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Determination of the blue phase II structure

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Résumé. — Plusieurs études précédentes de la structure de BPII ont donné trois symétries possibles : cs O\textsuperscript{2}, cfc O\textsuperscript{4} ou icosaédrique. Pour déterminer plus précisément cette structure, nous avons étudié expérimentalement les diagrammes de Kossel de BPII dans le MMBC et dans un mélange CB15/E9. La symétrie de ces diagrammes permet d'écarter la structure icosaédrique. Il manque deux lignes de Kossel attendues dans le cas de la symétrie O\textsuperscript{4} ; en revanche, les diagrammes observés sont identiques à ceux prévus par la théorie pour la symétrie O\textsuperscript{2}.

Abstract. — Different studies of the structure of BPII had previously given three different possible symmetries : sc O\textsuperscript{2}, fcc O\textsuperscript{4} or icosaedral. In order to discriminate between these three possibilities, we have studied the Kossel diagrams of BPII in MMBC and in a CB15/E9 mixture. The symmetry of these diagrams is completely inconsistent with an icosaedral structure. Two lines expected for O\textsuperscript{4} symmetry are missing ; the observed diagrams are identical to those of O\textsuperscript{2} symmetry.

1. Introduction : controversy about BPII structure.

Cholesteric liquid crystals are known to exhibit several mesophases : the Cholesteric Phase and three Blue Phases BPI, BPII and BPIII. BPI has a body-centred cubic (bcc) structure of space group O\textsuperscript{8} (I4\textsuperscript{1}32) ; BPIII is an amorphous phase whose structure has not yet been determined [1].

As far as BPII is concerned, its structure has given rise to much controversy :

1) The first observations of Bragg reflections and of crystal forms have indicated that the BPII structure is simple cubic (sc) of space group O\textsuperscript{2}(P4\textsuperscript{3}32) [1].

2) The polemic was initiated by Kuczynski who observed several IR and visible Bragg reflections in MMBC and concluded that BPII in this material cannot be cubic [2].

3) D. S. Rokhsar and J. P. Sethna in their paper devoted to a Landau theory of an icosaedral quasicrystalline Blue Phase, have suggested that Kuczynski’s results could be interpreted in terms of such a structure [3].

4) Using a technique similar to that of Kuczynski, P. Keyes has observed several visible Bragg reflections in MMBC [4]. His conclusion that the structure is neither icosaedral nor simple cubic O\textsuperscript{2} but face-centred cubic O\textsuperscript{4} was in contradiction with all previous studies (1°-3°).

5) Independently of Keyes’ studies, this last possibility that the Blue Phase II could have a face-centered cubic structure appeared on a quite different ground ; we have observed in 47 % mixture of CB15 in E9 that the transformation of single BPI crystals into single BPII crystals involves a very characteristic macroscopic finite variation of their shapes. Such a deformation is in fact reminiscent of the Bain transformation characteristic of a bcc-fcc phase transition.

The purpose of the present paper is to discriminate between all the above mentioned structures by means of a different experimental method — the Kossel diagram technique — which has been developed and used previously in a structural study of a field-induced phase transition BPI → BP X [5].

The principle of the method is explicit in section 2.1. In section 2.2, we give a short description of the experimental set-up. Experimental Kossel diagrams of the Blue Phase II in both MMBC and the mixture CB15/E9 [6] are shown in section 4. They are compared with theoretical diagrams for O\textsuperscript{2} and O\textsuperscript{4} structures ; the third possibility of an icosaedral structure can be discarded immediately.
for symmetry reasons (there are no four-fold axes in the icosahedral symmetry).

2. Experimental Kossel diagrams.

2.1 Principle of the method. — A beam of wave vector $k_i$ incident on a family of planes (hkl) corresponding to a wave vector $q$ in the reciprocal space is reflected into a wave vector $k_r$ if the Bragg relation: $k_r - k_i = q$ is satisfied, which implies:

$$\cos \theta = \frac{\lambda}{2an} \sqrt{h^2 + k^2 + l^2} = \frac{|q|}{2q_0}.$$  (1)

Here $\theta$ is the angle between $k_i$ and $q$, $\lambda$ the light wavelength, $a$ the lattice parameter and $n$ the refraction index.

