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Blue Phase one : first optical measurements of the order parameter

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Résumé. — Nous avons développé récemment une méthode de nucléation de gros monocristaux parfaits de Phase Bleue sur des surfaces de verre. Nous avons obtenu des spectres de lumière réfléchie sur de tels monocristaux de Phase Bleue I et montrons qu'ils peuvent être interprétés à l'aide de la théorie dynamique de la diffraction. Confrontant la théorie avec nos résultats expérimentaux, nous en déduisons la première mesure directe de la composante de Fourier dans la direction $\langle 110 \rangle$ du paramètre d'ordre de la Phase Bleue I.

Abstract. — We have recently developed a method of nucleation of large perfect monocrystallites of Blue Phases on glass surfaces. We have obtained spectra of Bragg-reflected light on such crystallites of BPI and show that they can be very easily interpreted in terms of the dynamical theory of light diffraction. From a comparison of this theory with our experimental data, we obtain the first direct measurement of the Fourier component in the direction $\langle 110 \rangle$ of the order parameter of BPI.

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 the wavelength of visible light [1-6]. However, in contrast with ordered suspensions like colloidal crystals, where one cubic unit-cell contains only two colloidal particles, one cubic unit-cell of the Blue Phase I (or II) contains about 10^7 rod-shaped chiral molecules. Moreover, the molecular order in Blue Phases is not positional but orientational : 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 allow one to consider Blue Phases as a continuum where the dielectric tensor $\hat{\epsilon}(\mathbf{r})$ is a smooth function of the position $\mathbf{r}$. Because of the periodicity of the lattice, one can develop $\hat{\epsilon}$ in a Fourier series [7, 8] :

$$\hat{\epsilon}(\mathbf{r}) = \epsilon \hat{I} + \sum_{\tau} \hat{\epsilon}_{\tau} e^{i2\pi\tau \cdot \mathbf{r}} \quad (1)$$

where τ 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 $\hat{I}$ because of the non-birefringence of BPI.

$\hat{\epsilon}(\mathbf{r}) - \epsilon_i$ may be chosen as the order parameter of the phase because it is a traceless tensor which is zero in the isotropic phase [7, 8].

Very recently [9], we have shown that it was possible to grow large perfect monocrystallites of BPI by nucleation on glass surfaces in the presence of a small temperature gradient. It seemed thus very interesting to try to obtain spectra of Bragg reflected light on such monocrystallites to interpret them in terms of the general theory of dynamical light diffraction and to extract direct information about the order parameter in BPI. In the present paper, we report the first experimental spectra obtained in back reflection (under normal incidence) on planes (110) of a large defectless monocrystallite of 58.8 % CB 15 in ZLI 1840 and, comparing them with theoretical spectra obtained by a calculation that will be detailed elsewhere [10], we determine the amplitude of the Fourier component $\hat{\epsilon}_{110}$.

Practically, application of the dynamical theory of light scattering is 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. Furthermore, in the presence of a small temperature gradient, the equilibrium shape of monocrystals grown on glass surfaces is well adapted for the present study because under such conditions, the facet parallel to the glass surface (perpendicular to 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, its orientation with respect to the glass surface can be determined without ambiguity from its shape. We have found that BPI monocrystals are oriented preferentially with (110) or (211) facets parallel to the glass surface S [9]. To apply the dynamical theory in an easy way, one must moreover ensure that there is only one Bragg reflection that occurs inside the crystal. In the case of normal incidence, double reflection of type (110)/(101) occurs [11] in the conditions of the (211) reflection, while no multiple reflection can occur in the conditions of the (110) reflection because it is the longest wavelength reflection from a BCC lattice. We have therefore worked only on perfect monocrystals with (110) facets parallel to the glass surface (Fig. 1).

Using a monochromator of a bandwidth $\delta\lambda = 2$ nm, we have obtained spectra shown in figure 2, for crystals of thicknesses ranging between 10 μm and 30 μm . All spectra shown both the well-known Pendellösung beats and a finite width of the central peak.

