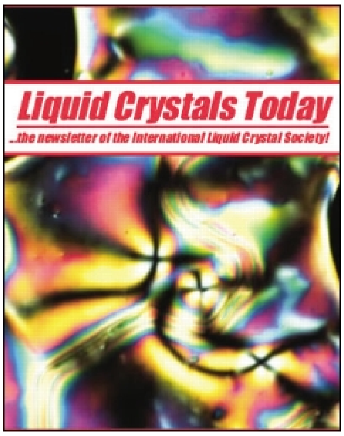

Liquid Crystals Today
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713681230

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To cite this Article Grelet, Eric(2003) 'Liquid-crystalline smectic blue phases', Liquid Crystals Today, 12: 4, 1 — 5
To link to this Article: DOI: 10.1080/14645180310001632636
URL: http://dx.doi.org/10.1080/14645180310001632636

LIQUID CRYSTALS TODAY, DECEMBER 2003, VOL. 12, NO. 4, 1–5

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Liquid-crystalline smectic blue phases

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(*Accepted 7 October 2003*)

Smectic blue phases (BP_{Sm}) are new mesophases of thermotropic liquid crystals, which exhibit a *double geometrical 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 existence of a quasi-long range smectic order in BP_{Sm} phases breaks the cubic symmetry of classical blue phases. The symmetries of these new phases have been determined by X-ray scattering and optical polarizing microscopy experiments.

1. Introduction

The discovery of new structures in liquid crystals turns out to be often associated with an increase of complexity. Smectic blue phases are the most recent example combining the properties of two types of frustrated mesophases: twist grain boundary (TGB) phases and blue phases (BP). Blue phases, which were the first reported liquid crystals [1], show an unusual cubic symmetry in which the orientational order is periodic and long range in three dimensions [2]. Thus, blue phases are exemplary *liquid crystals*: BPs exhibit three-dimensional cubic faceted monodomains as in a crystal [3], but the order at the origin of the cubic symmetry is not a positional order, but an orientational one. The naming of these phases as *blue* is due to their Bragg reflections in the visible range (and therefore also in the blue wavelengths) indicating a spatially periodic structure with lattice parameters of several hundreds nm. Saupe was the first to suggest a chiral cubic structure from the optical activity of the BPs and their lack of birefringence ($\Delta n = 0$) [4]. The structure of the BPs involves a radial twist of the director called a double cylinder. However, this double twisted structure cannot extend perfectly into three-dimensional space. Geometrical models of blue phases therefore consist of cubic networks of double twist cylinders separated by disclination lines (figure 1).

Twist grain boundary (TGB) phases represent a second example of a frustrated chiral system. TGB phases were predicted by Renn and Lubensky [6] and were experimentally observed by Goodby *et al.* in 1989 for TGB_A [7] and by Nguyen *et al.* in 1992 for TGB_C [8]. 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 (figure 2). Such a dislocation arrangement allows helical twist.

Thus, in TGB phases, as in blue phases, the frustration is relieved by the presence of defects.

In the last few years the Bordeaux group has synthesized new chiral liquid crystals exhibiting mesophases

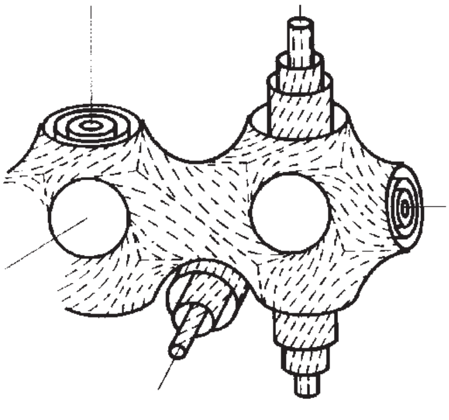

Figure 1. Geometrical model of blue phases involving double twist cylinders and a network of disclination lines [5].

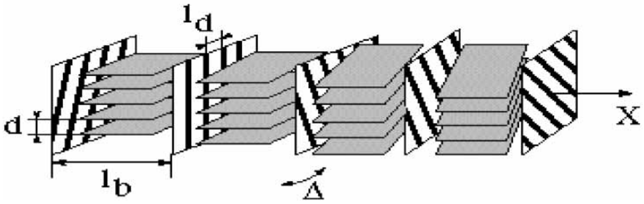

Figure 2. Sketch of the helical structure of the TGB_A phase [6].

