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OPTICAL PROPERTIES OF BLUE PHASE I:
MEASUREMENTS OF THE ORDER PARAMETER

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Résumé - Nous appliquons la théorie dynamique de la diffraction à la Phase Bleue I. Utilisant des spectres obtenus sur de gros monocristaux sans défaut nucléés sur des surfaces de verre, nous les comparons aux spectres théoriques et en déduisons la première mesure directe de la composante de Fourier dans la direction <110> du paramètre d'ordre de la Phase Bleue I. Enfin, nous montrons que ces résultats sont en accord avec la théorie développée par R.M. Hornreich et al.

Abstract - We apply the dynamical theory of diffraction to Blue Phase I. Using spectra we have got with large monocrystals without defect growth on glass surfaces, we compare them to the theoretical ones and obtain the first direct measurement of the Fourier component in the direction <110> of the order parameter of BPI. At least, we show that those results are in agreement with the theory proposed by R.M. Hornreich et al.

I - INTRODUCTION

Blue Phases I and II, occurring in a small temperature range between an isotropic and a cholesteric phase, have cubic structures with lattice constants of the order of wavelength of visible light /1-6/. On these scales (0.1-1 μm) the visible light is, like in colloidal crystals, a very convenient way of studying the crystal-line structure. However, in contrast with ordered suspensions where one (bcc) cubic unit-cell contains only two colloidal particles, one cubic unit-cell of the Blue Phase I (or II) contains about $10^7$ rodshaped chiral molecules. Moreover, the molecular order in Blue Phases is not positional but orientational what means that these molecules can move freely (like in a liquid) through the cubic lattice and only their orientations are correlated with their positions in the lattice. These characteristics, very different from usual colloidal crystals, allow one to consider Blue Phases as a continuum where the dielectric tensor $\varepsilon(\mathbf{r})$ is a smooth function of the position $\mathbf{r}$.

Because of the periodicity of the lattice one can develop $\varepsilon$ in a Fourier series /7,8/:

$$\varepsilon(\mathbf{r}) = \varepsilon_1 + \sum \varepsilon_\mathbf{T} e^{i2\pi \mathbf{T} \cdot \mathbf{r}}$$

where $\mathbf{T}$ is a reciprocal lattice vector of BPI (in this paper we are only interested in BPI).

The zeroth-component is proportional to the unit-tensor $\mathbf{1}$ because of non birefringence of BPI. $\varepsilon_1$ may be choosen as the order parameter of the phase, because it is a traceless tensor which is zero in the isotropic phase /7,8/.

The aim of the present paper is to apply the general theory of dynamical light diffraction to Blue Phases. It will be shown in the next section that this can be done in a very convenient way if one takes into account (1°) the lack of birefringence
(\varepsilon_0 = \varepsilon \hat{i}) characteristic of Blue Phases and (2°) a well-known experimental fact that Blue Phases reflect selectively almost uniquely a circulary polarized light of one chirality. As a theoretical result we will show how to get informations about the components \varepsilon_\text{T} of the order parameter from the spectral shapes of Bragg reflections.

Practically, the application of dynamical theory of light scattering is "ab initio" reserved to the case of defect-free monocrystals. Clearly, the development of the order parameter in a Fourier series (1) makes sense only when the crystal is perfect; any dislocation would break the phase relationship between different regions of the crystal.

Very recently, we have shown /9/ that this necessary condition can be satisfied in Blue Phases. In fact, we have developed a method of nucleation (on glass surfaces) and of growth of defectless monocrystals with well-known orientation with respect to the glass surface. In a presence of a small temperature gradient, these monocrystals can be made flat (limited by two strictly parallel crystal faces) and large, so they have ideal shapes suited for studies of dynamical light diffraction.

In section III, we report experimental spectra obtained in back-reflection (under normal incidence) from such perfect crystals of a well-known thickness L. These spectra are compared with the theoretical ones and (knowing the thickness L) the amplitude of the Fourier component \varepsilon_{10} is determined.

In the last section, we shall proceed to a confrontation of these experimental results with the Landau type theoretical approach by Hornreich et al /7/.

II - GENERAL THEORY OF DYNAMICAL DIFFRACTION BY PERFECT BP MONOCRYSTALS

II.1. Solutions of Maxwell's equations in a periodic medium

All the beginning of that theoretical work has been first made by Belyakov and related in a very interesting paper /8/. In the present paper, we have chosen Belyakov's way of considering BPs, and tried to develop the theory furthermore, using some interesting experimental results that greatly simplify the theory.

We consider an electric field of a plane wave:

\[ \hat{\varepsilon} = \varepsilon_0 e^{i2\pi(x, \hat{r} - \nu t)} \]

incident on the crystal, in such conditions that there is only one Bragg reflection that occurs inside the crystal. We assume moreover that this reflection is a back-reflection and is symmetric (Fig. 1a). This is a very restrictive condition that must be carefully controlled for each experimental data. For instance, if one looks at a Bragg peak in back-reflection with normal incidence corresponding to the family of planes (220), one could get in that peak a double successive reflection on planes (200) at 45° with the planes (220) and the two-wave approximation is thus not at all valid.