Following the approach made by Belyakov [8], we have developed a theoretical calculation [10] of those spectra that takes into account the very important experimental fact that all the Bragg reflections from Blue Phases observed 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 yet been detected. Thus, in the calculation, we suppose that left-handed circularly polarized light corresponds to an intrinsic polarization [8, 10] (σ) that is not reflected at all, while the other intrinsic polarization (σ') is a right-handed circular one of magnitude $F_{\sigma'}$, where $F_{\sigma'}$ is directly related to the tensorial Fourier component $\hat{\epsilon}_{110}$ of the order parameter [10]. With these hypotheses, using the notations of table 1 from the paper by Belyakov *et al.* [8], in the case of the O_8 symmetry group, we find that $|F_{\sigma'}| = 2 \frac{|I - I_1|}{\epsilon}$ and that $\begin{cases} R\sqrt{2} = I - I_1 \\ R^2 = I(I - I_1) \end{cases}$, so that the measurement of $F_{\sigma'}$ leads to the complete determination of $\hat{\epsilon}_{110}$. From the theory, we obtain the following expression of the reflected intensity $I(\lambda)$, if I_0 is the incident intensity and A^2 a term that concerns the incident polarization and is constant over all the experiments we have done:

$$- \delta < 2 |F_{\sigma'}|$$

$$I(\lambda) = I_0 A^2 \frac{\text{ch}[\pi\chi L(4 |F_{\sigma'}|^2 - \delta^2)^{1/2}] - 1}{\text{ch}[\pi\chi L(4 |F_{\sigma'}|^2 - \delta^2)^{1/2}] + 1 - \frac{\delta^2}{2 |F_{\sigma'}|^2}}. \quad (2)$$

a)

b)

c)

Fig. 1. — Fig. 1a shows one large-faceted monocrystal of BPI grown in a sample of 58.8 % CB 15 in ZLI 1840 submitted to a small vertical temperature gradient. The three-dimensional polyhedral shape of this monocrystal is represented schematically in two orthogonal projections on Figs. 1b and 1c. The facet (110) perpendicular to the thermal gradient is much larger than the others. Because the projection of the output slit of the monochromator (shaded rectangular area, on Fig. 1b) is smaller than the facet (110), the light is Bragg-reflected by a parallel monocrystalline slab of a well-defined thickness L , as required in the dynamical theory presented here. Fig. 1c shows that this largest facet (110) is parallel to the glass surface, and the incident light is perpendicular to it. These are conditions of back reflection under normal incidence assumed in the theory.

$$- \delta > 2 |F_{\sigma'}|$$

$$I(\lambda) = I_0 A^2 \frac{1 - \cos [\pi \chi L (\delta^2 - 4 |F_{\sigma'}|^2)^{1/2}]}{\frac{\delta^2}{2 |F_{\sigma'}|} - 1 - \cos [\pi \chi L (\delta^2 - 4 |F_{\sigma'}|^2)^{1/2}]} \quad (3)$$

where $\chi = \frac{1}{\lambda}$, L is the thickness of the crystal and δ measures the departure from Bragg law :

$$\delta = \frac{(\chi + \tau)^2 - \chi^2}{\chi^2} = \frac{\tau(\tau + 2\chi)}{\chi^2} \quad (4)$$

χ being the incident wave vector and τ the reciprocal lattice vector of the reflection.

For $\delta = 0$ this gives :

$$I_{\max} = I_0 A^2 \frac{\text{ch}[2 \pi \chi L |F_{\sigma'}|] - 1}{\text{ch}[2 \pi \chi L |F_{\sigma'}|] + 1} \quad (5)$$

And for $\delta = 2 |F_{\sigma'}|$:

$$I_{2|F_{\sigma'}|} = I_0 A^2 \frac{1}{1 + \frac{1}{\pi^2 \chi^2 L^2 |F_{\sigma'}|^2}} \quad (6)$$

Minima of the Pendellösung beats are related by :

$$\delta^2 = 4 |F_{\sigma'}|^2 + \frac{4 k^2}{\chi^2 L^2}; \quad k = 1, 2, 3... \quad (7)$$

With (4), this gives :

$$\left(\frac{\Delta \lambda}{\lambda_{\max}} \right)^2 \cong \frac{k^2 \lambda_{\max}^2}{4 L^2} + \frac{|F_{\sigma'}|^2}{4} \quad \text{where} \quad \Delta \lambda = \lambda - \lambda_{\max} \quad (8)$$

