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LIQUID CRYSTALS EXHIBITING A DOUBLE GEOMETRICAL FRUSTRATION: THE SMECTIC BLUE PHASES

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Smectic blue phases (BP_{Sm}) are original mesophases of thermotropic liquid crystals, which exhibit both three-dimensional orientational order, such as classical blue phases, and smectic positional order. The BP_{Sm} phases appear to be the three-dimensional counterpart of the twist grain boundary (TGB) phases. The symmetries of these new phases have been determined by X-ray scattering and optical polarizing microscopy experiments.

I. INTRODUCTION

The effect of chirality on the structure of liquid crystals [1] is presently a subject of intense interest. For chiral mesogens, a spontaneous twist of the molecular orientation appears. But this local orientational order can induce frustration, sometimes, resulting in complex structures. These include the blue phases (BP) located between the cholesteric phase and the isotropic phase [2]. Two of these blue phases, BP1 and BP2, exhibit an unusual cubic symmetry in which the orientational (but not the positional) order is periodic and long range in three dimensions. The blue phase structure involves a twist of the director (average molecular orientation) extending not only in one direction, as in the cholesteric phase, but radially in two directions of space. This is called a double twisted structure. This double twisted structure cannot extend perfectly into three-dimensional space. Geometrical models of the BP1 and BP2 phases consist of cubic networks of double twist cylinders separated by defect lines. Thus blue phases can also be seen as a periodic array of disclination lines. A second

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example of a frustrated chiral system is the twist grain boundary (TGB) phases predicted by Renn and Lubensky [3] and experimentally observed by Goodby *et al.* in 1989 for TGB_A [4] and by Nguyen *et al.* in 1992 for TGB_C [5]. Since smectic layers cannot be continuously twisted, the TGB phases consist of blocks of pure smectic material (which can be either smectic-A for TGB_A or smectic-C for TGB_C) separated by parallel, regularly spaced grain boundaries, formed by a periodic array of screw dislocations. Such a dislocation arrangement allows helical twist. In TGB phases, as in blue phases, the frustration is relieved by the presence of defects.

II. EXPERIMENTS AND RESULTS

Recently new chiral liquid crystalline phases, called smectic blue phases (BP_{Sm}), have been discovered in a very narrow temperature range (Fig. 1), with the following phase sequence: TGB-BP_{Sm}1-BP_{Sm}2-BP_{Sm}3-Iso, without any intermediate cholesteric state between the BP_{Sm} and TGB phases [6–8]. Contrary to classical blue phases, these phases exhibit quasi-long-range smectic order (with a typical persistence length of about 60 nm) that has been studied by x-ray scattering [9,10]. Information on the symmetry of these new phases was then obtained in growing *in situ* BP_{Sm} monodomains using a low cooling rate (0.01°C per 10 min). X-ray scattering studies have then been performed providing information on the order at the molecular level. The scattering patterns obtained exhibit pairs of peaks indicating that the smectic order is not isotropic, but extends in given directions of the three-dimensional unit cell (Fig. 2).

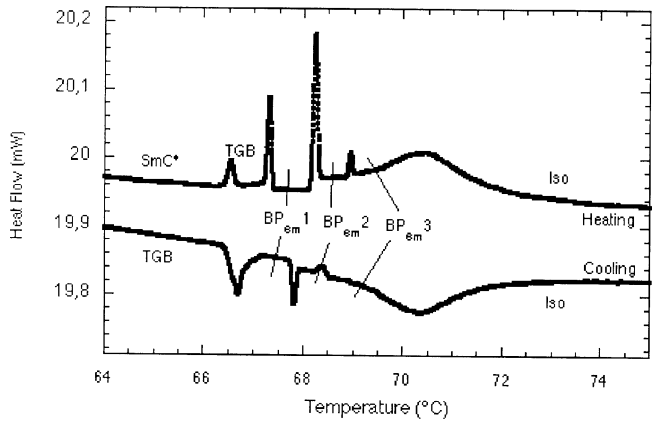

FIGURE 1 Typical differential scanning calorimetry thermograms of BP_{Sm} phases by heating and by cooling at 0.2°C/min (16FHFH-BTC1M8 compound [7]).

