Geometrical Model of the Tetragonal BPX Blue Phase
B. Pansu

To cite this version:

HAL Id: jpa-00248181
https://hal.archives-ouvertes.fr/jpa-00248181
Submitted on 1 Jan 1995

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Geometrical Model of the Tetragonal BPX Blue Phase

B. Pansu

Laboratoire de Physique des Solides LA02, Université Paris-Sud, 91405 Orsay Cédex, France

(Received 7 November 1994, revised in final form 10 January 1994, accepted 10 January 1995)

Résumé. — L’application d’un champ électrique suffisamment intense sur des monocristaux de phases bleues BP1 et BP2 provoque l’apparition de nouvelles structures cristallines. Notamment, une même phase BPX à symétrie tétragonale a été observée quand le champ est dirigé suivant un axe d’ordre 2 de la BP1 ou un axe d’ordre 4 de la BP2, ceci quand l’anisotropie diélectrique est positive. A partir de modèles géométriques des phases bleues basés sur l’analogie avec les phases cubiques lyotropes, nous proposons un modèle géométrique de la phase BPX et un mécanisme de transformation des phases bleues BP1 et BP2 en BPX.

Abstract. — Crystals of BP1 and BP2 blue phases exhibit different crystalline structures under sufficiently high electric field. When the dielectric anisotropy is positive, the same tetragonal phase, called BPX, has been observed when the field is applied, either along a two-fold axis of the BP1 phase, or along a four-fold axis of the BP2 phase. With the help of the geometrical models of cubic blue phases deduced from the analogy with the cubic lyotropic phases, we propose in this paper a geometrical model of the BPX phase and a mechanism for the transformations of BP1 and BP2 into BPX.

Introduction

Liquid crystals, despite a liquid-like positional short range order, can exhibit real 3D crystalline phases; this is the case for thermotropic blue phases [1]. Appearing in a very small domain of temperatures between the isotropic and the cholesteric phase, these phases, called BP1 and BP2, exhibit a typical crystalline behaviour (Bragg scattering, facetting ...). Both are cubic phases and are optically isotropic. The main difference with real crystals, besides the period scale (visible wavelength), is that the order which drives the periodicity is not linked to the position of the molecules which diffuse quite freely, but to their orientation. Indeed molecular chirality generates a twist in the local arrangement of the molecules. This twist creates a 1D periodic configuration of the molecular orientation in the cholesteric phase, and a 3D periodic configuration in blue phases: BP1 and BP2 have both a cubic symmetry with space groups I4,32 and P4232, respectively. An electric field applied to such phases disturbs the molecular orientation and therefore the structure itself. Many experiments on the effects of an electric
field on crystalline blue phases BP1 and BP2 have been performed [1-5]. For positive, as well as for negative, dielectric anisotropy of the molecules, three steps can be distinguished:

1) the reorientation of single crystallites of blue phases BP1 or BP2; one four-fold axis of the structure tends to align along the field. Single crystals grown in the electric field are found to be oriented in the same way;

2) the continuous deformation of the periodic network and therefore of the crystallites (electrostriction); during this transformation, the volume of the unit cell as well as that of the crystallites remain constant;

3) at higher fields, field-induced phase transitions, leading to a progressive unwinding of the twisted molecular organisation; for positive dielectric anisotropy, the final phase is the nematic phase as for a cholesteric phase under an electric field. This paper is focused on this third effect.