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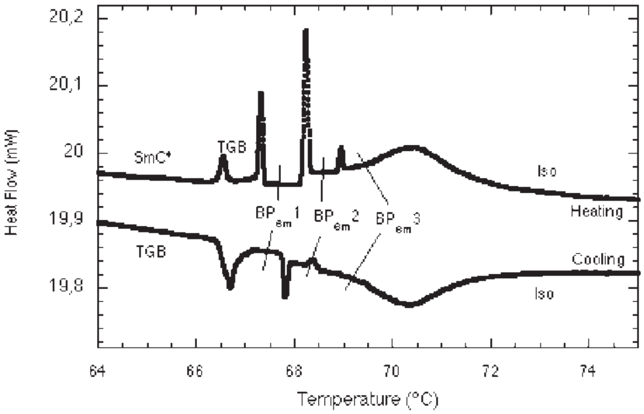

Figure 3. Typical differential scanning calorimetry thermograms in the temperature range of smectic blue phases performed by heating and by cooling at 0.2°C/min [10].

called smectic blue phases (BP_{Sm}), which appear in a very narrow temperature range (figure 3) 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 [9–11]. The evidence of a new phase sequence has stimulated further experimental studies by the Orsay group mainly based on optical techniques (polarizing microscopy and optical activity measurements) and on X-ray scattering from BP_{Sm} monodomains.

2. The discovery of new mesophases

2.1. *Optical experiments*

One of the first experiments used to characterize mesophases is to observe their texture under the polarizing microscope. The results of such an experiment are reported in figures 4 and 5 providing some important information on the BP_{Sm} structure.

When cooling from the isotropic phase, two smectic blue phases with detectable textures occur in a narrow temperature span (about 1°C): $BP_{Sm}2$ and $BP_{Sm}1$. The third smectic blue phase ($BP_{Sm}3$) has, like the classical BP3 phase [12], an amorphous structure of the same macroscopic symmetry as the isotropic phase [13]. As depicted in figure 4, a mosaic texture composed of grey platelets is observed for $BP_{Sm}2$. This texture looks at first sight very similar to the one of classical blue phases; however, what is the origin of the lack of bright colours observed in smectic blue phases? In BPs, the mosaic texture comes from selective Bragg reflections at visible wavelengths from domains with different orientations. In $BP_{Sm}2$ the existence of modulation in colours from light grey to black is due to a completely different optical feature: birefringence [14]. $BP_{Sm}2$ phase is thus optically anisotropic and the evidence of a non-cubic symmetry proves that smectic blue phases are really new mesophases, not merely atypical blue phases.

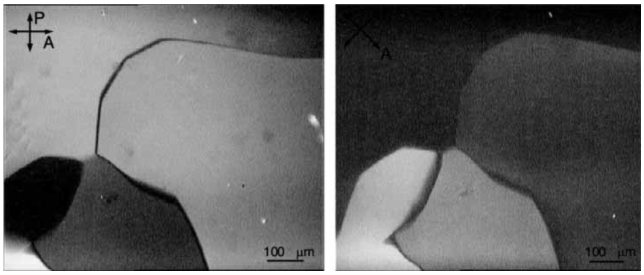

Figure 4. Birefringence of the $BP_{Sm}2$ phase observed in transmission by polarizing microscopy. The thickness of the sample is 100 microns.

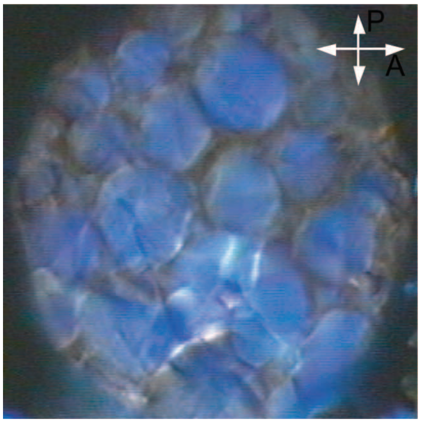

Figure 5. $BP_{Sm}1$ phase observed in transmission by polarizing microscopy. $BP_{Sm}1$ phase is optically isotropic, which shows a cubic symmetry, and the blue colour is due to its optical activity. The sample is 100 microns thick.

