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Faceted monodomains of liquid crystal smectic blue phases

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Smectic blue phases (BP_{Sm}) are 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 as the three-dimensional counterpart of the twist grain boundary phases. By growing large faceted monocrystals of BP_{Sm} phase, we provide, for the first time at the length scale of the lattice parameter, information on the symmetry of the orientational unit cell. This study leads us to suggest an orthorhombic structure, contrary to the previous results obtained by x-ray scattering at the length scale of the smectic order.

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Liquid crystals are phases of condensed matter in which the molecules possess long-range positional or orientational order along some directions of space even though the molecules undergo diffusion as in a simple isotropic liquid along at least one of the other directions [1]. 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 sometimes 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 example of a frustrated chiral system is the twist grain boundary (TGB) phase 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.

Recently new chiral phases, called smectic blue phases (BP_{Sm}), have been discovered in 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]. Contrary to classical blue phases, these phases exhibit quasi-long-range smectic order that has been studied by x-ray scattering. The smectic order seems to be correlated with the orientational three-dimensional order of the unit cell and is, therefore, enhanced in some directions, thus exhibiting particular symmetries: the $BP_{Sm}2$ phase then appears hexagonal (Fig. 1) [7] whereas the $BP_{Sm}1$ phase has a structure that depends on the phase sequence. The $BP_{Sm}1$ phase exhibits a cubic symmetry in the case of a TGB_A-BP_{Sm} transition (Fig. 1) [8] and is labeled $BP_{Sm(A)}1$; but the symmetry of the $BP_{Sm}1$ phase, then called $BP_{Sm(C)}1$, is hexagonal for a TGB_C-BP_{Sm} phase sequence [9]. The $BP_{Sm}3$ phase has, like the classical BP3 phase [10], an amorphous structure of the same macroscopic symmetry as that of the isotropic phase [11]. Up to now, the structural investigations of the smectic blue phases have been mainly carried out on monodomains by x-ray scattering, probing the structure at the length scale of the smectic order (with a typical layer spacing $d=4$ nm). This only provides indirect information on the symmetry of the orientational unit cell, which is at a much larger scale (200 nm, the dimension of the lattice constant) [12]. Indeed, this value of the BP_{Sm} lattice parameter in the UV range prevents study by optical scattering of visible light (Kossel diagram technique), which is commonly used to determine the symmetry of classical blue phases [13]. In this paper, we give, we believe for the first time, at the length scale of the lattice parameter, direct information on the symmetry of the

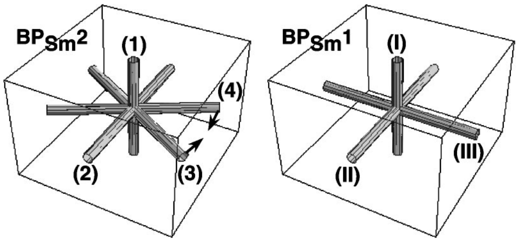

FIG. 1. Geometrical figures indicating the directions where the smectic order is enhanced, corresponding to the "Bragg peaks," for the $BP_{Sm}2$ and cubic $BP_{Sm(A)}1$ monodomains probed by x-ray scattering. The arrows show their evolution during the transition between the two smectic blue phases (from Ref. [8]).

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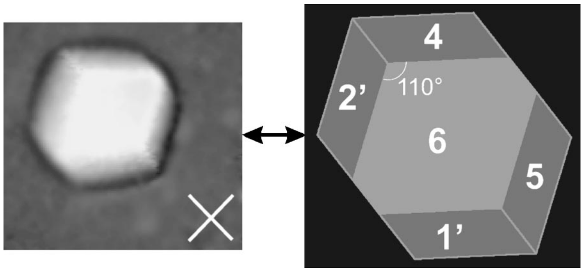

FIG. 2. Experimental and schematic view of a $\mathrm{BP}_{\mathrm{Sm}}2$ monocrystal floating in the supercooled $\mathrm{BP}_{\mathrm{Sm}}3$ and observed along a twofold axis in transmission between crossed polarizers. The white cross represents the projection (or the normal direction) of the optical axis in the observation plane.

