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Experimental evidence for a hexagonal Blue Phase

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Résumé. — On décrit la mise en évidence expérimentale d'une Phase Bleue de symétrie hexagonale. En accord avec les prédictions théoriques de Hornreich *et al.*, cette nouvelle Phase Bleue apparaît dans les cristaux liquides cholestériques de petit pas, d'anisotropie diélectrique positive et soumis au champ électrique d'intensité suffisante. La symétrie de cette phase est $P6_122$ ou bien $P6_222$. La Phase Bleue hexagonale est donc tridimensionnelle à la différence des modèles théoriques.

Abstract. — Experimental evidence for a Blue Phase of hexagonal symmetry is reported. In agreement with a theoretical prediction by Hornreich *et al.*, this new Blue Phase has been found in a short pitch cholesteric liquid crystal of positive dielectric anisotropy submitted to a large enough electric field. Its symmetry, compatible with crystal forms and with Bragg reflections, is either $P6_122$ or $P6_222$. The phase is three-dimensional in contradistinction with the theoretically considered two-dimensional models.

In cholesteric liquid crystals with a short enough pitch, the transition from the isotropic liquid phase (I.L.) to the usual helicoidal phase (C) is mediated by Blue Phases. In the framework of Landau theory, several possible symmetries of Blue Phases have been considered. In the first paper devoted to this problem [1], Brazovski and Dimitriev suggested a two-dimensional hexagonal symmetry (H_2^{2D}). This first possibility was critically examined and discarded by Grebel, Hornreich and Shtrikman [2], who showed that depending upon temperature and chirality, Blue Phases have cubic symmetries $O_5(I432)$, $O_8(I4_132)$ or $O_2(P4_232)$. Studies of Bragg reflections and of facetting, have shown that the last two symmetries correspond to the extensively studied Blue Phases I and II respectively. More recently, the possibility of the existence of a Blue Phase with a modified hexagonal structure (H_m^{2D}), introduced first in reference [3] and examined also in reference [2], was reconsidered by Hornreich *et al.* [4]. They pointed out that this phase should occur in materials, with a large positive dielectric anisotropy $\epsilon_a = \epsilon_{||} - \epsilon_{\perp}$, in a strong enough electric field, E .

In this Letter we present the first experimental evidence for a new Blue Phase, induced by an electric field. This new phase has either $P6_122$ or $P6_222$ symmetry. It resembles the hexagonal phases H_2^{2D} and H_m^{2D} mentioned above but differs in its three-dimensional character, i.e. the 6-fold axis is a screw axis.

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Our observation was made in a mixture of a nematic E9 with 49.3 % of a cholesterogene CB15. The sample was sandwiched between two parallel glass plates coated with semitransparent electrodes. The thickness (d) of the sample was typically 50 μm . The frequency of the applied voltage V was 10 kHz. The observation was made with monochromatic illumination in a reflecting microscope. Other details of the experimental set-up have been described elsewhere [5].

The phase diagram shown in figure 1 was obtained by setting different values of the electric field $E = V/d$ and cooling very slowly ($(dT/dt) < 10^{-2} \text{ }^\circ\text{C/min}$) from the isotropic phase. We found that Blue Phase monocystals nucleate at a given temperature, T_c , and the crystal size increases when the temperature is lowered. In this coexistence region the distinction between the different Blue Phases was evident from their different crystal forms with Bragg reflections of different wavelengths.

In zero field, Blue Phase II was identified by its characteristic crystal shape limited mainly by $\{110\}$ facets and small $\{111\}$ facets which disappeared during growth. In addition only (110) and (111) orientations are seen perpendicular to the glass plates.

Below a critical field E_1 , the effect of the field was to orient BP II monocystals with their fourfold axis $[001]$ parallel to the field [6, 7]. Furthermore, the zero field habit is modified by the appearance of (100) and (010) facets for $E = E_F$. Their size increases, progressively when $E > E_F$ while (110) and $(1\bar{1}0)$ facets decrease. Finally, the wavelength $\lambda_{001}^{\text{BP II}}$ of the Bragg reflection shifts continuously from $\lambda_{001}^{\text{BP II}}(0) = 600 \text{ nm}$ to $\lambda_{001}^{\text{BP II}}(E_1^-) = 628 \text{ nm}$.

At $E = E_1$ there is a discontinuity $\Delta\lambda(E_1)$ as $\lambda_{001}(E)$ jumps from $\lambda_{001}^{\text{BP II}}(E_1^-)$ to a larger value $\lambda_{001}(E_1^+) = 709 \text{ nm}$. The monocystals undergoing the phase transition still had a square shape indicating that the new phase is still oriented with a fourfold axis $[001]$ parallel to the field. It is not yet clear whether this phase is BPI so we call it BPX, for the time being.

