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## Orientation of crystals of blue phases by electric fields

P. Pierański (\*), P. E. Cladis, T. Garel (\*) and R. Barbet-Massin (\*)

AT & T Bell Laboratories, 600 Mountain Avenue, Murray Hill, 07974 New Jersey, U.S.A.

(\*) Laboratoire de Physique des Solides, Bâtiment 510, Faculté des Sciences, 91405 Orsay, France

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**Résumé.** — On trouve expérimentalement que dans deux systèmes étudiés les monocristaux des Phases Bleues soumis au champ électrique  $E$  s'orientent avec leurs axes  $[100]$  parallèlement à la direction du champ. En analysant la susceptibilité diélectrique non-linéaire, décrite par un tenseur du quatrième ordre, nous démontrons que, suivant son signe, les cristaux des Phases Bleues minimisent leur énergie électrostatique en s'orientant avec leurs axes quaternaires ou ternaires parallèlement au champ.

**Abstract.** — Blue Phases are cubic crystals with large unit cells. In two systems we studied we find experimentally that they orient with their  $[100]$  axis parallel to an electric field,  $E$ . By analysing the non-linear polarizability, which we describe in terms of the relevant fourth rank tensor, we show that cubic blue phase crystals are absolutely stable with their four-fold or threefold axis directed along  $E$ , depending on the sign of this tensor.

### 1. Introduction [1, 2].

In certain mixtures of nematic liquid crystals with a cholesterogenic agent there are large regions ( $\Delta T \sim \text{few } ^\circ\text{C}$ ) on phase diagrams ( $T$  versus concentration) where Blue Phases coexist with the isotropic liquid. Using transmission [3] and reflection [4] microscopy, it has been shown that faceted monocystals of Blue Phases I and II can be grown in these coexistence regions. As shown in figure 1, BPI monocystals are mainly limited by large  $(110)$  and  $(211)$  facets while the crystal habit of BPII is composed mainly of  $(110)$  facets.

Orientations of such monocystals are random when they float in the isotropic liquid but particular orientations occur for crystals nucleated and grown on glass surfaces. BPI crystals are oriented with their  $(110)$  and  $(211)$  facets parallel to the glass surface while crystals of BPII prefer  $(110)$ ,  $(111)$  or  $(100)$  crystal planes parallel to the glass surface (Figs. 1 and 2).

In the present paper we report on the orienting action of a homogeneous electric field on monocystals of Blue Phases. Our experimental results are interpreted in terms of a nonlinear polarizability of Blue Phases in the electric field.

### 2. Experimental

Our experimental set-up is shown schematically in figure 3. The materials were different mixtures, available from Merck, of E9 or ZLI 1840 with CB15.

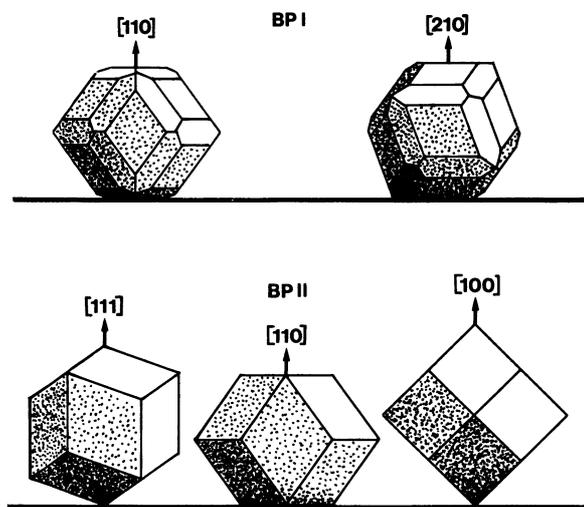


Fig. 1. — Spontaneous orientations of crystals of Blue Phases I and II on glass surfaces.