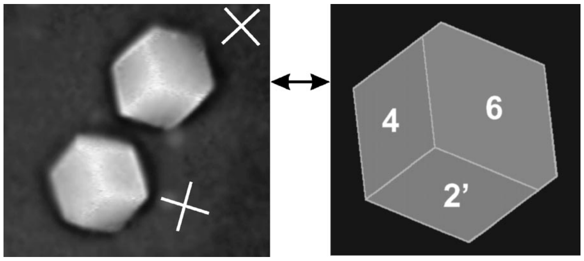

FIG. 4. Observation of two $\mathrm{BP}_{\mathrm{Sm}}2$ crystallites having almost the same orientation. They are seen along a pseudothreefold axis.

orientational unit cell by growing large faceted monocrystals of the $\mathrm{BP}_{\mathrm{Sm}}2$ phase. The faceting and birefringence of the $\mathrm{BP}_{\mathrm{Sm}}2$ monodomains contradict the results obtained by x-ray scattering at the length scale of the smectic order, and therefore the symmetry of the smectic blue phases will be discussed in the light of these new elements.

The nucleation and growth of single faceted crystals of the $\mathrm{BP}_{\mathrm{Sm}}$ phase to determine the symmetry of the orientational unit cell is a real experimental challenge. The classical method that uses a low cooling rate ($0.01\,^{\circ}\mathrm{C}$ per 10 min) to produce large monodomains gives rise to the birefringent ‘‘platelet’’ texture [14] that quickly fills whole of the experimental cell. In fact, faceted crystallites appear only if they are in coexistence with another phase (especially with an isotropic phase to avoid epitaxial correlations). This condition has been fulfilled by using the metastability of the $\mathrm{BP}_{\mathrm{Sm}}3$ phase with the molecules $n=13$ and $n=14$ of the series FH/FH/HH-*n*BTMHC, where *n* indicates the aliphatic chain length [6]. For these compounds, the $\mathrm{BP}_{\mathrm{Sm}}3$ can be supercooled from the isotropic phase using fast cooling (typically $\geqslant 0.5\,^{\circ}\mathrm{C/min}$), which has already been shown to produce single $\mathrm{BP}_{\mathrm{Sm}(A)}1$ monodomains [8]. Thus, the nucleation and growth of the single faceted $\mathrm{BP}_{\mathrm{Sm}}2$ monocrystals can be initiated by very slowly *heating* the supercooled $\mathrm{BP}_{\mathrm{Sm}}3$ phase. This kind of experiment is difficult because it is performed out of equilibrium in a very narrow temperature range ($0.15\,^{\circ}\mathrm{C}$) on heating and in a weak temperature gradient. The temperature must be increased enough to obtain large crystallites (between 100 and 150 μm in size), but not too much, otherwise the monodomains begin to melt. Four different crystalline shapes have been listed, and they are reported in Figs. 2–6. These large monocrystals with well-defined facets have been observed floating in the bulk in coexistence with the isotropic supercooled $\mathrm{BP}_{\mathrm{Sm}}3$ phase by transmission between crossed polarizers. On each picture, the white 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 compared to the faceting, due to the noncubic symmetry of the $\mathrm{BP}_{\mathrm{Sm}}2$ phase. The three-dimensional polyhedral habit of the $\mathrm{BP}_{\mathrm{Sm}}2$ monocrystals, however, seems close to a rhombic dodecahedron (Fig. 7) which is already observed for classical cubic blue phase [15]. In a first rough approximation, Figs. 2, 4, and 5 could be seen along, respectively, the twofold, threefold, and fourfold axes of a rhombic dodecahedron (corresponding to the directions OC, OB, and OA in Fig. 7). Nevertheless, the experimental crystallites cannot reproduce a perfect rhombic dodecahedron because their birefringence is incompatible with a cubic structure. It must be noted that the growth conditions certainly influence the size of the facets and the shapes of the monocrystals, as it is illustrated, for instance, by Figs. 2 and 3, but do not change the symmetry and especially the angles of the facets. Thus, the data of the birefringent faceted monodomains suggest that the crystal habit of the $\mathrm{BP}_{\mathrm{Sm}}2$ phase is formed by a structure close to a dodecahedron, whose cubic symmetry is, however, broken.