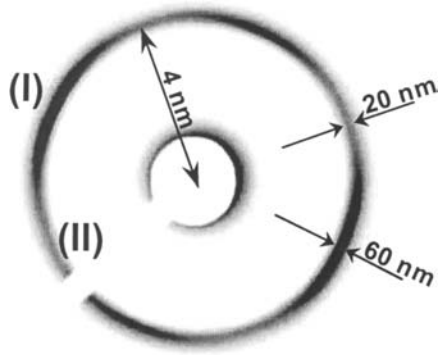

FIGURE 2 Experimental x-ray scattering patterns of $BP_{Sm}2$ monodomains. Parts of the ring with higher intensity are labeled (I) and parts with lower intensity are marked (II). The layer spacing and the correlation lengths of the smectic order are also indicated.

With the experimental setup we used in these x-ray scattering experiments, the molecules are contained in a glass capillary tube placed vertically inside a heating stage. Once the monodomain has been grown, the sample can be rotated around its main axis to explore the entire reciprocal space. Different scattering patterns are recorded on imaging plates by rotating the capillary by steps of 10° between two scans. The intensity along the smectic ring has been analyzed as a function of the angle with the vertical. By combining these various profiles, we can determine the directions of smectic order enhancement i.e., where the different smectic peaks are located and then deduce the angles between these peaks (Fig. 3). A monodomain of the $BP_{Sm}2$ phase exhibits four pairs of "Bragg peaks" (called (I) in Fig. 2) corresponding to four directions where the smectic order is enhanced: the first direction (T1) is perpendicular to three other directions (T2), (T3), and (T4), which are separated by angles of about 120° (Fig. 3) [11,12]. This result seems to indicate, within the precision of the experiment, a hexagonal or a trigonal symmetry of the $BP_{Sm}2$ phase. Note that due to the centrosymmetry of an x-ray diffraction setup, a sixfold axis cannot be distinguished from a threefold axis. This evidence of a non-cubic symmetry is consistent with the birefringence observed and measured in polarizing microscopy (Fig. 4) [12] and proves that smectic blue phases are really new phases, not merely classical blue phases with smectic fluctuations. The same kind of experiments on monodomains probing the smectic order by X-ray scattering has been performed on the $BP_{Sm}1$ phase, and the result is that this mesophase has a structure that depends on the phase sequence. Indeed,

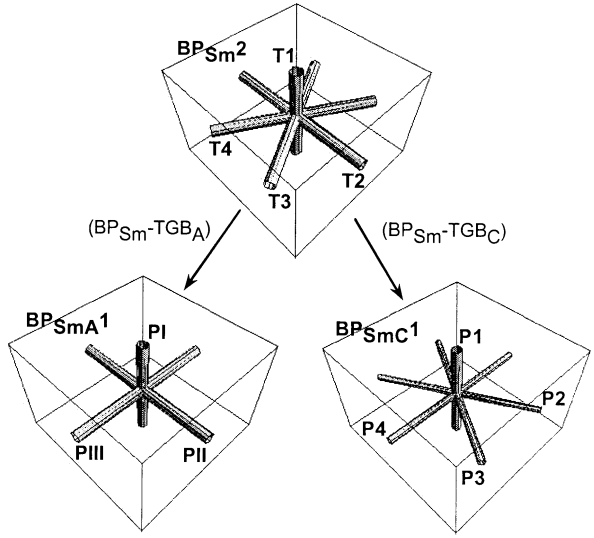

FIGURE 3 Geometrical figures indicating the directions along which the smectic order is enhanced, corresponding to the "Bragg peaks" (noted (I) in Figures 2 and 5), in monodomains of the $BP_{Sm}2$, $BP_{SmA}1$ and $BP_{SmC}1$ phases.

the $BP_{Sm}1$ phase exhibits a cubic symmetry in the case of a TGB_A-BP_{Sm} transition (Fig. 3) [12] and is labeled $BP_{SmA}1$; but the symmetry of the $BP_{Sm}1$ phase, then called $BP_{SmC}1$, is identical to the for $BP_{Sm}2$ phase for a TGB_C-BP_{Sm} phase sequence (Fig. 3) [16]. However, the structural anisotropy of the $BP_{SmC}1$ phase is much lower than in the $BP_{Sm}2$ phase. Only a very weak modulation of the "Bragg peaks" associated with a strong isotropic distribution of the smectic order between these peaks has been observed in the $BP_{SmC}1$ phase [16].