If this approximation is valid, we can solve Maxwell's equations /10/ considering the electric field amplitude inside the crystal as:

\[ \hat{\varepsilon}(\hat{r}, t) = (\varepsilon_0 e^{i2\pi k_0 \cdot \hat{r}} + \varepsilon_1 e^{i2\pi k_1 \cdot \hat{r}}) e^{-i\omega t} \]

We then obtain the system of equations (considering only the reflection due to the \text{T}-component of the reciprocal space of the lattice) /8/:

\[ \left( \frac{k_0^2}{\chi_\text{T}} - 1 \right) \varepsilon_0 - \varepsilon_\text{T} = 0 \]

\[ \left( \frac{k_1^2}{\chi_\text{T}} - 1 \right) \varepsilon_1 - \varepsilon_{-\text{T}} = 0 \]
where $\varepsilon_{-\tau} = \varepsilon^*$ because $\varepsilon$ is real and $\varepsilon = \varepsilon_0 n^2$, with $n$ the index of refraction.

If $\vec{e}_1^0$ and $\vec{e}_2^0$ are two perpendicular unit vectors so that $(\vec{e}_1^0, \vec{e}_2^0, \vec{k}_0)$ is a direct trihedral, and $\vec{e}_1^1$ and $\vec{e}_2^1$ two perpendicular unit vectors so that $(\vec{e}_1^1, \vec{e}_2^1, \vec{k}_1)$ is also a direct one (Fig 1b), we can project (2) along the directions $\vec{e}_1^0$ and $\vec{e}_2^0$ and (3) along those of $\vec{e}_1^1$ and $\vec{e}_2^1$ and obtain:

\begin{align*}
\varepsilon(1 - \frac{k_0^2}{\chi^2}) \begin{pmatrix} E_0^1 \\ \chi \end{pmatrix} + F_{01} \begin{pmatrix} E_1^1 \\ 0 \end{pmatrix} &= \begin{pmatrix} 0 \\ 0 \end{pmatrix} \\
\varepsilon(1 - \frac{k_1^2}{\chi^2}) \begin{pmatrix} E_0^1 \\ \chi \end{pmatrix} + F_{10} \begin{pmatrix} E_1^1 \\ 0 \end{pmatrix} &= \begin{pmatrix} 0 \\ 0 \end{pmatrix}
\end{align*}

with $(F_{01})_{ik} = \vec{e}_i^0 \cdot \varepsilon_+ \vec{e}_k^1$ and $(F_{10})_{ik} = (F_{01})_{ik}^* = \vec{e}_i^1 \cdot \varepsilon_+ \vec{e}_k^0$

Combining those equations, if we set:

\begin{align*}
\vec{S}_0 &= \hat{F}_{01} \hat{F}_{10} \\
\vec{S}_1 &= \hat{F}_{10} \hat{F}_{01}
\end{align*}

then we find that:

\begin{align*}
\vec{S}_0 \begin{pmatrix} E_0^1 \\ \chi \end{pmatrix} &= \varepsilon^2(1 - \frac{k_0^2}{\chi^2}) \begin{pmatrix} k_0^2 \\ \chi \end{pmatrix} \begin{pmatrix} E_0^1 \\ \chi \end{pmatrix} \\
\vec{S}_1 \begin{pmatrix} E_0^1 \\ \chi \end{pmatrix} &= \varepsilon^2(1 - \frac{k_1^2}{\chi^2}) \begin{pmatrix} k_1^2 \\ \chi \end{pmatrix} \begin{pmatrix} E_0^1 \\ \chi \end{pmatrix}
\end{align*}

So the very important result of that calculation is that $\vec{E}_0$ and $\vec{E}_1$ are eigenvectors of $\vec{S}_0$ and $\vec{S}_1$ for the same eigenvalue.

Let us call $\vec{n}_0^\sigma$ and $\vec{n}_1^\sigma$ the two unit-eigenvectors of $\vec{S}_0$ and $\vec{n}_1^\sigma$ and $\vec{n}_1'^\sigma$ the two corresponding ones of $\vec{S}_1$. The former are in the plane perpendicular to $\vec{k}_0$ and the latter in the plane perpendicular to $\vec{k}_1$. If we project the two equations (2) and (3) along those intrinsic directions of polarization, then we obtain unconnected equations between $E_0$ and $E_1$.