For a convergent beam produced by an objective lens (Fig. 1) and incident on the crystal planes (hkl) the reflected beams form a cone of half-aperture $\theta$ around $q$. The beams that have the same azimuthal angle $\Phi$ converge on the same point of the focal plane of the lens. When $\Phi$ varies of $2\pi$, this point describes a ring. Equation (1) implies that this ring exists only when $|q| < 2q_0$. The set of existing rings for a given $\lambda$ constitutes a Kossel diagram.

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2.2 Experimental setup. — We use a reflecting metallurgical microscope adding a Bertrand lens ($L$ in Fig. 2) to the eye-piece in order to observe the focal plane of the lens; the photographic pictures of this plane are obtained by means of a standard photographic camera equipped with a 135 mm focal objective (LFO) [5].

A detailed view of the sample is given in figure 3: the liquid crystal is located between a glass cylinder (GC) and a glass plate (GP); the temperature of these two parts are regulated separately with a precision of $10^{-3}$ K. We can nucleate and make monocrystals grow with a fixed orientation on one of the surfaces by introducing a small vertical temperature gradient and slowly cooling the whole cell.

On a clean glass, we obtain crystals orientated with the [111] or [110] axis perpendicular to the glass surface; the [111] orientation is much more frequent. In order to obtain crystals with the [100] axis perpendicular to the surface, we have coated the glass cylinder with an aqueous solution of polyvinylalcohol, let it dry, and rubbed it on a sheet of paper [7].
With this setup, we can obtain two sorts of diagrams depending on whether the upper surface of the cell is reflective (Fig. 4a) or not (Fig. 4b).

The second case is simpler as the crystal is illuminated only by one convergent beam coming from below so that only one set $S_1$ of Kossel lines, produced by reflected rays, is observed in the focal plane.

In the first case, the glass cylinder is coated by an evaporated Al film acting as a mirror: it creates a second convergent beam, coming from above, which gives rise to a second set $S_2$ of Kossel lines superposed on $S_1$. It can be shown that $S_1$ and $S_2$ are related by the inversion symmetry with respect to the center of the focal plane (when the mirror is perpendicular to the optical axis $O$).

Note that in both cases, we do not observe the whole sets of Kossel lines. We can only see the part of the diagrams created by rays making with $O$ an angle inferior to the aperture $\theta_0$ of the objective; this part is the inside of a circle whose center is the center of the focal plane and whose diameter is determined by the aperture of the objective.

3. Theoretical Kossel diagrams.

3.1 CONSTRUCTION OF KOSSEL LINES. — The Kossel lines can be drawn on a sphere $S$ of radius $2 q_0$ (see Eq. (1)) and center $O$.

A family of planes corresponding to a wave vector $\mathbf{q}$ generates a Kossel line only if $|\mathbf{q}| < 2 q_0$. This line is the circle determined by the intersection of the sphere $S$ with the plane $P$ perpendicular to $\mathbf{q}$ and containing the point $C$ such that $OC = q$ (Fig. 5); this point $C$ is the center of the Kossel ring.

For a given $q_0$, we can repeat the proceeding for all the possible wave vectors $\mathbf{q}$ and obtain all the existing lines on $S$. In order to obtain the Kossel diagrams for different orientations of the crystal, we can rotate this sphere $S$ and project its visible hemisphere on a plane perpendicular to the axis of observation.

These theoretical diagrams are shown in section 4 together with the experimental ones.

3.2 INTENSITY OF KOSSEL LINES. — For a fcc structure, the only possible lines are those corresponding to Miller indices all even or all odd; there is no such restriction for a sc structure.

Moreover, the Landau theory of Blue Phases shows that some lines are much weaker than others and may not be observed [8].

