shift of temperature of at least 0.25 °C between the two experiments is expected. We started from the isotropic phase at higher temperature and decreased the temperature very slowly (less than 0.02 °C per 3 minutes).

Some X-ray patterns are shown in Figure 3. At high temperature (75 °C), one recovers a broad diffuse ring characteristic of short range smectic order. When the temperature is lowered below 74 °C, the width of the ring decreases and its maximum intensity increases. At 72.5 °C, the ring becomes anisotropic: sharper peaks coexist with the ring and exhibit a clear four-fold symmetry as shown by the angular profile of Figure 4. In the first capillary

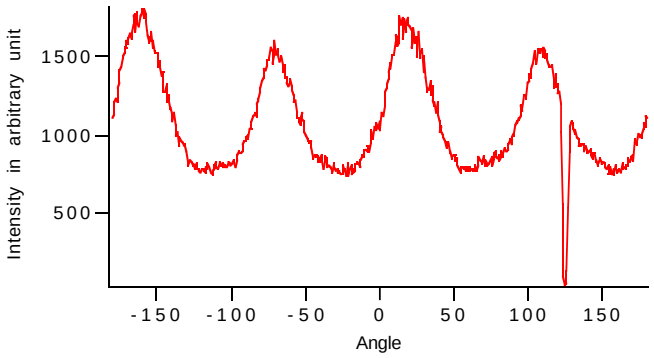

Fig. 4. Angular profile analysis over the whole diffuse ring showing the four-fold symmetry.

we have used, the same pattern with the same orientation has been detected when moving the capillary a few millimeters. We could reproduce the same pattern but with various orientations several times, either upon heating the same sample then cooling again, or when using another capillary filled with the same compound. This four-fold symmetrical pattern has been observed upon cooling up to 71.6 °C. This temperature range covers the BP2 and BP1 domain. Below 71.6 °C, one recovers the isotropic sharp ring observed in a powder-averaged TGB phase.

These observations clearly show that smectic order is present in these blue phases. It is important to notice that this is the first compound which offers stable blue phases with smectic order. Moreover the smectic order possesses the symmetry of the orientational order lattice. Indeed the orientational order in classical blue phases is cubic and the four-fold symmetry axis is linked to the blue phase lattice. In our experiment, although it was not possible to verify optically the size of the domains, the X-ray patterns prove that we have succeeded in growing large monodomains of blue phase filling nearly the whole capillary, and much larger than the beam size. Considering the phase diagram, we argue that the phase which gives such large monodomains is BP2. Indeed it is well known that, in classical blue phases, when both BP2 and BP1 exist, large domains of BP2 can be grown up but not of BP1. Monodomains of BP2 can be obtained by a very slow cooling of the isotropic phase, and our cooling rate was very low (0.01 °C per minute between exposure times). The four-fold symmetry pattern has been observed over a "large" range of temperature (0.9 °C), covering both BP2 and BP1 domains. But, in the lower temperature part of this domain, close to the transition towards the TGB_A phase, we have observed a very slow evolution with time (several hours) of the four-fold symmetrical pattern towards an isotropic ring pattern This can be interpreted as a very slow nucleation of BP1 inside a large monodomain of BP2. On the contrary, the transition towards the TGB_A phase occurs quickly. The blue phase monodomains are spontaneously well oriented compared to the X-ray beam since a four-fold axis is parallel to the beam. This perfect orientation of the monodomains can be explained by the existence of a temperature gradient along the beam direction since