In contrast to the grey colour of the $BP_{Sm}2$ phase, the blue colour of the $BP_{Sm}1$ phase shown in figure 5 originates from its optical activity; this can only be seen in the absence of high birefringence [15]. Moreover, in smectic blue phases the lattice parameter is in the near UV-range, and is therefore too small to generate selective reflections of visible light as in the BPs [16]. The BP_{Sm} lattice parameter has been measured by studying the wavelength dependence of the optical activity in $BP_{Sm}1$. A divergence of the optical activity is expected close to the selective reflection, λ_0, as has already been seen in the cholesteric phase and in the classical blue phases. The data for the 14BTMHC compound are plotted in figure 6, showing a rise of the optical activity when the wavelength decreases. A fit allows an estimate of the BP_{Sm} lattice parameter: $P = 0.21\,\mu m$ with $\lambda_0 = 320\,nm$ and $n = 1.5$.

The value of the BP_{Sm} lattice parameter in the UV range prevents study by optical scattering of visible

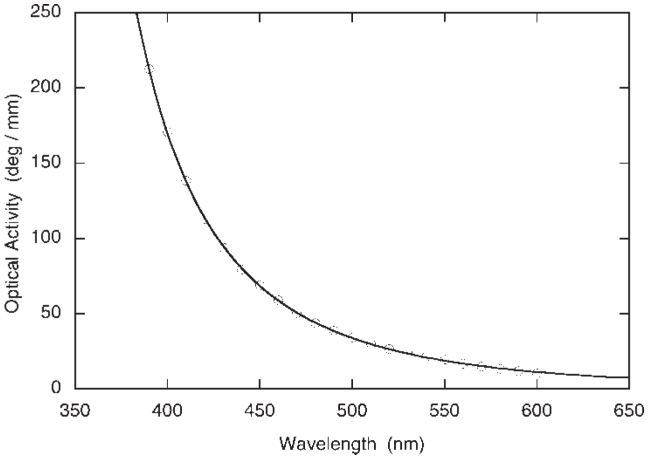

Figure 6. Optical activity as a function of wavelength for $BP_{SmA}1$ (14BTMHC; $T=72.8°C$). The solid line is a fit to $\rho=(C/\lambda)/[\lambda^2(\lambda_0^2-\lambda^2)]$ where ρ is the optical activity, $\lambda=2\pi/k$ is the wavelength of the light (k being the wavevector of the light), and $\lambda_0=nP$ (P being the lattice parameter and n the average refractive index) [16].

light (Kossel diagram technique), which has been used to determine the symmetry of classical blue phases [17]. Therefore, other ways had to be found to study the orientational symmetries of smectic blue phases, such as the growth of faceted crystallites.

The nucleation and growth of such single faceted crystals of BP_{Sm} phases represent 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 (figure 4) that quickly fills the entire experimental cell. However, by using the metastability of the $BP_{Sm}3$ phase occurring in some compounds, we succeeded in producing large faceted crystallites of the $BP_{Sm}2$ phase [18]. This kind of experiment is difficult because it is performed out of equilibrium in a very narrow temperature range (0.15°C). Different crystalline shapes have been listed, as reported in figures 7 to 10. 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. In each picture, the white cross represents the positions of the crossed polarizers needed to ensure *extinction* of the birefringent domains, i.e. it represents the projection (or the normal direction) of the optical axis in the observation plane. The three-dimensional polyhedral habit of the $BP_{Sm}2$ monocrystals shown in figures 7 to 10 seems close to a rhombic dodecahedron, which has already been observed for classical cubic blue phase [3]. Nevertheless, the experimental crystallites cannot reproduce a perfect rhombic dodecahedron

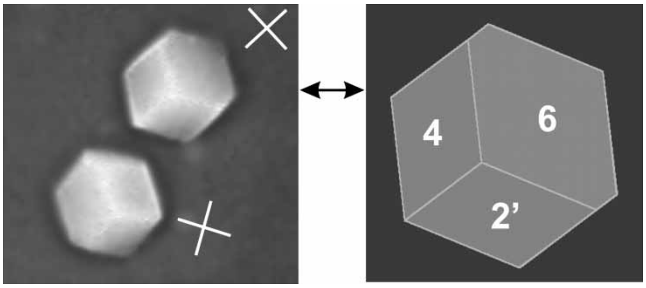

Figure 7. Experimental and schematic view of $BP_{Sm}2$ monocrystals having almost the same orientation floating in the isotropic supercooled $BP_{Sm}3$ and observed along a pseudothreefold axis in transmission between crossed polarizers [18]. The white cross represents the projection (or the normal direction) of the optical axis in the observation plane.