The intensity of the reflected light is proportional to the square of the Fourier components of the order parameter, the anisotropic part of the dielectric tensor; these components may be developed in a basis of five $[M_m]$ traceless symmetric tensors, with $m = -2$ to 2. It can be shown [8] that $m = 2$ is the leading term of the development.
Fig. 6. — Non zero components of the Fourier coefficients of the order parameter (a) for a sc $O^2$ structure ; (b) for a fcc $O^4$ structure. $F_2(q)$ is the coefficient of the quadratic term in the Landau free energy.

Fig. 7. — Four-fold symmetry diagrams obtained without mirror : (a) MMBC, $\lambda = 500$ nm ; (b) CB15/E9 48,05 %, $\lambda = 373$ nm ; (c) theory for $O^2$ structure ; (d) theory for $O^4$ structure.
If \([M_2]\) is not invariant by the symmetry elements associated with a wave vector \(q\) of the reciprocal space, the \(m = 2\) term of the Fourier coefficient of the component \(e^{-iq\cdot r}\) is equal to zero (Fig. 6): the intensity of the associated Kossel line is expected to be much lower than that of the lines for which the \(m = 2\) component is not equal to zero.

Table I lists the possible lines for \(O^2\) and \(O^4\) symmetries. We can see that the only difference between the sequences of lines for the two structures is the presence or absence of the \((111)_f\) and \((311)_f\) lines. The absence of the \((111)_f\) lines is not a relevant difference because it may be due to their extrem weakness; on the contrary, the \((311)_f\) lines, if they exist, are expected to be of comparable intensity to that of the \((200)_f\) and \((220)_f\) lines.

Table I. — Possible lines for \(O^2\) and \(O^4\) structures and the corresponding main component.

<table>
<thead>
<tr>
<th>Possible Lines</th>
<th>(100)_f)</th>
<th>(110)_f)</th>
<th>(111)_f)</th>
<th>(200)_f)</th>
<th>(220)_f)</th>
<th>(311)_f)</th>
<th>(222)_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lines sc (O^2)</td>
<td>((100)_f)</td>
<td>((110)_f)</td>
<td>((111)_f)</td>
<td>((200)_f)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lines fcc (O^4)</td>
<td>((111)_f)</td>
<td>((200)_f)</td>
<td>((220)_f)</td>
<td>((311)_f)</td>
<td>((222)_f)</td>
<td>((400)_f)</td>
<td></td>
</tr>
<tr>
<td>Leading component</td>
<td>(m = 0)</td>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(0)</td>
<td>(0)</td>
<td></td>
</tr>
</tbody>
</table>

4. Comparison of the experimental and theoretical diagrams.

A set of Kossel diagrams obtained both with MMBC and a 48.05% in weight CB15/E9 mixture, for \([100]\), \([111]\) and \([110]\) orientations are shown in figures 7 to 12. On the same figures, we show the theoretical diagrams for the \(O^2\) and \(O^4\) symmetries; the part corresponding to the experimental diagrams is drawn with thick lines.

In these experimental diagrams, we can see the following lines:

1) The \((100)_f\) or \((200)_f\) lines can be observed in figures 9a and b, figures 10a and b, figures 11a and b and figure 12a.

2) As expected from the selection rules (Sect. 3.2), the \((110)_f\) or \((220)_f\) lines are of comparable intensity as the previous lines \((1°)\); they can be seen in all the experimental diagrams.

3) The \((111)_f\) or \((222)_f\) line is entirely visible in figure 10a; its intensity is even comparable to that of the \((100)_f\) or \((200)_f\) and \((110)_f\) or \((220)_f\) lines. Parts of the \((111)_f\) or \((222)_f\) lines can also be observed in figure 8a at the intersection of these lines with the \((110)_f\) or \((220)_f\) lines.

Both figure 10a and figure 8a have been obtained without the mirror. In the diagrams obtained with the mirror (Fig. 10b and Fig. 12a), the \((111)_f\) or \((222)_f\) lines are not visible at all.