We first attempted to interpret these optical observations of faceted monodomains in the ‘‘most obvious’’ manner consistent with our previous x-ray scattering results, by distorting a rhombic dodecahedron habit along a threefold axis (OB in Fig. 7). In the x-ray scattering experiments probing

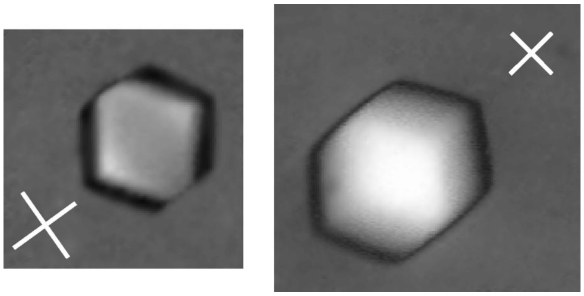

FIG. 3. Two other examples of the $\mathrm{BP}_{\mathrm{Sm}}2$ monodomains observed along a twofold axis. An apex angle of about 110° can also be found as in Fig. 2.

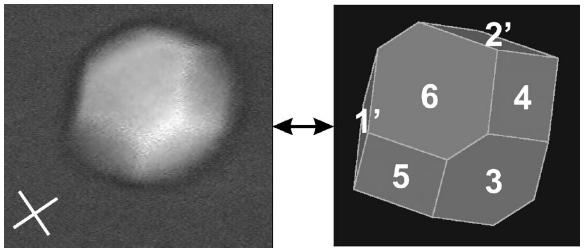

FIG. 5. Faceted monodomain of the $\mathrm{BP}_{\mathrm{Sm}}2$ phase exhibiting four large and two small facets, as schematically shown in the corresponding pictures.

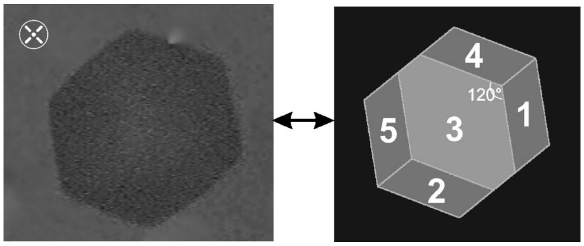

FIG. 6. Crystal shape of the BP$_{\mathrm{Sm}}$2 phase, which stays dark for all the positions of the crossed polarizers. The optical axis is then perpendicular to the plane of the figure. An angle of about 120° is observed in this picture.

the BP$_{\mathrm{Sm}}$ structure at the scale of the smectic order, the BP$_{\mathrm{Sm}}$2 monodomain exhibits four pairs of "Bragg peaks" corresponding to four directions where the smectic order is enhanced; the first direction (1) is perpendicular to three other directions (2), (3), and (4), which are separated by angles of about 120° (Fig. 1) [8]. Note that due to the centrosymmetry of an x-ray diffraction experiment, a sixfold axis cannot be distinguished from a threefold axis. However, the correspondence between a dodecahedron distorted along a threefold axis cannot account for the optical data, as is shown, for instance, in Fig. 5 where the projection of the optical axis (which must also be the distortion axis of the rhombic dodecahedron) should then be rotated by 45° to be consistent with the suggested structure. Moreover, up to now, all the other attempts to find a polyhedral habit with a threefold or sixfold axis describing both the symmetries of the optical and of the x-ray scattering experiments have failed.

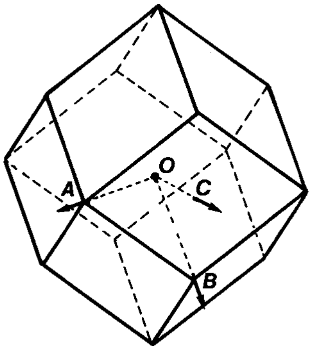

FIG. 7. Perfect rhombic dodecahedron limited by 12 (110) facets. OA, OB, and OC are the directions of the fourfold, threefold, and twofold axes, respectively.

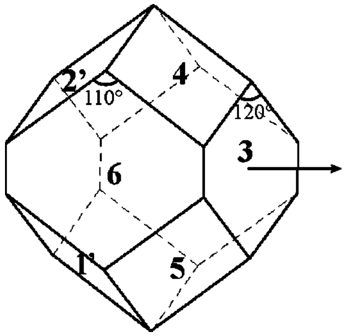

FIG. 8. Orthorhombic dodecahedral crystal habit formed by four (100) facets (labeled 3 and 6) and eight (111) facets (labeled 1, 2, 4, and 5) accounting to the experimentally observed monocrystals of the BP$_{\mathrm{Sm}}$2 phase. For this model, the parameters of the unit cell are $a=1$, $b=0.82$, and $c=0.58$ and the optical axis is located perpendicular to the normal of the facet labeled 3.