Phase diagrams of crystalline blue phases under an electric field are rather complex and reveal a rich polymorphism. The main parameters are the strength of the field, the chirality of the medium, the orientation of the field compared to that of the crystallites and the dielectric anisotropy of the molecules. The Landau theory has been extensively used to explain these diagrams theoretically but, as far as we know, no geometrical model of blue phases under an electric field has yet been proposed. One interesting feature of these phase diagrams is that the same tetragonal phase BPX has been observed in mixtures with positive dielectric anisotropy, by applying an electric field on either BP2 oriented with one four-fold axis parallel to the field, or BP1 oriented with one two-fold axis along the field. The aim of this paper is to propose a geometrical model in order to understand how BP1 and BP2 can be transformed into the same BPX phase. The basic feature of all the geometrical models of blue phases is the assumption that the local orientational order follows a more or less perfect double-twist rule: the mean orientation of the molecules, called the director, tends, at each point, to rotate in all directions perpendicular to it. Section 1 will be devoted to a short review of geometrical models of BP1 and BP2, focusing on the particular aspect of these two structures along the four-fold axis for BP2 and the two-fold axis for BP1. In Section 2, we shall analyse the effect of an electric field on the standard double-twisted configuration, i.e. a double-twist cylinder, in the case of positive anisotropy. This will lead to interpret, in Section 3, the structure of BPX as resulting from a mixture of both BP1 and BP2 architectures.

1. Geometrical Models of Crystalline Blue Phases

The basic feature of the geometrical models which describes these chiral phases is the use of a director \( \mathbf{n} \) \(( \mathbf{n} = -\mathbf{n} \)) where \( \mathbf{n}(r) \) represents the mean orientation of the molecules at point \( r \). In the cholesteric phase, as well as in blue phases, the long-range order results from the twist of the director. In the cholesteric phase, twist occurs in only one direction of the space, the \( z \)-direction for instance. Then a perfect configuration is given by:

\[
\begin{align*}
    n_x &= \cos (qz) \\
n_y &= \sin (qz).
\end{align*}
\]

Since \( \mathbf{n} \) and \( -\mathbf{n} \) are equivalent, the spatial periodicity is half of the cholesteric pitch \( p = 2\pi/q \). When the range of the pitch lies in the visible length domain, Bragg diffraction occurs in this domain and the cholesteric phase appears colored. The basic assumption to understand why blue phases exist is that twist happens, not only in one direction like in the cholesteric phase, but in all directions perpendicular to the director. This geometrical constraint can be justified with use of the free energy per unit volume usually expended in terms of \( \mathbf{n} \) as:
\[ F = K_1 (\text{div } n)^2 + K_2 (n \cdot \text{rot } (n) - q)^2 + K_3 (n \wedge \text{rot } n)^2 \\
- K_4 \text{ div } (n \cdot \nabla (n) + n \text{ div } n). \quad (1) \]

The last term is a surface contribution and is often omitted, but in blue phases, it plays an important role. In the following, we shall neglect elastic anisotropy and take: \( K_1 = K_2 = K_3 = K_4 = K \). The free energy can then be written as:

\[ F = K \sum_{ij} (\partial_i n_j - q \epsilon_{ijkl} n_k)^2 - q^2. \]

An absolute minimum of this energy is given by

\[ \partial_i n_j = q \epsilon_{ijkl} n_k. \]

This equation expresses that the director \( n \) twists in all directions perpendicular to \( n \): this is called double-twist. Let us notice that the cholesteric configuration also corresponds to an energy minimum, but the corresponding energy is higher for simple twist than for double-twist.

The problem is that this local condition cannot be extended over long distances. If one knows the orientation of the director at a point \( A \) and applies the double-twist rule continuously from \( A \) to another point \( B \), the orientation of the director at point \( B \) depends on the path followed to go from \( A \) to \( B \): there is frustration. This implies that double-twist cannot be satisfied everywhere. The geometrical models which have been proposed are built with finite regions like spheres or cylinders [6–8], where double-twist is more or less perfect. In a double-twist cylinder, the configuration is axially symmetrical. Around the \( z \)-axis for instance, one can consider a director field of the following form:

\[ n_\theta = \sin (qr) \]
\[ n_z = \cos (qr), \]