This phenomenon does not occur for the \((100)_f\) or \((200)_f\) and \((110)_f\) or \((220)_f\) lines: they are both visible on the diagrams obtained with the mirror (Fig. 11a and Fig. 12a).

The reasons for the unexpected behaviour of the \((111)_f\) or \((222)_f\) lines are not clear.

4) The \((200)_f\) or \((400)_f\) line is visible in figure 8a though it is extremely weak.
Fig. 9. — Three-fold symmetry diagrams obtained with the mirror: (a) MMBC, $\lambda = 597$ nm; (b) CB15/E9 48.05%, $\lambda = 428$ nm; (c) theory for $O^2$ structure; (d) theory for $O^4$ structure.

Fig. 10. — Three-fold symmetry diagrams: (a) MMBC, $\lambda = 470$ nm without mirror; (b) MMBC, $\lambda = 470$ nm with the mirror; (c) theory for $O^2$ structure; (d) theory for $O^4$ structure.
Fig. 11. — Two-fold symmetry diagrams: (a) MMBC, \( \lambda = 602 \text{ nm} \) without mirror; (b) CB15/E9 48.05\%, \( \lambda = 433 \text{ nm} \) with the mirror; (c) theory for O\(^2\) structure; (d) theory for O\(^4\) structure.

The last two sets of lines (3° and 4°) have only been observed in MMBC; in the CB15/E9 mixture they appear in the UV light.

The only lines that have not been observed are the (111)\(_f\) and (311)\(_f\) lines: they appear in none of the experimental diagrams.

Fig. 12. — Two-fold symmetry diagrams obtained with the mirror: (a) MMBC, \( \lambda = 476 \text{ nm} \); (b) theory for O\(^2\) structure; (c) theory for O structure.
5. Conclusion.

We have obtained Kossel diagrams of the Blue Phase II in two different materials (MMBC and CB15/E9) for three different crystal orientations ([100], [110] and [111]) and for several wavelengths of light (370 nm ≤ λ ≤ 800 nm).

These experimentally obtained Kossel diagrams were compared with theoretical ones expected for the two competing isocahedral symmetries O^2 and O^4. (The third possibility of an icosahedral structure was discarded for simple symmetry reasons.)

Our results are the following:

1) All Kossel lines visible on experimental diagrams can be identified one by one, with the (100)_s, (110)_s, (111)_s and (200)_s lines expected theoretically for the O^2 structure.

2) Reciprocally: all theoretically expected lines for the O^2 structure have been found on our experimental diagrams.

3) All experimental lines can also be identified one by one, with the (200)_t, (220)_t, (222)_t and (400)_t lines expected theoretically for the O^4 structure.

4) However, the inverse statement is not true: (111)_t and (311)_t lines expected theoretically for the O^4 structure are missing on our experimental diagrams.

The impossibility to detect the (111)_t line could be explained by its weakness resulting from selection rules, but there is no such reason to explain the absence of the (311)_t line. In view of these facts, we may conclude that only the first possibility, that is the O^2 structure, is compatible with our results.

However, it must be emphasized that the difference between O^2 and O^4 symmetries is extremely small. The BPII structure may be represented by a network of disclinations [9]. in the case of O^4 symmetry, this network is composed of two different interwoven diamond lattices; in the case of O^2 symmetry, these two lattices are identical. O^2 symmetry can be broken into O^4 symmetry by introducing an infinitesimal difference between the two disclination lattices. This fact can also be understood in terms of space groups: the O^4 space group is a subgroup of the O^2 space group.

Because of this extremely small difference between O^2 and O^4 symmetries, the intensity of the (311)_t line can be arbitrarily small. However, if BPII was fcc, this intensity would be expected to be temperature dependent; thus, there is no reason for it to remain small in the whole temperature range of existence of BPII. So we must conclude that, in the limit of our experimental accuracy, BPII has a sc O^2(P4_232) symmetry.

References

[6] MMBC is the 2-methylbutyl p[N-(p-methoxybenzyli-dene)-amino] cinnamate. CB15 and E9 are produced by BDH.