Along the $\sigma$ directions ($\vec{n}_0^\sigma$ for (2) and $\vec{n}_1^\sigma$ for (3)):

\begin{align*}
(1 - \frac{k_0^2}{\chi^2}) E_0^\sigma + F_{\sigma}^* E_1^\sigma &= 0 \\
F_{\sigma}^* E_0^\sigma + (1 - \frac{k_1^2}{\chi^2}) E_1^\sigma &= 0
\end{align*}

with $F_{\sigma}^* = \frac{\vec{n}_0^\sigma \cdot \varepsilon \vec{n}_1'^\sigma}{\varepsilon}$

\begin{align*}
(1 - \frac{k_0^2}{\chi^2}) E_0^\sigma + F_{\sigma}^* E_1^\sigma &= 0 \\
F_{\sigma}^* E_0^\sigma + (1 - \frac{k_1^2}{\chi^2}) E_1^\sigma &= 0
\end{align*}
Along the $\sigma'$ directions ($\tilde{\alpha}_0^\sigma$ for (2) and $\tilde{\alpha}_1^\sigma$ for (3)):

$$
(1 - \frac{k_0^2}{\chi^2}) E_0^\sigma + F_0^\sigma \cdot E_1^\sigma = 0
$$

(11)

$$
F_0^\sigma \cdot E_0^\sigma + (1 - \frac{k_1^2}{\chi^2}) E_0^\sigma = 0
$$

(12)

with $F_0^\sigma = \frac{\tilde{\alpha}_0^\sigma}{\tilde{\alpha}_1^\sigma} \frac{\tilde{\alpha}_0^\sigma}{\tilde{\alpha}_1^\sigma}$

(13)

The dispersion equations are:

$$
(1 - \frac{k_0^2}{\chi^2}) (1 - \frac{k_1^2}{\chi^2}) = F_0^\sigma \cdot F_0^\sigma \quad \text{for the } \sigma \text{ direction}
$$

(14)

$$
(1 - \frac{k_0^2}{\chi^2}) (1 - \frac{k_1^2}{\chi^2}) = F_0^\sigma \cdot F_0^\sigma \quad \text{for the } \sigma' \text{ direction}
$$

(15)

One polarization gives than two couples ($\tilde{\alpha}_0^\sigma$ and $\tilde{\alpha}_1^\sigma$) (by permutation) and we call them ($\tilde{\alpha}_0^\sigma(1)$, $\tilde{\alpha}_1^\sigma(1)$) and ($\tilde{\alpha}_0^\sigma(2)$, $\tilde{\alpha}_1^\sigma(2)$), and the same for $\sigma'$.

So, inside the crystal we get by superposition of the solutions:

$$
\tilde{\mathbf{E}}(\mathbf{r},t) e^{i\omega t} = C_0^\sigma (\tilde{\alpha}_0^\sigma \exp [i2\pi \tilde{\alpha}_0^\sigma(1) \cdot \mathbf{r}] + B_1^\sigma \tilde{\alpha}_1^\sigma \exp [i2\pi \tilde{\alpha}_1^\sigma(1) \cdot \mathbf{r}])
$$

$$
+ C_2^\sigma (\tilde{\alpha}_0^\sigma \exp [i2\pi \tilde{\alpha}_0^\sigma(2) \cdot \mathbf{r}] + B_2^\sigma \tilde{\alpha}_1^\sigma \exp [i2\pi \tilde{\alpha}_1^\sigma(2) \cdot \mathbf{r}])
$$

$$
+ C_0^{\sigma'} (\tilde{\alpha}_0^{\sigma'} \exp [i2\pi \tilde{\alpha}_0^{\sigma'}(1) \cdot \mathbf{r}] + B_1^{\sigma'} \tilde{\alpha}_1^{\sigma'} \exp [i2\pi \tilde{\alpha}_1^{\sigma'}(1) \cdot \mathbf{r}])
$$

$$
+ C_2^{\sigma'} (\tilde{\alpha}_0^{\sigma'} \exp [i2\pi \tilde{\alpha}_0^{\sigma'}(2) \cdot \mathbf{r}] + B_2^{\sigma'} \tilde{\alpha}_1^{\sigma'} \exp [i2\pi \tilde{\alpha}_1^{\sigma'}(2) \cdot \mathbf{r}])
$$

(16)

II.2. Boundary conditions

We know that on the upper surface of the crystal, the incident electric field of the plane wave in direction $\chi$ is $\varepsilon$, and on the lower surface, there is no incident wave with direction $\chi_1$ /11/.

If we make the assumption that we are in normal incidence, or that the index of refraction of the outside region is nearly equal to that of the inside region, then the electric field must be continuous at the surfaces between the two regions. In the experiments described in next section, we are always in such cases. A classical calculation /10,11/ gives then for boundary conditions:

- At the upper surface : $\sum C_p \exp (i2\pi \hat{k}_0^P \cdot \mathbf{r}) \hat{\mathbf{r}}_0^P = \varepsilon_0 \exp (i2\pi \chi \mathbf{r})$

and so $\hat{k}_0^P = \chi + \chi \mathbf{p}$ (for $\hat{k}_0^P \cdot \mathbf{r} = \chi \mathbf{r}$ on the surface)

(17)

and $\varepsilon_0 = \sum C_p \hat{\mathbf{r}}_0^P$

(18)
At the lower surface: \( \sum \beta_p B_p \exp (i2\pi k_1^p \cdot \hat{r}) \hat{n}_1^p = \hat{0} \)

with \( k_1^p = k_1^0 + \hat{z} = \hat{x} + x_p \hat{z} + \hat{y} \) from Bragg law. \( \) (19)