For E in a narrow interval between E_2 and E_3 , the Blue Phase crystals nucleating in the isotropic phase obviously had sixfold symmetry (Fig. 2). They grew rapidly in the direction of the sixfold axis to finally form long hexagonal prisms with their bases on the glass plates. In the vicinity of critical fields E_2 and E_3 , these hexagonal crystals coexisted with crystals of BPX and cholesteric phases respectively.

The hexagonal Blue Phase observed is three dimensional. This is evident from the circularly polarized Bragg reflection ($\lambda = 658 \text{ nm}$) exhibited by crystals oriented with their hexagonal axis parallel to the incident light beam. In the Fourier expansion for the order parameter $\hat{\epsilon}(\mathbf{r})$ (the anisotropic part of the dielectric susceptibility tensor) :

$$\hat{\epsilon}(\mathbf{r}) = \hat{\epsilon}_0 + \sum_{\mathbf{q}_\perp} \epsilon_{\mathbf{q}_\perp} e^{i\mathbf{q}_\perp \cdot \mathbf{r}} + \sum_{q_\parallel} \hat{\epsilon}_{q_\parallel} e^{iq_\parallel z}, \quad (1)$$

Fig. 1. — Phase diagram of a 49.8 % mixture of CB15 in E9. The diagram was obtained by setting the voltage V and cooling very slowly from the isotropic liquid phase. The shadowed region of the phase diagram corresponds to the coexistence of different cholesteric phases with the isotropic liquid phase. Monocrystals of BP II, BPX, H and C differ either by their shapes (shown schematically at the top) or by the wavelength of the Bragg reflection (see text).

Fig. 2. — Monocrystals of Hexagonal Blue Phase grown in the isotropic phase (dark background). The monocrystals exhibit brilliant circularly polarized Bragg reflection of wavelength $\lambda = 658$ nm.

besides the first two terms with $\mathbf{q} = 0$ and $\mathbf{q}_\perp$ perpendicular to the hexagonal axis (z) there is a third contribution with wavevector, $\mathbf{q}_\parallel$ parallel to z . Since the Bragg reflected light is circularly polarized in this direction the hexagonal axis is a screw axis.

Of the 27 space groups of hexagonal systems, only $P6_122$ ($P6_522$) and $P6_222$ ($P6_422$) have screw axes compatible with $m = 1$ or $m = 2$ (Ref. [2]) $\hat{\epsilon}_{q_\parallel}$ Fourier components. The choice of $P6_122$ is more general than that of $P6_222$ because it allows both $m = 1$ and $m = 2$ components. The selection rules for Fourier components of the order parameter, required by $P6_122$ and $P6_222$ symmetries, are summarized in figure 3.

The difference between the present model of hexagonal Blue Phases and that considered by Hornreich *et al.* [4] consists in the introduction of the $\epsilon_{q_\parallel}$ component in the Fourier series (1). Despite this difference, the physical reasons for the appearance of the hexagonal Blue Phase, in reference [4], are unchanged. Compared to cubic Blue Phases, the hexagonal phase has an additional $\mathbf{q} = 0$ Fourier component corresponding to a symmetry allowed average dielectric anisotropy, $\hat{\epsilon}_0^H$. In an electric field, the Landau expansion of the free energy has an additional term :

$$F = F_0 - \frac{1}{8\pi} \mathbf{E} \cdot \hat{\epsilon}_0^H \cdot \mathbf{E} \tag{2}$$

which is zero in the case of Blue Phases I and II where the dielectric energy is only fourth order in E [7]. In a large enough field, the dielectric energy term lowers the total free energy of the hexagonal Blue Phases and makes it more favourable than cubic phases. On the other hand,

Fig. 3. — Wave vector $\{q\}$ and eigenvalue (m) dependence of the quadratic part of the Landau energy, showing states $[q, m]$ allowed by $P6_122$ and $P6_222$ symmetries. Note the presence of the $q = 0$ state corresponding to an average dielectric anisotropy of the hexagonal Blue Phase. This figure is to be compared with figure 3 of reference [2] and with theoretical considerations of reference [4].

the helicoidal phase (C) as well as the nematic phase have also average dielectric anisotropies $\hat{\epsilon}_{0C}$ and $\hat{\epsilon}_{0N}$ so they also compete with the hexagonal phase. The Hornreich *et al.* theory, based on the two-dimensional model H_m^{2D} indicates that there is a finite range of fields where the hexagonal phase minimizes the total free energy. The present observations bring a confirmation of this basic physical idea.

Phase diagrams of the cholesteric liquid crystals in an electric field have also been studied recently by Stegemeyer and Porsch [8]. Compared with our results their phase diagram is much simpler as it contains neither the hexagonal phase nor the intermediate phase BPX. Due to the narrow range of its existence, the hexagonal phase can be easily missed. On the other hand, the discontinuity of the Bragg reflection (100) at the transition between BP II and BPX is very clear and confirms the results of Heppke *et al.* [9] contested in reference [8].

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