where \( r \) is the distance to the axis and \( \theta \) is the polar angle. Along the axis of the cylinder, the director lies parallel to the axis; it twists when moving radially and the twisting rate depends on the twist parameter \( q \). It is worth noticing that in such cylinders the double-twist condition is not perfectly fulfilled; the energy vanishes only in the vicinity of the axes \((r \to 0)\), of the cylinders where double-twist is perfect. In order to build periodic architectures, double-twist cylinders are then packed in cubic arrays. Two conditions are required for a good packing: (i) achieve the same symmetry group as the one experimentally observed and (ii) fit the orientation of the director at the points where the cylinders are tangent. Most of the figures of this paper deal with projections of 3D structures involving pieces of cylinders. To help the reader, we give in Figure 1 the different ways used in this paper to represent these cylinders. Large circles correspond to cylinders parallel to the projection axis (called \( z \)); other cylinders are represented by pieces of lines and the arrows indicate decreasing \( z \). Small circles show junctions between cylinders. The location \( z \) of the center of the cylinders or of the junctions will sometimes be given and will be correlated with the "color" of the circles.

In the classical models of BP1 and BP2 (Fig. 2), three sets of cylinders lie along the three axes of the cubic cell. When two identical cylinders are perpendicular and tangent, the orientation at the surface of each one must be tilted \( (45^\circ) \) with respect to the axes. This imposes that the radius of these cylinders, and therefore the size of the cell, depends on the cholesteric pitch. In such configurations frustration then appears between the cylinders. To illustrate this,
Fig. 1 — Rules for representing pieces of cylinders in projection drawings: In a) (left), a cylinder parallel to the projection axis (called $z$) is represented by a large circle, the coordinate $3/4$ corresponds to the position of its center along the $z$-axis. Other cylinders are represented by lines and the arrow indicates decreasing $z$. In b) (left), the small circle is associated to a junction between cylinders; the coordinate $1/2$ corresponds to its position along the $z$-axis. The lines with arrows represent the cylinders which join at this point.

Fig. 2. — Classical models for BP2 (a) and BP1 (b). Double twist cylinders lie parallel to three perpendicular edges of the cubic cell; the symmetry groups are $P4_232$ for BP2 and $I4_132$ for BP1.

Let us consider three double-twist cylinders which are perpendicular and tangent. Between these cylinders lies a three-fold axis. Depending on the arrangement of the cylinders, two configurations exist [9]. If the director field can be extended between the cylinders, one can consider another double-twist tube along the three-fold axis. If the director field cannot be extended, it generates a defect line along the three-fold axis. This defect line is a $s=-1/2$ disclination line. It is impossible to build an array of double-twist cylinders without generating disclination lines. Therefore each cubic structure is associated with an array of disclination lines along the three-fold axes. These defect lines do not intersect in BP1 as they do in BP2 (Fig. 3). The presence of defect lines is imposed by double-twist but, from an energetical point of view, costs a lot. Since this cost decreases near the isotropic transition, blue phases appear there. These phases thus result from an energetical balance between the energy lost due to the presence of defects lines and the one saved in the double-twist cylinders compared to simple twist configuration.

These geometrical models of BP1 and BP2 coincide with the space groups which have been determined experimentally: $I4_132$ and $P4_232$, respectively. But they cannot explain the structural change of these two phases into the same BPX structure when an electric field is applied. Improving these models requires to fill the space between the double-twist cylinders, which is quite large, especially in the BP1 model. In a previous paper [9], we have shown that the space left between the cylinders could be partially filled with other double-twist cylinders. In BP1, as
Fig. 3. — Corresponding arrays of disclination lines for BP2 (a) and BP1 (b).