If the origin is taken on the upper surface, with a crystal of thickness \( L \) we get then:

\[ \sum \gamma_p \beta_p B_p \hat{n}_1^p = \hat{0} \] \( \) (20)

or \( \sum \gamma_p C_p \beta_p \hat{n}_1^p = \hat{0} \) \( \) (21)

We now set:

\[ k_0^p = x (1 + \xi_0^p) \] \( \) (22)

\[ k_1^p = x (1 + \xi_1^p) \] \( \) (23)

and \( \delta = \hat{z} (\hat{t} + 2\hat{x}) \) (that measures the departure from Bragg law). \( \) (24)

Then, from equations (17) and (19) we obtain:

\[ \xi_0^p = q^p \cos \theta_0 \] \( \) (25)

\[ \xi_1^p = \frac{\delta}{2} - \xi_0^p \] \( \) (26)

The dispersion equations (14,15) then become:

\[ \xi_0^p (\frac{\delta}{2} - \xi_0^p) = \frac{1}{4} F_o \] \( \) \( \xi_o^* \) for \( p = 1, 2 \)

\[ \xi_0^p (\frac{\delta}{2} - \xi_0^p) = \frac{1}{4} F_o, \xi_o^* \) for \( p = 3, 4 \)

So \( \xi_0^{1,2} = \frac{\delta}{4} \pm \frac{\sqrt{2}}{4} (6^2 - 4|F_o|^2)^{1/2} \) if \( |\delta| \geq 2|F_o| \) \( \) (27)

\[ \xi_0^{3,4} = \frac{\delta}{4} \pm \frac{\sqrt{2}}{4} (4|F_o|^2 - \delta^2)^{1/2} \) if \( |\delta| \leq 2|F_o| \) \( \) (28)

and

\[ \xi_0^{3,4} = \frac{\delta}{4} \pm \frac{\sqrt{2}}{4} (4|F_o|^2 - \delta^2)^{1/2} \) if \( |\delta| \leq 2|F_o| \) \( \) (29)

II.3. Meaning of the experimental data of BPI

All the Bragg reflections from Blue Phases observed up to date seemed to be chiral: if one uses right-handed circularly polarized light under normal incidence, it is strongly reflected, while the left-handed reflection has not been yet detected. So in following we will suppose that left-handed circularly polarized light corresponds to an intrinsic polarization that is not reflected at all. In the calculation this is obtained by making \( F_o = 0 \) (or \( F_{o'} = 0 \)). Then only one intrinsic polarization is reflected.

Furthermore, when \( \theta_0 = 0 \) (normal incidence), observing in back reflection \( (\theta_2 = 0) \), the reflected polarization is circular so if \( F_o = 0 \), we also get:

\[ n_1^{o'} = \frac{1}{\sqrt{2}} (e_1^1 + i e_2^1) e^{i\eta} \]

Using these two conditions and the boundary conditions, we can then calculate the reflected intensity, in the case \( \theta_0 = 0 \).
II.4. Reflected intensity with normal incident light

If the incident electric field has the polarization:
\[ \hat{e} = \cos \varphi \hat{e}_1 + e^{i\beta} \sin \varphi \hat{e}_2 \]

We set:
\[ A^2(\alpha, \beta) = \left| \frac{\det (\tilde{n}_0, \hat{e})}{\det (\tilde{n}_0, \tilde{n}_0)} \right|^2 \]

Then a fastidious calculation using the above conditions gives, if the incident intensity is \( I_0 \):

\[ I(\lambda) = I_0 A^2(\alpha, \beta) \frac{\cosh \left( 2\pi \lambda L \left| 4|F_\sigma| - \delta^2 \right|^{1/2} \right) - 1}{\cosh \left( 2\pi \lambda L \left| 4|F_\sigma| - \delta^2 \right|^{1/2} \right) + 1 - \frac{\delta^2}{2 |F_\sigma|}} \]

For \( \delta = 0 \), this gives:
\[ I_{\text{max}} = I_0 A^2(\alpha, \beta) \frac{\cosh \left( 2\pi \lambda L |F_\sigma| \right) - 1}{\cosh \left( 2\pi \lambda L |F_\sigma| \right) + 1} \]

And for \( |\delta| = 2|F_\sigma| \) this gives:
\[ I_{2|F_\sigma|} = I_0 A^2(\alpha, \beta) \frac{1}{1 + \frac{1}{\pi^2 \chi^2 L^2 |F_\sigma|^2}} \]

If \( L \) is small enough (less than hundred times the lattice constant) the spectra shows the well-known Pendelösung beats, with minima related by:
\[ \cos \left( 2\pi \lambda L \left| 4|F_\sigma| - \delta^2 \right|^{1/2} \right) + 1 \]

or \( \delta^2 = 4|F_\sigma|^2 + \frac{4k^2}{\chi^2 L^2} \) with \( k \) integer.