The first theoretical approach for combining smectic order with three-dimensional orientational order has been proposed by Kamien [17] with a model of smectic double twist cylinders combining smectic A order and twist not only in one direction as in TGB phases, but in two spatial directions (Fig. 5). Our experimental results can be interpreted in terms of this geometrical model by assuming that the regions where the smectic order easily extends, are the smectic double twist cylinders cores, corresponding to the "Bragg peaks". In the annular and concentric domains wrapping around this perfect smectic core, the smectic layers are distorted by the twist (Fig. 5). A geometrical model of the structure of smectic blue phases can be sketched by packing these smectic double twist cylinders according to the observed symmetries [11,12] as in Figure 6. However, this model is

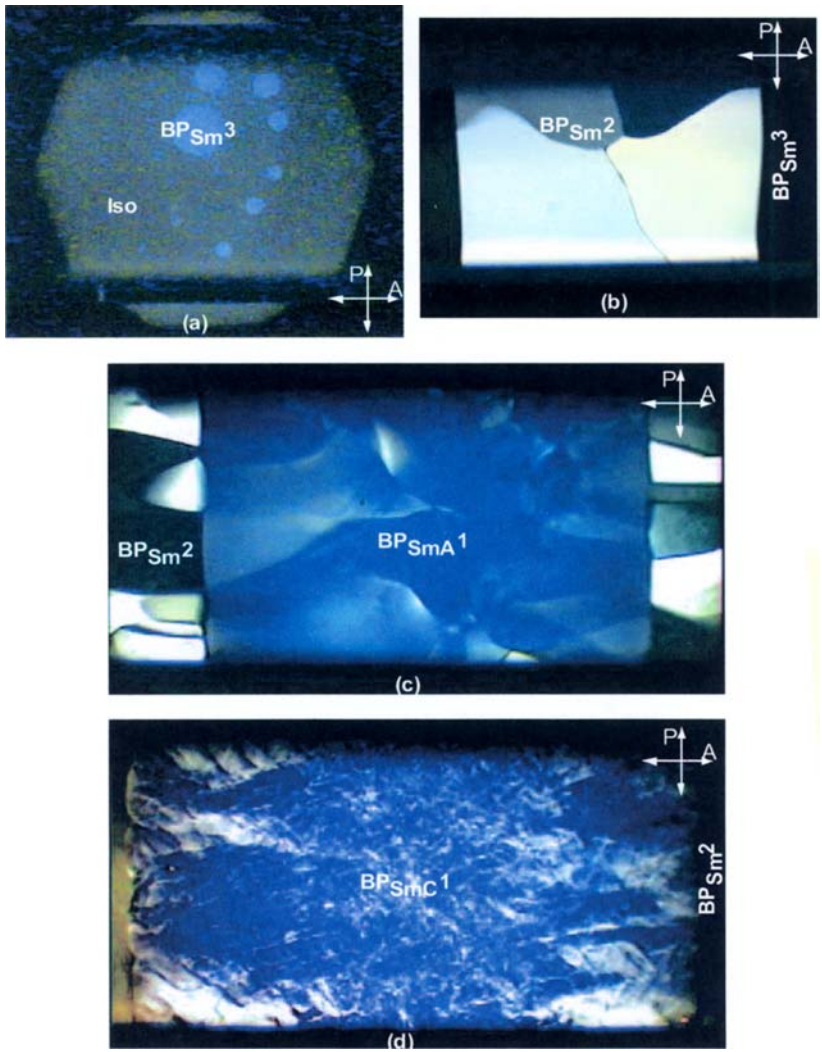

FIGURE 4 Typical textures of the smectic blue phases observed in transmission by polarizing microscopy. When cooling from the isotropic phase, two smectic blue phases with detectable textures occur in a narrow temperature span: $BP_{Sm}2$ and $BP_{Sm}1$. The third smectic blue phase ($BP_{Sm}3$) has, like the classical BP3 phase [13], an amorphous structure of the same macroscopic symmetry as that of the isotropic phase [14]. Contrary to the gray color of the $BP_{Sm}2$ phase coming from its birefringence, the blue color of the $BP_{SmA}1$, $BP_{SmC}1$, and $BP_{Sm}3$ phases originates from their optical activity; this can only be seen in absence of high birefringence. Moreover, the BP_{Sm} lattice parameter is in the near UV-range, and is therefore too small to generate selective reflections of visible light [15]. The thickness of the samples is 100 microns and their vertical size is 1 mm. (See COLOR PLATE IV)