Fig. 4. — Geometrical models for BP2 deduced from the analogy with lyotropic cubic phases. Pieces of double-twist cylinders build two intertwined networks (a and b): one is in black, the other in white. The two networks are perfectly identical.

well as in BP2, the new double-twist cylinders are only intersecting pieces of cylinder, they lie along the three-fold axes in BP2 (Fig. 4) and along the two-fold axes for BP1 (Figs. 5 and 6). In BP1, as well as in BP2, they weave two similar but non-connected infinite tridimensional nets which are periodically intertwined. These new cylinders fit perfectly well with the cylinders which lie along the four-fold axes and also with the disclination lines. Let us just point out that these new architectures are reminiscent of that of the cubic bicontinuous lyotropic

Fig. 5. — Geometrical models for BP1 deduced from the analogy with lyotropic cubic phases. Pieces of double-twist cylinders build two intertwined networks (a and b): one is in black, the other in white.
phases. In direct lyotropic phases, the amphiphilic molecules form cylindrical aggregates: the core of the cylinders is a melt of paraffinic chains and their surface is covered with polar heads. These cylinders build the skeleton of cubic arrays identical to those of blue phases. The main difference between the two systems is that, in the lyotropic phases, the cylinders are real entities: they are filled with paraffinic chains and dipped in water. In blue phases, mean density is uniform and not spatially modulated; the cylinders are only images which help to visualize molecular orientations.

The tentative description of BPX given in the following will be done using the models of BP1 and BP2 based on a double network of intersecting double-twist cylinders. Experiments have shown that BPX can be obtained, either from BP1 under a field parallel to one two-fold axis, or from BP2 under a field parallel to one four-fold axis. Therefore we first have to focus on the architecture of both BP1 and BP2 along these axes. Figure 7 shows a projection of four cells of the BP2 structure perpendicularly to a four-fold axis. In this model of BP2, pieces of cylinders lie along the main diagonals of the cubic array and join four by four (this junction will be called a 4-junction in the following). The cylinder pieces are neither parallel nor perpendicular to the projection axis (called z). In Figure 7 the two networks that they build are represented in separate drawings. Each cylinder is tilted with respect to the projection plane: it is represented by a piece of line, the arrow on this line indicating decreasing z. The z position of points where four cylinders intersect is also shown. The visualisation of the architecture of BP1 along a two-fold axis is much harder. Along this axis, the structure can be described with the use of a tetragonal cell (Fig. 8c) with parameters \(a_R = a_1\), \(b_R = \sqrt{2}a_1\) and \(c_R = \sqrt{2}a_1\) where \(a_1\) is the cubic parameter. The projection of this cell perpendicularly to the axis leads to a rectangular cell with parameters \(a_R\) and \(b_R\). In the model of BP1 derived from the analogy with lyotropic cubic phases, pieces of cylinders lie along the six different two-fold axes. They join three by three in planes perpendicular to some three-fold axes along which the disclination lines are located. Such junctions will be called 3-junctions in the following. In a projection along a two-fold axis, called \(z'\), some pieces of cylinder are perpendicular to the projection plane, some lie in the projection plane and the other ones are tilted. This is shown in Figures 8a and 8b,
Fig. 7. — Projection of four cubic cells of BP2 perpendicularly to a four-fold axis (called z). The two networks are shown separately in (a) and (b) and correspond to the networks (a) and (b) in Figure 4. The pieces of double-twist cylinders are tilted with respect to the projection plane; they are represented by lines with the arrow indicating decreasing z. The z position of the junctions in-between the double-twist cylinders (small circles) is also given.

where the two networks are shown separately. The cylinders are represented by circles when they are parallel to the projection axis and by pieces of lines when they are not; when they are tilted with respect to the projection plane, the arrows still indicate decreasing z'. The positions z' (in the orthorhombic cell) of the cylinders perpendicular to the projection axis and those of the middle of the pieces of cylinder parallel to the axis are also given.

Both architectures of BP1 and BP2 are characterized by intersections of double-twist cylinders. These intersections concern three pieces of cylinders in BP1 and four pieces of cylinder in BP2. BPX will also be described by a double network of double-twist cylinders, intermediate between those of BP1 and BP2. The main difference between the double networks of BP1 and BP2 is the number of pieces of cylinder involved in the junctions. Since BPX can be grown either from BP1 or from BP2 by applying an electric field, one effect of the field, as we shall see in next section, is to modify the junctions between the cylinders.