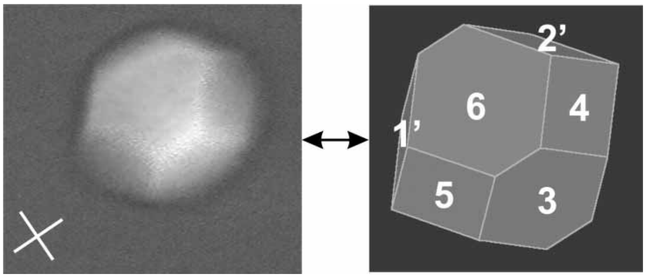

Figure 8. Faceted monodomain of the $BP_{Sm}2$ phase exhibiting four large and two small facets [18].

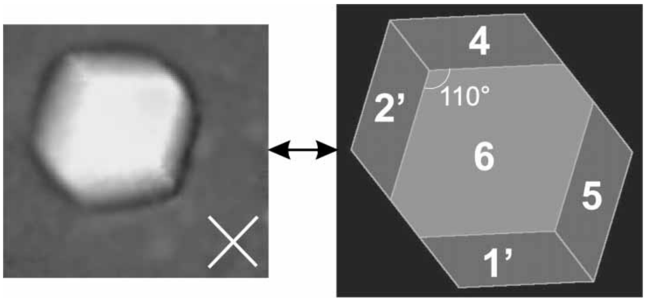

Figure 9. $BP_{Sm}2$ monocrystal floating in the supercooled $BP_{Sm}3$ and observed along a two-fold axis in transmission between crossed polarizers [18].

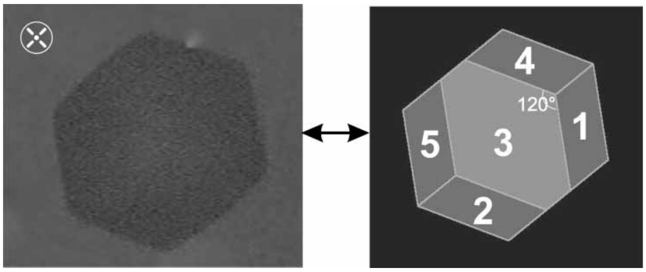

Figure 10. Crystal shape of $BP_{Sm}2$ which stays dark for all the positions of the crossed polarizers [18]. The optical axis is then perpendicular to the plane of the figure. An angle of about 120° is observed on this picture.

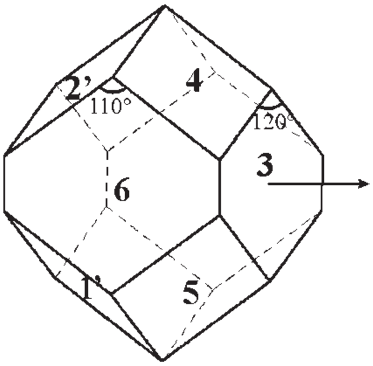

Figure 11. Orthorhombic dodecahedral crystal habit formed by four (100) facets (labelled 3 and 6) and eight (111) facets (labelled 1, 2, 4, and 5) accounting for the experimentally observed monocrystals of the $BP_{Sm}2$ phase [18]. For this model, the parameters of the unit cell are $a=1$, $b=0.82$, and $c=0.58$ and the optical axis is located perpendicular to the normal of the facet labelled 3.

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 dodecahedral structure made from an orthorhombic unit cell (figure 11). This interpretation of an orthorhombic symmetry is also consistent with the X-ray scattering experiments and especially with the epitaxial relation observed at the transition from $BP_{Sm}2$ to $BP_{Sm}1$ phases [15, 18].