We have \( \tau = \frac{2}{\lambda_{\text{max}}} \) and \( \chi = \frac{1}{\lambda} \) so with equation (24) we get:
\[ \left( \frac{\Delta \lambda}{\lambda_{\text{max}}} \right)^2 = \frac{k^2 \lambda_{\text{max}}^2}{4 L^2} + \frac{|F_\sigma|^2}{4} \]

II.5. Discussion of theoretical results

Using equations (33) and (34), we have computed numerically the spectra of the relative intensity \( I(\lambda)/I_0 A^2 \) for several values of the crystal thickness \( L \) (\( nL = 10, 30, 50 \) and \( 70 \) \( \mu m \)) and for four different values of the parameter \( F_\sigma \) (\( F_\sigma = mx 0.0145 ; m = 1, 2, 3, 4 \)). The central wavelength \( \lambda_{\text{max}} = 567 \) nm was chosen to correspond to the \( \{110\} \) reflection observed experimentally (section III.2). These theoretical spectra (in Fig. 2) show the Pendelösung beats which, as indicated by equation (37) are denser either for larger thickness \( L \) or for larger amplitudes \( \epsilon_\tau \) (\( F_\sigma \) is related to \( \epsilon_\tau \) by equation (13)) of the dielectric constant. The central peak, for large values of \( L \) or \( F_\sigma \), has a finite width and shows a flattening of its top. The general shapes of these spectras, are in agreement with previous theoretical works concerning Blue Phases (Belyakov /8/ /14/) cholesteric liquid crystals (Chandrasekhar /12/) or X ray
Fig. 1 - (la) Conditions of the theoretical calculation 
(1b) Triedras referred to incident and reflected plane waves inside the crystal diffraction by ordinary crystals (Zachariasen /13/). It is important to emphasize that this similarity with the case of X-ray diffraction rests on the condition that only one of eigen polarizations, $a'$, was supposed to be reflected.

In general, in the case of the Blue Phases, the reflectivity coefficient $F_\sigma$ of the other eigen polarization $\alpha$ is certainly much smaller than $F_\sigma'$, \((F_\sigma/F_\sigma') < 10^{-1}\) but in the limit of a thickness $L$ large enough, it could give rise to a measurable Bragg reflection.

If one supposes that the incident beam is not polarized, then the reflected intensity can be calculated as a simple superposition of two spectra $I_{\sigma'}(\lambda)$ and $I_\sigma(\lambda)$ corresponding to the same parameters of equations (33) and (34) except for $F_\sigma$ which should be taken much smaller than $F_\sigma'$. The total intensity $I(\lambda) = I_{\sigma'}(\lambda) + I_\sigma(\lambda)$ should then show a narrow peak, corresponding to $F_\sigma'$, sitting on the large peak corresponding to $F_\sigma'$, as depicted in Figure 3. This result is in agreement with an analogous plot shown in Figure 2 of the paper by Belyakov /8/.

III - DETERMINATION OF THE ORDER PARAMETER COMPONENTS

III.1. Nucleation and growth of perfect BPI monocrystals

In a recent article /9/, we have pointed out that large perfect facetted monocrystals of BPI, coexisting with the isotropic phase, can be grown in a material being a mixture of 58.8% CB 15 in ZLI 1840. In presence of a small temperature gradient, the equilibrium shape of monocrystals grown on glass surfaces is well adapted for the present study of Bragg reflection. In these conditions, the facet parallel to the glass surface (perpendicular to the temperature gradient) is much larger than all other facets so that the monocrystal acts on light as a lamella of perfectly uniform thickness $L$. Moreover, their orientation with respect to the glass surface can be determined without ambiguity from their shapes. We have found that BPI monocrystals are oriented preferentially with (110) or (211) facets parallel to the glass surface $S$. 
Fig. 2 - Theoretical spectra of the reflected intensity when $F_0 = 0$. Each figure is made for a given value of the thickness $L$ of the crystal:
A. $L = 7300$ nm; B. $L = 21900$ nm; C. $L = 36500$ nm; D. $L = 51100$ nm and four different values of $|F_\sigma'|$: a. $|F_\sigma'| = 1.45 \times 10^{-2}$; b. $|F_\sigma'| = 2.9 \times 10^{-2}$; c. $|F_\sigma'| = 4.35 \times 10^{-2}$; d. $|F_\sigma'| = 5.8 \times 10^{-2}$.

The wavelength of the maximum is $\lambda = 567$ nm like in experiments.

We have drawn $R = \frac{I}{I_0 A^2}$ vs. $\Delta \lambda$ where the origin of $R$ is waving of 0.1 when passing from one spectrum to the following one.
Theoretical spectra of the reflected intensity with $|F_\sigma| = \frac{1}{10} |F_\sigma'|$ for two different values of the thickness $L$ of the crystal: A. $L = 21900$ nm; B. $L = 43800$ nm and for the same four different values of $|F_\sigma'|$ as on Fig. 2.