Typically, in a mixture of 42.5 % CB15 in E9 (sample C in Ref. [4]) only the Blue Phase I occurred between the isotropic liquid and cholesteric phases, while in a mixture of 50 % CB15 in E9 the Blue Phase II, appearing the first under cooling from the isotropic liquid phase, was followed by the Blue Phase I. Due to a multicomponent character of our samples, there was a relatively wide region ( $\Delta T = T_{IL/BP} - T$ ) on phase

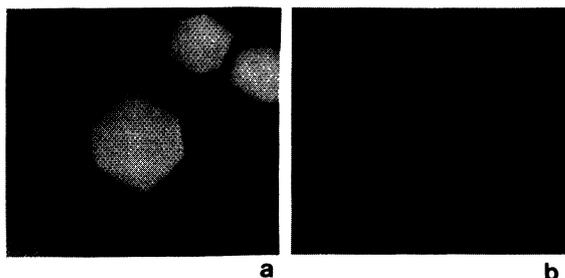


Fig. 2. — Crystals of the Blue Phase II in a mixture of 50 % of CB15 in E9 observed along their two-fold (a) and three-fold (b) axes. This observation combined with the four-fold symmetry shown in figure 4 evidences the  $O(432)$  symmetry of the Blue Phase II.

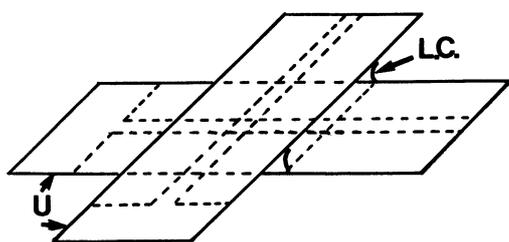


Fig. 3. — Geometry of the experiment.

diagrams where monocrystals of the Blue Phases coexisted with the isotropic phase. In the present paper we are dealing with the behaviour of such monocrystals, surrounded by the liquid isotropic phase, submitted to an electric field. The liquid crystal sample (of a typical thickness 50  $\mu\text{m}$ ) is sandwiched between two parallel glass plates coated with transparent electrodes. The electrodes have shapes of narrow stripes 1 mm wide so that a homogeneous electric field is applied to a small square (1 mm  $\times$  1 mm) region in the centre of the sample where the electrodes overlap. By this means, it is possible to compare the behaviour of BP crystals with and without field. In order to avoid electrohydrodynamic instabilities the frequency of the applied AC voltage was set between 1 and 20 kHz. The observations were made using a transmission microscope in polarized light or a reflection microscope and monochromatic illumination.

### 3. Orientation of BP crystals by a field.

Two different types of experiments are distinguished :

- a) The field is applied to crystals grown without the field.
- b) The field is applied to the completely isotropic sample and crystals are grown in the field.

The first case (a) is more complex as one has to consider the action of the field on crystals with different initial orientations. We have found however that all initial orientations  $[211]_{\text{BPI}}$ ,  $[110]_{\text{BPI}}$ ,  $[111]_{\text{BPII}}$

and  $[110]_{\text{BPII}}$  (Fig. 1) were unstable with respect to the orientation  $[100]_{\text{BPI,BPII}} \parallel \mathbf{E}$ . We have observed that the transition to the stable orientation can take place in two ways :

**3.1 CRYSTALS ROTATE AS A WHOLE.** — This kind of reorientation applied to crystals floating in the isotropic liquid and was most frequent for crystals nucleated on surfaces when their size was smaller than the distance between the two glass plates. In contrast to floating crystals, the orientation of crystals on surfaces required an applied electric field larger than thresholds  $E_{[hkl]}^{\text{BPI,BPII}}$  and different for each of the initial orientations  $[hkl]_{\text{BPI,BPII}}$ . The absolute values of threshold  $E_{[hkl]}$  depended upon the detailed shapes of crystals but, in general, the following relationships were satisfied :

$$\begin{aligned} E_{[211]}^{\text{BPI}} &< E_{[110]}^{\text{BPI}} \\ E_{[111]}^{\text{BPII}} &< E_{[110]}^{\text{BPII}}. \end{aligned} \quad (1)$$