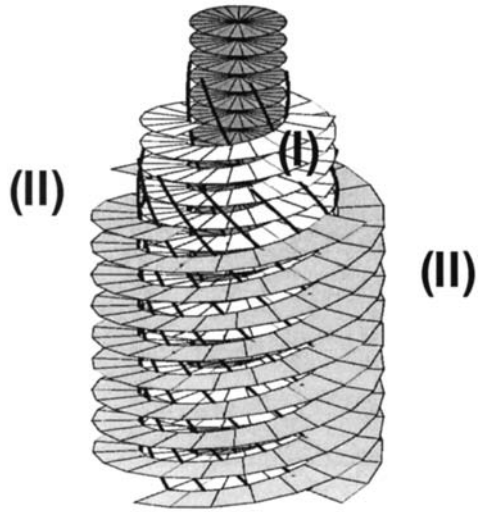

FIGURE 5 Geometrical model of a smectic double twist cylinder giving rise to the experimental smectic peaks (called region (I) in Figure 2). In this picture, the surfaces represent the smectic layers and the black lines wrapping around the cylinder represent the screw dislocations. These cylinders can be packed together according to the observed symmetry, as described for instance in Figure 6. However, smectic order persists between cylinders and gives rise to the continuous smectic ring (region labeled (II) in Figure 2). (Courtesy of Kamien).

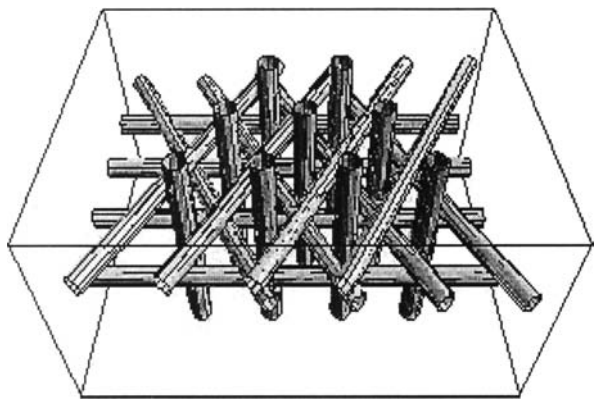

FIGURE 6 Geometrical model of an array of smectic tubes.

not fully compatible with the experimental results [11] and recently a new geometrical model has been suggested [18].

It is important to note here that the Bragg scattering is not due to the periodicity of the orientational order, which is at the length scale of the unit cell (200 nm, the dimension of the lattice constant) [15]. We detect the Fourier transform of some pattern in the unit cell linked to a periodicity of 4 nm and a correlation length of about 60 nm (Fig. 2), that is the smectic order. Therefore, these x-ray scattering experiments only provide indirect information on the symmetry of the orientational unit cell. In particular, the value of the BP_{Sm} lattice parameter in the UV range (200 nm) prevents study by optical scattering of visible light (Kossel diagram technique), which is commonly used to determine the symmetry of classical blue phases [19]. However, the symmetry of the orientational unit cell can be determined by growing large faceted monocrystals of the $BP_{Sm}2$ phase.