III.2. Measurements of $F_\sigma$, corresponding to (110) reflection

Using a microspectroscope (see the present proceedings), we have measured the spectra of light reflected under normal incidence from such flat monocrystals of the orientation (110) // S. Using a monochromator of a bandwidth $\delta \lambda = 2$ nm, we have obtained spectra, shown in Fig. 4, for crystals of thickness ranging between 10 $\mu$m and 30 $\mu$m. All spectra show both the Pendellösung beats and the finite width of the central peak predicted theoretically in the previous section.

In order to determine the amplitude of the order parameter, we have proceeded as follows:

First, by plotting $(\frac{\Delta \lambda_k}{\lambda_{\text{max}}})^2$ vs. $k^2$ ($\lambda_k$ is the wavelength of the $k^{\text{th}}$ minimum) we have verified that the theoretical relationship given by equation (37) is satisfied (figure 5). From the slopes of the linear plots we have determined the values of the product $\lambda_{\text{max}} L$ for each of the spectra.

Then, knowing $\lambda_{\text{max}} L$, we have calculated the value of $F_\sigma'$, on each spectra by a succession of approximations: a value of $F_\sigma'$, gives us $\frac{I_2 |F_\sigma'|}{I_{\text{max}}}$ and we find on the given spectrum the corresponding width $\Delta \lambda_F$. The iterative process was well converging and we stopped the iteration when $\frac{\Delta \lambda_F}{\lambda_{\text{max}}} = |F_\sigma'| \pm 1\%$. The average value for $F_\sigma'$ was found:

$|F_\sigma'| = 1.45 \times 10^{-2} \pm 10^{-3}$
This value of $F_{\text{a}}$, determined experimentally, was used precisely in computing the theoretical spectra shown previously in Fig. 2. When comparing these spectra with experimental ones, one observes first of all that Pendelössung beats are less deep in experiments than in theory. This effect, due to the finite monochromator bandwidth, can be calculated by a convolution of the theoretical spectra (equations (33) and (34)) with a triangular shaped pass-band of the monochromator. The resulting convoluted spectra, shown in figure 6 are in a much better agreement with the experimental ones.

The second observation concerns the shape of the top of the central peak. It does not seem to have a tendency to flatten for large thicknesses but on the other hand, it does not show any marked narrow peak which could be attributed to the contribution of the second eigen polarization $\sigma$. We concluded that the value of $F_{\sigma}$ must be less than $F_{\text{a}}$, by a factor larger than 10.

III.3. Calculation of $\tilde{r}_{110}$ in the $0_8$ space group

In ref. 8, Belyakov has given on Table 1 the restrictions imposed by the symmetry on the components of $\tilde{r}$ for different cubic space groups. Following Belyakov, let us
choose the coordinate frame in the following manner: the axes $x$, $y$, $z$ are parallel to the edges of the cubic unit-cell, and the origin lies on a three fold axis (Fig. 7a).

Most of experimental and theoretical studies indicate that BP1 has a cubic centered Bravais lattice and its space group assignment is $O_8$. This comes from Laudau theory approach /7/ as well as from the experiments on crystal habit /9/. In this paper, we will therefore interpret our results of the dynamical light scattering as due to a
The general form of the Fourier component $\tilde{\varepsilon}_{110}$ compatible with the $O_8$ space group, given by Belyakov, is:

$$
\tilde{\varepsilon}_{110} = \begin{bmatrix}
    iI & iI_1 & R \\
    iI_1 & iI & -R \\
    R & -R & -2iI
\end{bmatrix}
$$

(38)

where $I, I_1, R$ are real parameters to be determined.

In agreement with the experimental condition of the normal incidence ($\theta_0 = 0$) we take (Fig. 7b):

$$
\tilde{\varepsilon}_{e0}^1 = \frac{\vec{Y} - \vec{X}}{\sqrt{2}} \quad \text{and} \quad \tilde{\varepsilon}_{e1}^1 = \vec{Z}
$$

The above mentioned experimental fact that only one $(\sigma')$ of the eigen polarizations is strongly reflected, reduces the number of the independent parameters. The theoretical approximation $F_{\sigma} = 0$ leads to the following relation:

$$
R^2 = I(I - I_1)
$$

(39)

Also the fact that the reflected eigen polarization $\sigma'$ is circular gives a second relation:

$$
R/\vec{Z} = I - I_1
$$

(40)

With the one independent parameter left we get:

$$
\tilde{\varepsilon}_{110} = I_0 \begin{bmatrix}
    i/2 & -i/2 & -i/21/\sqrt{2} \\
    -i/2 & 1/2 & -1/\sqrt{2} \\
    1/\sqrt{2} & -1/\sqrt{2} & -i
\end{bmatrix}
$$

(41)

Using the definition of $F_{\sigma}$, (equation (13)) we calculate:

$$
|F_{\sigma'}| = 2 \sqrt{I_0} \varepsilon = 0.0145 \pm 10^{-3}
$$

Fig. 7 - (7a) coordinate frame used for calculations of $\tilde{\varepsilon}_{110}$ and $\tilde{\varepsilon}_{200}$