Using equations (2) and (3), we have numerically computed 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 $70 \mu\text{m}$) and for four different values of the parameter $F_{\sigma'}$ ($F_{\sigma'} = m \times 0.0145$; $m = 1, 2, 3, 4$). The central wavelength $\lambda_{\max} = 567 \text{ nm}$ was chosen to correspond to the (110) reflection observed experimentally (Fig. 2). These theoretical spectra (Fig. 3) show the Pendellösung beats which, as indicated by equation (8), are denser either for larger thicknesses L or for larger amplitudes $|F_{\sigma'}|$. 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 spectra are in agreement with previous theoretical work concerning Blue Phases [8], cholesteric liquid crystals [12] or X-ray diffraction by ordinary crystals [13]. It is important to emphasize that this similarity with the case of X-ray diffraction rests on the condition that only one of the eigen-polarizations, σ' , was supposed to be reflected. In general, in the case of the Blue Phases, the reflectivity coefficient $F_{\sigma'}$ of the other eigen-polarization σ 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 (2) and (3) except for F_{σ} which should be taken much smaller

Fig. 2. — Experimental spectra of light Bragg-reflected by planes (110) of a large monocrystal in conditions of normal incidence and back reflection. The wavelength of the maximum is $\lambda = 567$ nm. The thickness L of the crystal varies as follows : A — $L = 9\,800$ nm ; B — $L = 11\,400$ nm ; C — $L = 12\,900$ nm ; D — $L = 17\,900$ nm ; E — $L = 21\,400$ nm ; F — $L = 28\,100$ nm. The vertical scale of intensity is arbitrary but the same for all of the spectra.

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_{σ} , as depicted in figure 4. This result is in agreement with an analogous plot shown in figure 2 of the paper by Belyakov [8].

In order to determine the amplitude of the order parameter from the experimental spectra we have proceeded as follows :

— First, by plotting $\left(\frac{\Delta\lambda_k}{\lambda_{\text{max}}}\right)^2$ vs. k^2 (λ_k is the wavelength of the k th minimum) we have verified that the theoretical relationship given by equation (8) is satisfied.

Fig. 3. — Theoretical spectra of the reflectivity $R = \frac{I}{I_0 A^2}$ calculated for $F_o = 0$. Each figure is made for a given value of the thickness L of the crystal and for four different values of $F_{\sigma'}$: A — $L = 7\,300$ nm; B — $L = 21\,900$ nm; C — $L = 36\,500$ nm; D — $L = 51\,100$ nm. a — $F_{\sigma'} = 1.45 \times 10^{-2}$; b — $F_{\sigma'} = 2.90 \times 10^{-2}$; c — $F_{\sigma'} = 4.35 \times 10^{-2}$; d — $F_{\sigma'} = 5.80 \times 10^{-2}$. The wavelength of the maximum, $\lambda = 567$ nm, was chosen to be the same as in experiments. Plots b, c and d are shifted vertically by 0.1, 0.2 and 0.3 respectively.

Fig. 4. — Theoretical spectra of the reflectivity R calculated for $F_{\sigma} = \frac{F_{\sigma'}}{10}$, for two different values of the thickness L of the crystal : A — $L = 21\,900$ nm ; B — $L = 43\,800$ nm and for four values of $F_{\sigma'}$ (the same as in Fig. 3).

From slopes of the linear plots we have determined the values of the product $\chi_{\max} L$ for each spectrum.

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

$$|F_{\sigma'}| = 1.45 \times 10^{-2} \pm 10^{-3}.$$

This value of $F_{\sigma'}$, determined experimentally, was used precisely in computing the theoretical spectra shown in figure 3. When comparing these spectra with experimental ones, one observes first of all that Pendellösung 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 (Eqs (2) and (3)) by a triangularly shaped pass-band of the monochromator. The resulting convoluted spectra, shown in figure 5, 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 σ . We concluded that the value of F_{σ} must be less than $F_{\sigma'}$ by a factor larger than 10.

In conclusion, we reported here the first direct measurement of one component of the order parameter in BPI. In the case of the (110) reflection, precise experimental measurements of the polarization of reflected light are being developed to determine the exact contribution of the

Fig. 5. — Convolution of the theoretical spectra of Figs. 3B and 3D by the triangularly shaped pass-band of the monochromator set at 2 nm : A — $L = 21\,900$ nm ; B — $L = 51\,100$ nm.

second eigen-polarization σ , and then, studies of BPI under various conditions of oblique incidence of light will probably allow us to get analogous information about other components of the order parameters such as $\langle 211 \rangle$, $\langle 200 \rangle$, or $\langle 220 \rangle$ by avoiding multiple reflections. Then, an interesting and precise comparison of the experimental results with the different theories [7, 14] will be possible.

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