2.2. *X-ray scattering experiments*

The new phase sequence (TGB–BP_{Sm}–Iso) has stimulated X-ray scattering studies, especially to investigate whether the smectic order existing in the TGB phases persists in smectic blue phases. The experiments show that the BP_{Sm} phases exhibit, in contrast to BPs, quasi-long-range smectic order with a typical persistence length of about 60 nm. Information on the symmetry of these new phases has then been obtained by growing BP_{Sm} monodomains to explore the entire reciprocal space [5, 14, 19]. The scattering patterns obtained exhibit pairs of Bragg peaks indicating that the smectic order is not isotropic, but extends in given directions of the three-dimensional unit cell (figure 12). By combining these various profiles, the directions of smectic order enhancement, i.e. those in which the different Bragg peaks are located, have been determined and the angles between these directions have been deduced, providing the symmetry of each BP_{Sm} phase.

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 (about 200 nm, the dimension of the lattice parameter) (figure 6) [16]. Only the smectic order has been probed, defined by a periodicity of 4 nm and a correlation length of about 60 nm, three times smaller than the size of the unit cell (figure 12). Therefore, these X-ray scattering experiments only provide *indirect* information on the symmetry of the orientational unit cell, in contrast to the faceted monocrystals of the $BP_{Sm}2$ phase.

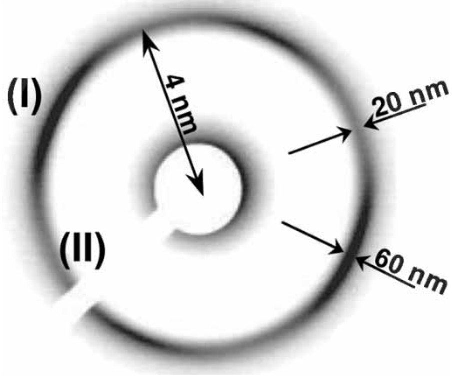

Figure 12. Experimental X-ray scattering patterns of $BP_{Sm}2$ monodomains. Parts of the ring with higher intensity (labelled (I)), where the smectic order is enhanced, correspond to the Bragg peaks, and parts with lower intensity are marked (II). The layer spacing and the correlation lengths of the smectic order are also indicated [14, 19].

These results by X-ray scattering point to the main unsolved theoretical question dealing with smectic blue phases: why does the smectic order break the cubic symmetry of blue phases?

3. Geometrical models of smectic blue phases

The first theoretical approach for combining smectic order with three-dimensional orientational order was proposed by Kamien [20] with a model of smectic double twist cylinders linking smectic A order and twist not only in one direction as in TGB phases, but also in two spatial directions (figure 13). The smectic double twist cylinder is the counterpart in the smectic blue phases of the double twist cylinder in the BPs.

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 and correspond to the Bragg peaks in figure 12. 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 [5, 14]. Thus, some topological defects exist both *in* the smectic double

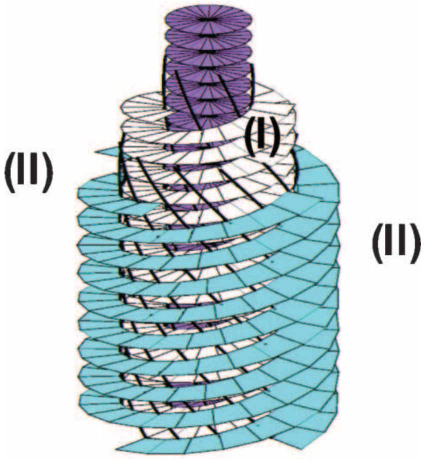

Figure 13. Geometrical model of a smectic double twist cylinder giving rise to the experimental smectic peaks (called region (I) in figure 12). In this picture, the surfaces represent the smectic layers and the black lines wrapping around the cylinder represent the screw dislocations. However, smectic order persists between cylinders and gives rise to the continuous smectic ring (region labelled (II) in figure 12) [20].

twist cylinder for combining twist and smectic order, and *between* the cylinders as in blue phases.

Recently another geometrical model based on minimal surfaces has also been suggested [21].

4. Conclusion

In the same way as a classical blue phase can be seen as the three-dimensional counterpart of the cholesteric phase, a smectic blue phase can be regarded as the extension to 3D of the TGB phase. Indeed, in contrast 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 represent an original physical system of condensed matter exhibiting a *double frustration*: the extension of chirality in three spatial dimensions, and helical twist competing with smectic order.

Peter J. Collings, Randall D. Kamien, Min-Hui Li, Huu Tinh Nguyen and Brigitte Pansu are acknowledged for their contributions to the research on the smectic blue phases.

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