(7b,c) Vectors $\tilde{\varepsilon}_{110}^1$ of the wave planes of the incident and reflected waves inside the crystal for (110) reflection (b) and (200) reflection (c).
III.4. Calculation of \( \varepsilon_{200} \) in the O\(_8\) Space Group

From Belyakov, the general form of \( \varepsilon_{200} \) compatible with the O\(_8\) space group is:

\[
\varepsilon_{200} = \begin{bmatrix}
0 & 0 & 0 \\
0 & R & iI \\
0 & iI & -R
\end{bmatrix}
\]

when R and I are real parameters. (42)

Again in agreement with the experimental condition \( \theta_0 = 0 \), we take (Fig. 7c):

\[
\varepsilon_0 = \gamma, \quad \varepsilon_1 = \hat{\gamma} \\
\varepsilon_2 = \hat{\gamma}, \quad \varepsilon_1 = \gamma
\]

The condition that \( F_0 = 0 \) implies that \( R = I \) (This condition corresponds to the same chirality of reflection as that for (110) reflection in the above paragraph).

Then \( \eta_{10}' \) is automatically a circular polarization. We have then from equation (13)

\[
|F_0| = \frac{2|R|}{\varepsilon}
\]

and \( \varepsilon_{200} = R \)

\[
\begin{bmatrix}
0 & 0 & 0 \\
0 & 1 & i \\
0 & i & -1
\end{bmatrix}
\]

(43)

So if we would get spectra from a perfect monocrystal with the suitable orientation (planes (200) parallel to the glass surface), we could obtain the value of R. Here the results about polarization implied a drastic simplification of the component \( \varepsilon_{200} \), with just one independent parameter left (and the same for \( \varepsilon_{110} \)). Unfortunately, up to date, the spectra we got from perfect monocrystallites with this orientation differ from the ideal theoretical shapes for two main reasons: (1°) the crystals of such an orientation have been only nucleated in volume so that their orientation changes very easily under Brownian rotational motion; (2°) their forms, as seen from (100) direction are not flat because the (100) facets are missing /9/. Consequently, the interpretation of these spectra in view of determining the value of \( \varepsilon_{200} \) is not possible using the present theory.

IV - CONFRONTATION WITH LANDAU THEORY

IV.1. Components (110) and (200) of the order parameter

As we have shown in the previous section, experimental results concerning polarization of reflected light at normal incidence, applied to the O\(_8\) group, lead to a drastic simplification of the components \( \varepsilon_{110} \) and \( \varepsilon_{200} \) (eq. (41) and (43)) of the order parameter.

Other Fourier components of the series (1) corresponding to the same type of reciprocal lattice vector, can be obtained from \( \varepsilon_{110} \) and \( \varepsilon_{200} \) by applying the symmetry operations of the O\(_8\) group (Fig. 8). For instance, if one makes a translation of the origin from \((0,0,0)\) to \((1/4,3/4,1/4)\) and a rotation of axes of 90° around \( \gamma \), in the new coordinates frame \( \varepsilon_{020} \) is the same as was \( \varepsilon_{200} \) in the original frame. By this mean, we can calculate contributions of all terms of type (110) ((1TO), (011), ...) id est 12 terms, to the order parameter:

\[
\varepsilon(110) = -2T_0 \begin{bmatrix}
\varepsilon_2-3s_2C_3, & \varepsilon_2S_2S_3+C_1C_3-S_2C_1, & \varepsilon_2C_3C_2+S_1-S_2, & \varepsilon_2C_3C_2+S_1, \\
\varepsilon_2S_2S_3+C_1C_3-S_2C_1, & \varepsilon_2-3s_2C_1, & \varepsilon_2C_3C_2+S_1-S_2, & \varepsilon_2C_3C_2+S_1, \\
\varepsilon_2S_2S_3+C_1S_2-S_1C_3, & \varepsilon_2C_3C_2+S_1S_2-S_3C_3, & \varepsilon_2-3s_1C_2
\end{bmatrix}
\]

(44)
Fig. 8 - A cubic unit-cell of the $O_8$ symmetry space group showing all the axes of symmetry.

where $C_1 = \cos qx, ...$

$S_1 = \sin qx, ...$ and $q = 2\pi/a$, $a$ being the lattice constant

and $E_2 = S_1C_2 + S_2C_3 + S_3C_1$

The expression (44) is exactly the same as that found by Hornreich and al./7/, keeping only the lowest energy harmonic (110) in a Landau theory approach.

The contribution of the six terms of type (200) is:

$$\tilde{\epsilon}(200) = \begin{bmatrix}
  C_3' - C_2' & -S_3' & -S_2' \\
  -S_3' & C_1' - C_3' & -S_1' \\
  -S_2' & -S_1' & C_2' - C_1'
\end{bmatrix}$$ (45)

where $C_1' = \cos 2qx ...$

$S_1' = \sin 2qx ...$

and is also in agreement with that found by Hornreich et al./7/. So far, the optical theory, taking into account experimental datas, fits very well the Landau theory in the sense that only the spherical harmonics of lowest energy ($m = 2$) are present in each component $\tilde{\xi}_r$ of the order parameter.