**3.2. REORIENTATION BY MOTION OF A GRAIN BOUNDARY.** — This mechanism occurred in large crystals in contact with both glass plates. The reorientation consisted in the nucleation of a small domain of orientation  $[100] \parallel \mathbf{E}$  on the border of the crystal and in the subsequent slow propagation of the grain boundary. An example of this kind of reorientation is shown in figure 4 where one of the crystals has in its centre a rectangular domain of the initial orientation  $[110] \parallel \mathbf{E}$  which is surrounded by a reoriented region.

In case (b), when crystals were nucleated and grown in a field, the orientation  $[100] \parallel \mathbf{E}$  occurred exclusively.

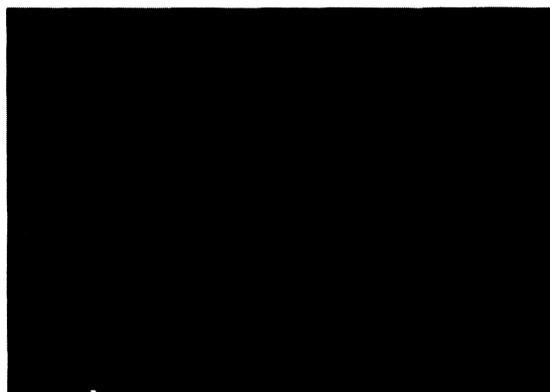


Fig. 4. — Crystals of the Blue Phase II in a mixture of 50 % of CB15 in E9 reoriented by the electric field. The orientation of all crystallites is  $[100] \parallel \mathbf{E}$  except for the one indicated by an arrow. In spite of the four-fold symmetry of the  $[100]$  axis several crystals have allongated rectangular shapes due to two effects : (1) — fusion of neighbouring square crystals ; (2) — reorientation by the field of crystals of different initial orientations. This is evident in particular for the crystal indicated by the arrow where the central rectangular domain has the initial orientation  $[110] \parallel \mathbf{E}$  while the surrounding regions are reoriented by the field.

All observations clearly indicate that both BPI and BPII crystals are oriented by the field in the same way i.e.,  $[100] \parallel \mathbf{E}$ .

**4. Torques due to a nonlinear electric polarization of blue phases.**

Explanation of this orienting action of the electric field involves consideration of a torque  $\Gamma = \mathbf{P} \times \mathbf{E}$  exerted on the polarization  $\mathbf{P}$  by the field  $\mathbf{E}$  [5].

Due to the cubic symmetry  $O(432)$  of Blue Phases their average (zero field) dielectric constant  $\overline{\epsilon_{\alpha\beta}}$  is an isotropic tensor  $\epsilon\delta_{\alpha\beta}$ . The value of  $\epsilon$  must be approximately the same as that of the isotropic fluid coexisting with Blue Phases because in a nonuniform field (when electrodes are not parallel) crystals of Blue Phases do not migrate in the field gradient. Consequently, we suppose that the field inside the crystals is the same as outside.

The polarization  $\mathbf{P}$  induced by the field  $\mathbf{E}$  in a crystal of volume  $V$  is then :

$$P_\alpha = V(\chi_{\alpha\beta} E_\beta + \chi_{\alpha\beta\gamma} E_\beta E_\gamma + \chi_{\alpha\beta\gamma\delta} E_\beta E_\gamma E_\delta + \dots). \quad (2)$$

Due to the above mentioned isotropy of  $\epsilon_{\alpha\beta}(E = 0)$ ,  $\chi_{\alpha\beta}$  is an isotropic tensor and cannot contribute to the orientation of the crystal. The tensor  $\chi_{\alpha\beta\gamma}$  and  $\chi_{\alpha\beta\gamma\delta}$  must be :

1) invariant under operations of the point group  $O(432)$  which characterizes the symmetry of Blue Phases;

2) symmetric with respect to any exchange of indices when the frequencies of all fields  $E_\beta, E_\gamma, E_\delta$  are the same [6].