Therefore, we must reinterpret our experimental data. Some questions arise when the transition between the BP$_{\mathrm{Sm}}$2 phase and the BP$_{\mathrm{Sm}(A)}$1 phase is analyzed in more detail. The assumed sixfold axis of the BP$_{\mathrm{Sm}}$2 phase becomes a fourfold axis in BP$_{\mathrm{Sm}(A)}$1 phase (Fig. 1). But why do we then observe no degeneracy in BP$_{\mathrm{Sm}(A)}$1? Or why is one direction of the enhancement of the smectic order privileged by remaining unchanged, whereas the two others merge [16]? Indeed, three equivalent possibilities should exist to transform a hexagonal BP$_{\mathrm{Sm}}$2 phase into a cubic BP$_{\mathrm{Sm}(A)}$1 phase (or four possibilities in the case of a threefold axis for the BP$_{\mathrm{Sm}}$2 phase). This assumption is substantiated by the fact that in classical blue phases, a degeneracy between a fourfold axis of the BP2 phase and a twofold axis in the BP1 phase exists, which is illustrated under the polarizing microscope by "cross hatching" in the BP1 texture [17]. But nothing similar has been observed in the smectic blue phases, either by optical experiments [14] or by x-ray scattering [8]. It means that one of the directions of the smectic order enhancement, (2), is slightly different from the two other directions, (3) and (4) (Fig. 1). This suggests that the assumed sixfold axis of the BP$_{\mathrm{Sm}}$2 phase is only a twofold axis: the symmetry of the BP$_{\mathrm{Sm}}$2 phase is then *orthorhombic*. Therefore, the crystal habit we propose is formed by a dodecahedral structure made from an orthorhombic unit cell. In this way, we succeed in reproducing all the birefringent shapes observed for the BP$_{\mathrm{Sm}}$2 crystallites and in explaining the nondegeneracy seen in the transition to the BP$_{\mathrm{Sm}(A)}$1 phase. We have drawn a polyhedral shape limited by four (100) and eight (111) facets and made from the orthorhombic unit cell $(\mathbf{a},\mathbf{b},\mathbf{c})$, where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ 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 in Figs. 2, 3, and 6. The result is reported in Fig. 8, where $a=1$, $b=0.82$, and $c=0.58$. Each experimental picture can then find a correspondence to the crystal shape of Fig. 8: the schematic figures with the labeled facets reported in Figs. 2–6 are all issued from Fig. 8, but are seen from different points of view. 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 plane of Fig. 6 and to the facet (100) labeled 3 in Fig. 8 (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. Indeed, Figs. 2 and 3 almost represent the same faceting as that of Fig. 6, but the optical axis in this case is in the observation plane. Figure 4 corresponds to a view rotated, comparing with Fig. 2, by about 30° around the optical axis. Figure 5 is the experimental picture where the greatest number of facets (six) has been found, and provides the most general view of the BP$_{\mathrm{Sm}}$2 faceting. The resolution of the experimental pictures is not high enough to measure with accuracy the angles of the different facets. Nevertheless, the angles of 120° between three directions of smectic order enhancements (Fig. 1) can also be found in Fig. 6; whereas Figs. 2 and 3 show an apex angle of about 110°. These two angles are also reproduced by the orthorhombic model described in Fig. 8, where the adjusted parameters $c/a = 0.58 \approx 1/\sqrt{3}$ and $b/a = 0.82$ correspond to the angles of 120° and 110°, respectively.

Thus the smectic blue phases are original physical systems of condensed matter with a *double frustration*: the extension of chirality in the three spatial dimensions like the classical blue phases, and the helical twist competing with smectic order, as in the TGB phases. The $\mathrm{BP_{Sm}}$ phases can, therefore, be seen as the three-dimensional counterpart of the TGB phases. In this paper, we report the orientational symmetry of the $\mathrm{BP_{Sm}}2$ phase, which is orthorhombic. We thus provide a consistent description of the smectic blue phases *in terms of symmetry* at two different length scales (smectic order and unit cell); however, the physical models have 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 phases, and the main unsolved question is probably the theoretical origin of the orthorhombic symmetry observed in the smectic blue phases. Indeed, why does the smectic order break the cubic symmetry of the blue phases?

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