Fig 8. — The structure of BP1 can be described with the use of an orthorhombic cell parallel to a two-fold axis (c) The projection of the two networks (a) and (b) of BP1 perpendicularly to a two-fold axis (called z') are represented separately in (a) and (b). Some pieces of cylinders are parallel to the projection plane, and are represented by a piece of line; their z' position is given. Some pieces of cylinders are tilted with respect to the projection plane: they are also represented by pieces of line and the arrow indicates decreasing z'. Some pieces of cylinders are perpendicular to the projection plane: they are represented by a large circle and the z' position of their center is given.
2. Field Effect on the Twist

The effect of an electric field has been largely studied in liquid crystal phases [10]. The electric field which is applied is not static (few kHz) to prevent charge motion and instabilities. A volume of liquid crystal where the molecular mean orientation is \( \mathbf{n} \) behaves like an anisotropic dielectric medium characterized by two dielectric constants \( \varepsilon_\parallel \) (in the \( \mathbf{n} \) direction) and \( \varepsilon_\perp \) (perpendicular to \( \mathbf{n} \)). The dielectric anisotropy, \( \varepsilon_\parallel - \varepsilon_\perp \) is either positive or negative depending on the chemical properties of the material. In the following we shall consider only positive dielectric anisotropy. In this case, the director \( \mathbf{n} \) tends to align parallel to the applied field and, at first order, the interaction between the director and the field can be described by an energy term proportional to the dielectric anisotropy and to \( - (\mathbf{n} \cdot \mathbf{E})^2 \). In the cholesteric phase, the effect of an electric field has largely been studied in thick samples in order to neglect surface and anchoring effects. In a non-oriented sample, a large enough field tends to orient the twist axis perpendicularly to the field. With increasing field, distortion appears in the helical structure. The regions where \( \mathbf{n} \) is nearly parallel to \( \mathbf{E} \) extend: the increase of the elastic energy is balanced by the decrease of the electrostatic one. Whereas, if the period remains constant, twist increases in the regions where \( \mathbf{n} \) is perpendicular to \( \mathbf{E} \); then the elastic energy increases without any compensation of the electrostatic one. The overall result is an increase of the pitch under field and thus the untwisting of the cholesteric spiral leading to a nematic phase above some critical value of the field.

In blue phases, the cubic long-range orientational order is also disturbed by electric field. For low values of the field, BP1 and BP2 tend to be oriented with the four-fold axis parallel to the field. This can be deduced from several experimental facts: one observes a rotation of free crystallites grown up in the isotropic bulk at zero field and the nucleation at non zero field of crystallites with the preferred orientation. This effect can be explained by the presence of a torque \( \Gamma \) acting on the crystallites. Due to the cubic symmetry, \( \Gamma \) varies as \( \mathbf{E}^4 \). As for the cholesteric case, higher fields induce distortions in the cubic structure: for instance, cubic cell of BP2 (P\(4_l\)32) is continuously transformed into a tetragonal one (P\(4_l\)22) when \( \mathbf{E} \) is applied along the four-fold axis. Then a real phase transition occurs towards a new tetragonal phase, BPX, with symmetry group I \( 4_l\)22. For larger fields untwisting gradually appears, since a cholesteric phase appears before the nematic one. For some values of the pitch, hexagonal phases, tridimensional first, then bidimensional only, have also been observed. The aim of this paper is not to explain the full phase diagram but focus to only on the BPX structure.