It has been shown [6] that there is no third rank tensor satisfying these conditions but there are two independent fourth rank tensors  $\chi_{\alpha\beta\gamma\delta}$ .

Let us introduce three orthogonal unit vectors  $\hat{\mathbf{n}}^1, \hat{\mathbf{n}}^2$  and  $\hat{\mathbf{n}}^3$  parallel to fourfold axes of the crystal. Using  $n$ 's and Kronecker symbols two independent symmetric and invariant tensors can be constructed :

$$\chi_{\alpha\beta\gamma\delta}^{(1)} = \sum_{i=1}^3 n_\alpha^i n_\beta^i n_\gamma^i n_\delta^i \quad (4)$$

and

$$\chi_{\alpha\beta\gamma\delta}^{(2)} = \delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}.$$

The susceptibility  $\chi_{\alpha\beta\gamma\delta}$  can therefore be represented as a linear combination :

$$\chi_{\alpha\beta\gamma\delta} = A\chi_{\alpha\beta\gamma\delta}^{(1)} + B\chi_{\alpha\beta\gamma\delta}^{(2)}. \quad (5)$$

Due to isotropy of  $\chi_{\alpha\beta\gamma\delta}^{(2)}$ , the coefficient  $B$  is not affected by the IL-BP transition. Its order of magnitude is therefore the same as that determined from the Kerr effect in the isotropic liquid. Also, as the polarization  $\mathbf{P}$  due to it is parallel to  $\mathbf{E}$ , it contributes no torque,  $\Gamma$ .

The coefficient  $A$  and in particular its sign is a critical parameter that determines the orientation of Blue Phase crystals in the field. The torque  $\Gamma$  exerted on the crystal of volume  $V$  by the field  $\mathbf{E}$ , can finally be written as :

$$\Gamma = VA \sum_{i=1}^3 (\mathbf{n}_i \cdot \mathbf{E})^3 (\mathbf{n}_i \times \mathbf{E}). \quad (6)$$

The discussion of the above expression is straightforward in reference frame (1, 2, 3) of vectors  $\mathbf{n}_i$ . One has obviously :

$$\Gamma = VA\mathbf{h} \times \mathbf{E} \quad (7)$$

where

$$\mathbf{h} = [(E_1)^3, (E_2)^3, (E_3)^3]$$

or

$$\begin{aligned} \Gamma_1 &= VA(E_2^3 E_3 - E_3^3 E_2) = VAE_2 E_3 (E_2^2 - E_3^2). \\ \Gamma_2 &= VA(E_3^3 E_1 - E_1^3 E_3) = VAE_3 E_1 (E_3^2 - E_1^2) \\ \Gamma_3 &= VA(E_1^3 E_2 - E_2^3 E_1) = VAE_1 E_2 (E_1^2 - E_2^2). \end{aligned} \quad (8)$$

The torque  $\Gamma$  vanishes when :

- (a)  $|E_1| = |E_2| = |E_3|$
  - (b)  $E_i = 0$  and  $|E_j| = |E_k|$ ;  $i = 1, 2, 3$ ;  $j \neq k \neq i$
  - (c)  $E_i \neq 0, E_j = 0, E_k = 0$ ;  $i = 1, 2, 3$ ;  $j \neq k \neq i$ .
- (9)

The cases a, b and c correspond respectively to the following geometries :

- (a)  $\mathbf{E} \parallel$  threefold axes
  - (b)  $\mathbf{E} \parallel$  twofold axes
  - (c)  $\mathbf{E} \parallel$  fourfold axes.
- (10)

For intermediate directions of the field  $\mathbf{E}$ , there will be nonzero torques acting in a way to bring  $\mathbf{E}$  into the « nearest » stable position where  $\Gamma$  is zero. A simple representation of this behaviour is obtained using a crystallographic stereogram of figure 5. Directions of  $\mathbf{E}$  corresponding to zero torques are represented by dots, while the evolution of  $\mathbf{E}$  (for  $A > 0$ ) is visualized by arrows. Clearly, for  $A > 0$ , the orientation of the field is absolutely stable when it is directed along fourfold axes. Orientations of  $\mathbf{E}$  along twofold axis are relatively unstable.