Nucleation and growth of single faceted crystals of BP_{Sm} phases is a real experimental challenge. Using a low cooling rate (0.01°C per 10 min) to produce large monodomains gives rise to the birefringent "platelet" texture (Fig. 4) that quickly fills the entire experimental cell. However, by using the metastability of the $BP_{Sm}3$ phase occurring in some compounds (as FH/FH/HH-14BTMHC), we succeeded in producing large faceted crystallites of the $BP_{Sm}2$ phase [20]. This kind of experiment is difficult because it is performed out of equilibrium in a very narrow temperature range (0.15°C on heating). Different crystalline shapes have been listed, and two examples reported in Figures 7 and 8. These large monocrystals, between 100 and 150 μm in size and with well-defined facets, have been observed floating in the bulk in coexistence with the isotropic supercooled $BP_{Sm}3$ phase by transmission between crossed polarizers. On each picture, the white

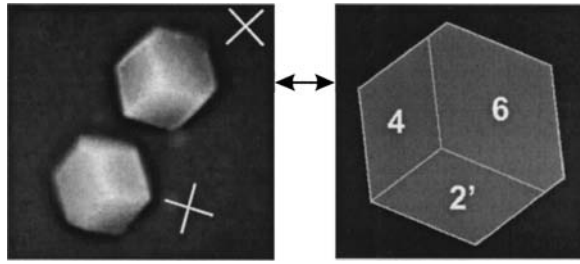

FIGURE 7 Experimental and schematic view of $BP_{Sm}2$ monocrystals having almost the same orientation floating in the isotropic supercooled $BP_{Sm}3$ and observed along a pseudothreefold axis in transmission between crossed polarizers. The white cross represents the projection (or the normal direction) of the optical axis in the observation plane.

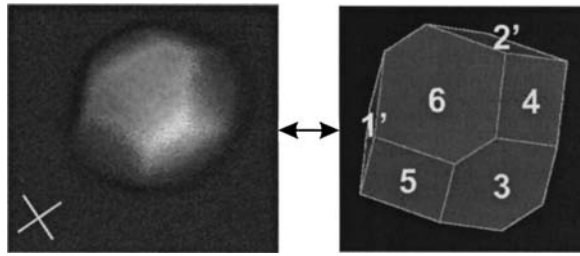

FIGURE 8 Faceted monodomain of the $BP_{Sm}2$ phase exhibiting four large and two small facets, as schematically shown in the corresponding picture.

cross represents the positions of the polarizers needed to assure *extinction* of the birefringent domains, i.e., it represents the projection (or the normal direction) of the optical axis in the observation plane. This provides additional information to the faceting, due to the non-cubic symmetry of the $BP_{Sm}2$ phase. The three-dimensional polyhedral habit of the $BP_{Sm}2$ monocrystals seems close to a rhombic dodecahedron, which has already been observed for classical cubic blue phase [21]. Nevertheless, the experimental crystallites cannot reproduce a perfect rhombic dodecahedron because their birefringence is incompatible with a cubic structure. Thus, the data of the birefringent faceted monodomains suggest that the crystal habit of the $BP_{Sm}2$ phase is formed by a structure close to a dodecahedron, whose cubic symmetry is however broken.

III. DISCUSSION

We first attempted to form a consistent interpretation of these optical observations of faceted monodomains with our x-ray scattering results by, for instance, distorting a rhombic dodecahedron along one of its threefold axis. However, all attempts to find a polyhedral habit with a three or sixfold axis describing both the symmetries of the optical and of the x-ray scattering experiments have failed. Therefore, we must reinterpret our experimental data. Some questions arise when the transition between the $BP_{Sm}2$ and $BP_{SmA}1$ phases is analyzed in more detail. The assumed sixfold axis of the $BP_{Sm}2$ phase becomes of a fourfold axis in the $BP_{SmA}1$ phase (Fig. 3). But why do we then observe no degeneracy in $BP_{SmA}1$? Or why is one direction of the enhancement of the smectic order privileged by remaining unchanged, whereas the two others merge? Indeed, three equivalent, possibilities should exist to transform a hexagonal $BP_{Sm}2$ phase into a cubic $BP_{SmA}1$ phase. This assumption is substantiated by the fact