The Landau theory [11] has elucidated some of the features of this phase diagram, but no geometrical model has been proposed yet. Let us first consider a single double-twist tube with a fixed configuration and a given radius \( R \). Minimizing the electrostatic energy obviously implies that such a cylinder tends to orient itself parallel to the field. But, due to the cubic symmetry, the cylinders are entangled and cannot rotate freely. Moreover, as in the cholesteric case, the configuration inside the cylinders can be disturbed. When the cylinder is parallel to the field, the region close to the axis expands; this means that the radial variation of the tilt of the director decreases. Keeping the tilt angle of the director at the surface constant, to fit with other cylinders, induces an increase of the radius of the cylinder; this is equivalent to the increase of the pitch in the cholesteric phase. When the entangled cylinder remains perpendicular to the field, it looses its axial symmetry or tends to disappear if possible. With such considerations, the full prediction of the phase diagrams under an electric field is not possible. Nevertheless these simple ideas, as shown in the next section, lead to a geometrical description and interpretation of the structure of the BPX phase.
3. BPX Structure

As previously said, the tetragonal phase BPX can be obtained either from BP1 or BP2. The distortion of the cubic cells of BP1 and BP2 when the field is applied along given axes (two-fold axis for BP1 and four-fold axis for BP2) must then generate the same tetragonal structure. Let us start from the BP2 model, which is built by two networks of double-twist cylinders parallel to the three-fold axes of the structure, that is, along the main diagonal lines of the cubic cell. As the two sets of cylinders are perfectly identical, the cell is simple cubic (with parameter $a_2$). Under an electric field, double-twist cylinders rise in the direction of the field and the cubic cell can be continuously deformed into a tetragonal phase. If the deformation is too large, elastic constraint can split a 4-junction of double-twist cylinders into two 3-junctions separated by a new piece of double-twist cylinder parallel to the field (Fig. 9). One thus recovers some 3-junctions characteristic of the BP1 structure. This cannot occur in all the cells, otherwise the resulting cell would be simple tetragonal. The transformation has to be different for the two networks of cylinders. The structural phase transition process is, in fact, easier to understand starting from the BP1 structure. Let us now examine the transformation of the BP1 structure under an electric field and we shall come back later to the transformation of BP2 into BPX.

In our model of the BP1 structure, pieces of cylinders parallel to the two-fold axes join three by three weaving two disconnected networks. Each of these two networks is the mirror image of the other one. One is wrapped around the $4_1$ axes, the second one around the $4_3$ axes. When the field is applied along the two-fold axis, the ratios between the three parameters of the tetragonal cell ($a_R = a_1$, $b_R = \sqrt{2}a_1$ and $c_R = 2a_1$), introduced in Section 1, vary and the cell becomes orthorhombic ($b_R$ and $c_R$ are no longer equal). The cylinders which lie in planes perpendicular to the two-fold axis, that is, to the electric field, tend to disappear (Fig. 10). Thus the ratio between the two parameters of the 2D rectangular cell ($\sqrt{2}$ at zero-field) decreases. When it reaches 1, the cylinders perpendicular to the field have disappeared. Therefore two 3-junctions are replaced by one 4-junction (Fig. 10c). The cell is tetragonal and BPX corresponds to this stage. The director configuration can be described as shown in Figure 11 by two networks of cylinders, as in BP1 and BP2. Figure 11a can be deduced from Figure 8a: the cylinders perpendicular to the field ($z = 3/4$, $z = 1/4$) vanish and are replaced by 4-junctions. Similarly, Figure 11b is obtained from Figure 8b by removing the cylinders located at $z = 0$ and $z = 1/2$. The two networks are now built from pieces of cylinders which

![Fig. 9. — Effect of an electric field on double-twist cylinders in BP2 (a) represents part of one of the two networks contained in a cubic cell. When the dielectric anisotropy is positive, the double-twist cylinders tend to be parallel to the field. One possible effect is thus the nucleation of a new double-twist tube which transforms one junction of four cylinders into two junctions of three cylinders (b)](image)
Fig. 10. — Effect of an electric field on double twist cylinders of BP1. (a) represents part of one of the two networks contained in a one-eighth of the orthorhombic cell. When the dielectric anisotropy is positive, the double-twist cylinders perpendicular to the field tend to disappear (b). The ratio $a'/b'$ of the cell parameters decreases. When this ratio is equal to 1 (c), the double-twist cylinders perpendicular to the field vanish, and two junctions of three cylinders are replaced by one junction of four cylinders: the cell is tetragonal.

join either three by three or four by four. The cell corresponding to Figure 11a and Figure 11b is drawn in Figure 12, where both networks are shown, but only the cylinders parallel to the field are represented. Symmetry axes are also indicated and the resulting symmetry group $I4_{1}22$ corresponds to the experimental observations. This cell is face-centered and thus the conventional cell is a smaller tetragonal cell (with half volume) which is centered. This cell is represented in dotted lines in Figure 12.