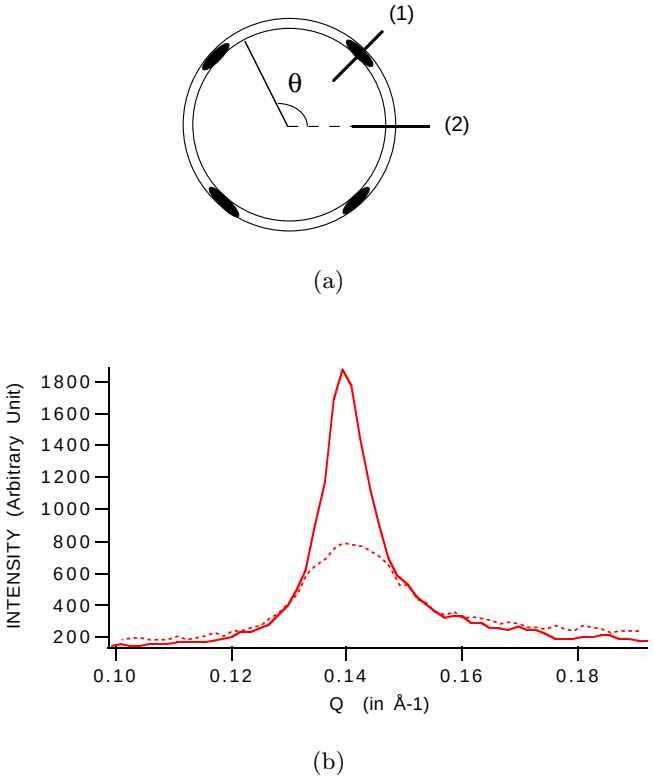

Fig. 5. (a) Different profiles: (1): longitudinal profile of a peak, (2): longitudinal profile of the diffuse part of the ring. (b) Longitudinal profiles of a peak (1) (full line) and of the diffuse part (2) of the ring (dotted line) for $T = 72.1$ °C.

the metallic oven which surrounds the capillary is closed by kapton windows in this direction. The preferred orientation of monodomains of classical BP2 phase is aligning a four-fold axis along the temperature gradient. This would then also be the case in BP2 with smectic ordering since we have obtained these four-fold symmetry patterns.

Growing a monodomain of BP2 thus reveals that the smectic order is not isotropic but possesses the symmetry of the blue phase lattice. Quantitative information can be obtained from the X-ray pattern on one monodomain: several profiles (Fig. 5a) have been fitted using a Gaussian function. At $T = 72.1$ °C, the longitudinal profile (Fig. 5b) of one of the four peaks give the maximum position at $Q_1 = 0.1405$ Å^{-1} with a FWHM (full width at medium height) equal to $\Delta Q_1 = 9 \times 10^{-3}$ Å^{-1}. The profile analyse of the "diffuse" part of the ring (Fig. 5b) gives a maximum at $Q_2 = 0.1425$ Å^{-1} and $\Delta Q_2 = 1.8 \times 10^{-2}$ Å^{-1}. The extension of the peaks perpendicularly to the smectic direction can be estimated to $\Delta Q_3 = 10^{-1}$ Å^{-1}. In all the patterns, we observe that Q_2 is always greater (about 1.5%) than Q_1. Compared to the TGB phase, the width of the four peaks is larger than the width of the ring observed with the TGB phase ($\Delta Q = 3 \times 10^{-3}$ Å^{-1}). As was already deduced from powder patterns, the smectic order coherence length is smaller in the blue phases than in the TGB phase, but much larger than in the isotropic phase. Moreover, in the blue phase, it can extend over longer range along given directions of the cubic double twist cell which are probably the four-fold symmetry axes.

A first approach to understand why smectic order is anisotropic can be proposed using the double twist model valid at low chirality. Indeed, it seems reasonable to assume that the smectic order can extend more easily along the direction of the double twist tube axes which, in BP2, are expected to lie along the four-fold axes. The smectic order range would therefore be different in the core of the double-twist tubes and in between the tubes. A local geometrical model combining double twist and smectic order was sketched by Gilli and Kamaye [14] and the first cubic model of these phases has been proposed by Kamien [15]. Nevertheless the pitch measured in the TGB phase is small and this double twist model is perhaps not the most appropriate to the system under study.

This experiment opens a new and perhaps wide field in the field of chiral liquid crystals. The blue phases we have observed are probably cubic but the pitch value is so low that we cannot use visible light to determine the symmetry of these blue phases *via* the Kossel diagram method. In this paper, we have presumed that they have the same symmetry group as classical blue phases, but this must be experimentally checked. The theoretical approach of these phases is still an open question: are they new phases or only blue phases with smectic fluctuations? Can the continuous model based on a tensorial field predict their thermodynamic stability and the smectic order anisotropy?

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