that in classical blue phases, a degeneracy between a fourfold axis of the BP2 phase and a twofold axis in the BP1 phase exists, which is illustrated under a polarizing microscope by "cross hatching" in the BP1 texture [22]. However, nothing similar has been observed in the smectic blue phases, either in optical experiments (Fig. 4) [7] or by x-ray scattering (Fig. 3) [12]. It means that one of the directions of the smectic order enhancement, (T2), is slightly different from the two other directions, (T3) and (T4) (Fig. 3). This suggests that the assumed sixfold axis of $BP_{Sm}2$ is only a twofold axis: the symmetry of the $BP_{Sm}2$ phase is then *orthorhombic* [20]. Therefore, the crystal habit we proposed is formed by a dodecahedral structure made from an orthorhombic unit cell. In this way, we succeed in reproducing all the birefringent shapes observed for the $BP_{Sm}2$ crystallites and in explaining the nondegeneracy seen in the transition to the $BP_{SmA}1$ phase. We have drawn a polyhedral shape limited by four (100) and eight (111) facets and made from the orthorhombic unit cell (**a**, **b**, **c**), where **a**, **b** and **c** are three perpendicular vectors of different length. The values of a, b, and c have been adjusted to reproduce all the experimental crystallites and especially the angles of the facets observed on the crystallites (Fig. 9) [20] which are also correlated with the angles between the directions of the smectic order enhancements. The structure can be considered as mainly uniaxial by locating the optical axis parallel to one of the basis vector, i.e. perpendicular to the facet (100) labelled 3

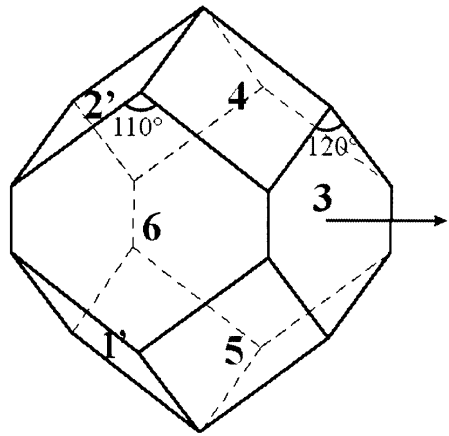

FIGURE 9 Orthorhombic dodecahedral crystal habit formed by four (100) facets (labeled 3 and 6) and eight (111) facets (labeled 1, 2, 4, and 5) accounting for the experimentally observed monocrystals of the $BP_{Sm}2$ phase. For this model, the parameters of the unit cell are a = 1, b = 0.82, and c = 0.58 and the optical axis is located perpendicular to the normal of the facet labeled 3.

in Figure 9 (Note that the orientation of the optical axes of biaxial crystals depends, in fact, on the values of the refractive indices). The projections of the optical axis associated with each experimental crystallite are thus consistent with this suggested orthorhombic structure.

IV. CONCLUSION

As classical blue phases can be seen as the three-dimensional counterpart of the cholesteric phase, smectic blue phases can be pictured as the extension of 3D of the TGB phase. Indeed, contrary to the cholesteric and to the blue phases where the twist occurs at the "molecular level", the twist occurs at the scale of the smectic slabs for both TGB and smectic blue phases. Thus smectic blue phases are original physical systems of condensed matter with a *double frustration*: the extension of chirality in three spatial dimensions like the classical blue phases, and helical twist competing with smectic order, as in the TGB phases. The experimental results reported in this paper provide a consistent description of the smectic blue phases *in terms of symmetry* at two different length scales (smectic order and unit cell); bowever, a complete physical model of the BP_{sm} phases has still to be proposed. Both theoretical and experimental investigations, such as the determination of the space groups, should be developed to improve our understanding of these new liquid crystalline phases.

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