Fig. 11. — Projection of BPX perpendicularly to the four-fold axis (called $z$). The two networks resulting from the transformation of the networks of Figures 8a and b are shown separately in Figures 10a and 10b and correspond. As in BP1, some pieces of cylinders are perpendicular to the projection plane; they are represented by a large circle and the $z$ position of their center is given. The other pieces of cylinders are tilted with respect to the projection plane: they are also represented by pieces of line and the arrow indicates decreasing $z$. Some junctions involve four pieces of cylinders and their $z$ position is given.
Let us come back to BP2 and imagine the scenario which leads from BP2 to BPX. BP2 can be described by two identical networks of cylinders joining four by four. In perfect BP2, each network is deduced from the other one by a cubic translation. But, for each network, each set of cylinders inside a cubic cell is connected to the set of cylinders of the second neighboring cells and not of the first ones as shown in Figure 7. To describe only one set of cylinders, one needs a cubic cell twice as large in each of the three directions of space. This cell is represented in Figure 13. The two networks are represented separately in Figures 13a and b.

**Fig. 13 — BP2 blue phase: cubic cell with parameter twice as larger as in the primitive one.** The two networks are shown separately in (a) and (b). The small circles represent the junctions of four pieces of double twist cylinders. The transition from BP2 to BPX is characterized by a splitting of half of the four-junctions of each network into two three-junctions and the appearance of a new double-twist tube parallel to the four-fold axis. This splitting is such that the two networks are no longer identical up to a cubic translation. For the network in (a), splitting occurs for the junctions located at $z = 0$ or $z = 1/2$ and one thus recovers the network of Figure 11(a). For the network in (b), the splitting only occurs for the junctions located at $z = 1/4$ or $z = 3/4$: the resulting network is that of Figure 11(b).
In Figure 13, the small circles are located at the tube junctions and their position along the four-fold axis is indicated. Under a sufficiently large electric field, half of the 4-junctions of each network split into two 3-junctions and a new double-twist tube parallel to the four-fold axis appears. This splitting is such that the two networks are no longer identical up to a cubic translation. For the network of Figure 13a, splitting occurs, for instance, for the junctions located at \( z = 1/4 \) or \( z = 3/4 \) whereas for the network of Figure 13b, splitting occurs for the junctions located at \( z = 0 \) or \( z = 1/2 \). It is now easy to see that one recovers the two networks of the BPX architecture shown in Figure 11: half of the junctions of Figure 13 represented by small circles are transformed into double-twist tubes perpendicular to the figure plane (large circles of Fig. 11). For the other junctions, splitting does not occur. This mechanism proves that the same structure corresponding to the BPX phase can be obtained either from BP1 or BP2. In BP1, the cylinders perpendicular to the field vanish whereas, in BP2, cylinders parallel to the field appear.

Three-dimensional architectures of double-twist cylinders must contain disclination lines. In BP2, they join four by four at the same junction points, as the double-twist cylinders do. Each piece of defect line thus connects two junctions belonging to each of the two networks of double-twist tube. In BP1 they do not intersect, but still link the two networks. When the splitting of half of the four by four junctions of cylinders occurs in BP2, the four pieces of disclination lines which were joining at the junction points generate two pieces of defect line which are no longer intersecting. Each of these two pieces crosses one of the two new 3-junctions of double-twist tubes which appear during the splitting. Since the splitting occurs only for half of the functions, this means that some disclination lines still intersect. Let us now consider what happens when starting from BP1: when the cylinders perpendicular to the field vanish, some disclination lines must therefore intersect four by four. Then, in a cell of the BPX structure, some disclination lines intersect four by four, and some do not. That implies the co-existence of a connected network of disclinations lines joining four by four like in BP2 and of an array of infinite disclination lines as in BP1. In BP2, the disclination lines weave two identical networks which are mirror images of the two networks of double-twist tubes. In BPX, these two networks are different. One network of disclination lines remains the same (junctions four by four), whereas the other is fully transformed into a periodic array of non-intersecting disclination lines.