If measurements of the ratio $I_0/R$ were possible, then we should be able to compare it to the ratio obtained by the Landau theory of minimization of the free energy.

IV.2. Visualization of the order parameter

Although the analytic expressions (44) and (45) of the order parameter $\tilde{\xi}_r(\hat{r})$ have been derived above, it is still not easy to imagine what is a 3D orientational order
corresponding to them. Therefore we have developed a graphic representation of the tensorial order parameter. At each point of the unit cell, the tensor $\varepsilon(r)$ is diagonalized and represented by plotting a brick, which orientations are eigen directions of the tensor $\varepsilon(r)$ and dimensions are proportional to the corresponding eigen values.

Using only the first matrix (eq. (44)), corresponding to the contribution of terms of (110) type, we have got the results of figure 9. This visualization is a very convenient way to find the place of disclination lines in the lattice and to determine of what kind they are. If one looks in (111) direction (Fig. 9b) and turns around such a three fold axis, one can see there is a $s = -1/2$ disclination near to it. The three-fold axis is necessarily a place where the dielectric tensor is uniaxial, so the disclination line (where the tensor must also be uniaxial) is situated precisely on the three-fold axis.

**Fig. 9a** - A cubic unit-cell where only planes of type (100) are drawn. Binary axes are indicated by (b), screw axes of the same sign as that of cholesteric twist are indicated by (+), screw axes of the opposite sign by (-).

In the $O_8$ group of symmetry, there are two sorts of screw axes of opposite sign parallel to the (100), (010) and (001) directions (Fig. 8). One of those signs is
Also the sign of the natural twist of the cholesteric material. Around that type of axis, one cannot see any disclination, but around the other type of screw-axis, there is a disclination of strength - 1/2 (Fig. 9c). If one looks at the matrix, one can see that along such a screw-axis, the tensor is not uniaxial, thus the disclination line is not on it. Moreover, on fig. 9b, one can see that the tensor turns there twice faster than just off the axis, and in the opposite sense. By computing $\varepsilon(r)$ in the neighbourhood of this screw axis, we have found that the order parameter is uniaxial on a spiral line that turns three times around the screw axis over a lattice period, and in the sense of the cholesteric twist (which is the opposite sign of that of the screw axis itself). Over that period, tensor on the screw axis turns of $-2\pi$, while off the axis it turns of $+\pi$. The rotation of $6\pi$ of the spiral line around the screw axis is the minimum rotation imposed by the symmetry corresponding to the screw axis, and over a period, the disclination turns of $16\pi/3$ around the spiral line to allow the opposite rotations of the tensor described just above (Fig. 10). This result is quite an interesting one, you cannot find by only looking at the matrix (44), so visualization of such tensors is very helpful for comprehension of the orientational order in BPI in such a model.

V - CONCLUSIONS

In this paper, we have tried to develop the dynamical theory of light diffraction in its application to BPs in our original way, taking into account the experimental results on polarization of Bragg reflected light on BPs. From experimental spectras
obtained on large perfect monocrystals, and from their comparison with the theoretical ones, we have deduced the first measurement of the Fourier component $\xi_{110}$, and shown that one of the two eigen polarizations was certainly very weakly reflected while the other one was strongly. Further measurements of the polarization of the reflected light are necessary and being developed, to evaluate the exact contribution of the $\sigma$ polarization to the Bragg reflections.

Measurements for other Fourier components such as (200), (211) and (220) need important modification of the experience, because under normal incidence, multiple reflections occur that forbid easy interpretation of experimental spectra, while with oblique incidence, it is possible to avoid such multiple reflection. Such experiments will be developed in the near future.

Then a more precise confrontation with theory than that done in section IV.1 will be possible and perhaps will allow to distinguish within the various models /15, 16/ what is the most realistic.

We wish to acknowledge R.M. Hornreich for stimulating discussions and P.P. Crooker for a private communication about multiple reflections. Last, but not least, we want to underline that this work could not have been done without the contribution of P. Cladis who gave us the material and stimulated our interest about that study.
Fig. 10 - Spiral disclination line round a screw axis of opposite sign of that of the cholesteric twist. Along the screw axis the tensor turns of $-2\pi$ over a period while off the axis, it turns of $+\pi$ over the same period. The spiral makes three turns around the screw axis over a period because of the $4_1$ symmetry.

REFERENCES

/10/ Batterman B.W. and Cole H., Rev. Of Mod. Phys. 36 (1964) 681
In the expression given by Belyakov in (8), p. 326, we have noticed that $P$ should be equal to $\sin^2(\chi L)\Delta^2 b_{\alpha} + \sin^2(\chi L)\Delta^2 \frac{1}{|F_{\alpha}|^2}$ and not to $\sin^2(\chi L)\Delta^2 b_{\alpha} + \sin^2(\chi L)\Delta^2 \frac{1}{|F_{\alpha}|^2}$. 