4. Conclusion

Cubic blue phases exhibit many structural transformations under an electric field. Notably the same phase BPX can be obtained either from BP1 or BP2 for materials with positive dielectric anisotropy. The existence of this phase cannot be explained by using the classical models built with tangent double-twist cylinders. In order to interpret the structural changes from BP1 to BPX and from BP2 to BPX under an electric field the classical models need to be improved. This has been done using the analogy between cubic blue phases and cubic lyotropic phases. The classical models of cubic blue phases can be filled out with other pieces of double-twist cylinders which join together and thus build the same interwoven networks as the surfactant cylinders of the cubic lyotropic phases with corresponding symmetry. In blue phases, the cylinders are virtual and describe some double-twist configuration, whereas lyotropic cylinders are built by amphiphilic molecules. In BP1, the architecture of the two networks is characterized by junctions of three pieces of cylinders; in BP2 junctions concern four pieces of cylinders. As in the cholesteric phase, it is easy to predict the behaviour of a single double-twist tube when applying an electric field: both the orientation and the shape of the double-twist cylinders are modified. But the tricky entanglement of cylinders in the cubic
architectures prevents us from a full understanding of the behavior of blue phases under an electric field. Nevertheless simple considerations lead to the description of a possible mechanism for the phase transformations of both BP1 and BP2 into BPX. The resulting architecture of BPX is then a subtle compromise between the two cubic phases, where some junctions concern three pieces of cylinders like in BP1, and some concern four pieces of cylinders like in BP2. It is also worth noting that this mechanism is in agreement with the (positive) sign of the electrostriction coefficient for the lattice constant of BP1 and BP2 along the field. The sign of the dielectric anisotropy (positive) is important in this mechanism. In the case of negative anisotropy, the cylinders tend to orient perpendicular to the field and the cylinders parallel to the field tend to disappear. With arguments identical to those presented above, one can at least understand the field-induced decrease of the lattice constant of both BP1 and BP2.

Without an external field, there is some epitaxial relation between BP1 and BP2: a four-fold axis of BP2 corresponds to a two-fold axis of BP1 [3]. These two orientations are the same as those giving birth to the BPX phase under an electric field. One can thus imagine that a mechanism as that described in this paper can play a role when the BP2-BP1 transition occurs. Also, can this mechanism explain transitions in cubic lyotropic phases? The lyotropic phases corresponding to BP1 and BP2, respectively, are the so-called Ia3d and Pn3m phases (their name is associated with the corresponding space groups). Indeed, removing the mirror operations incompatible with chirality leads to the equivalence between Ia3d and BP1 (symmetry group I4132) and between Pn3m and BP2 (symmetry group P4232). In some systems like mixtures of monolein and water, a transition between these two bicontinuous cubic phases can be observed as a function of temperature [12]. In this case, the epitaxial relation between the two structures is different from that in blue phases: that is, a three-fold axis of Pn3m corresponds to a two-fold axis of Ia3d. The difference between the two systems is probably due to density problems. It seems that in lyotropic phases epitaxial relations concern the densest planes, whereas in blue phases, the molecular density is uniform at the scale of the cell and has no effect. This shows the limit of the analogy between the two systems and therefore the difficulty to predict the behavior of lyotropic cubic phases under uniaxial constraint.

Acknowledgments

The author would like to thank E. Dubois-Violette for a critical reading of the manuscript.

References

[12] Rawiso M., private communication