**5. Microscopic mechanism of the nonlinear dielectric susceptibility  $\chi_{\alpha\beta\gamma\delta}$ .**

In view of the above considerations the constant  $A$  must be positive (orientation  $[100] \parallel \mathbf{E}$  stable) in samples of Blue Phases prepared by mixing nematics E9 or ZLI 1840 with the cholesterogene CB15. The order of magnitude of  $A$  can be estimated from a time  $\tau_r$  of reorientation of a crystal which has been slightly turned around  $\mathbf{n}_3$  out of its equilibrium position

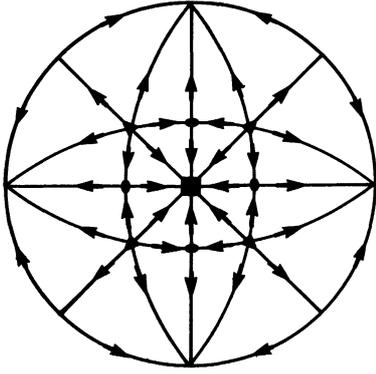


Fig. 5. — Stereogram of stability of Blue Phases in an electric field for  $A > 0$ . The evolution of the crystal with respect to the field, due to the torque  $\Gamma$  given in equation (6), is shown in the reference frame of the crystal. The corresponding trajectories of the field direction with respect to the crystal axes are indicated by arrows. Only the orientations of the field parallel to the fourfold axes are absolutely stable.

$\mathbf{n}_1 \not\parallel \mathbf{E}$  (Fig. 6). The crystal is subjected to the electric torque (Eq. (8)) which for small angle  $\phi$  is :

$$\Gamma_1^{e1} = \Gamma_2^{e1} = 0, \quad \Gamma_3^{e1} \approx VAE^4 \phi. \quad (11)$$

This restoring torque is opposed by a viscous torque due to the surrounding isotropic fluid of viscosity  $\mu$  [7] :

$$\Gamma_3^v = 6V\mu\dot{\phi}. \quad (12)$$

The relaxation time  $\tau_r$  is then :

$$\tau_r = \frac{6\mu}{AE^4}. \quad (13)$$

With a typical time  $\tau_r \approx 1$  s observed for crystals in a field  $E = \frac{30 \text{ V}}{100 \mu\text{m}} = 10$  esu and for  $\mu \approx 1$  poise, one gets  $A \approx 6 \times 10^{-4} \left[ \frac{\text{cm}^3}{\text{erg}} \right]$ .

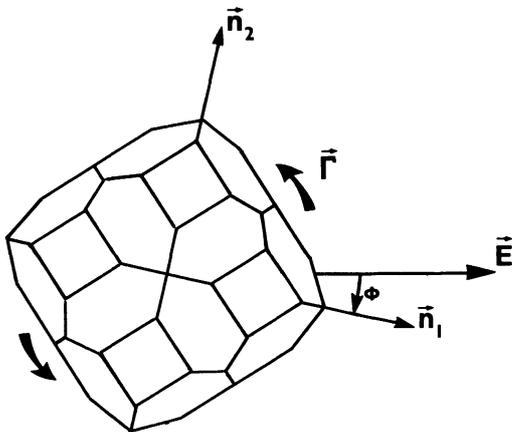


Fig. 6. — Reorientation of a crystal by the electric torque.

The constant  $A$  has dimension of  $E^{-2}$ . The characteristic electric field  $E_c = A^{-1/2}$  which is of the order of  $50 \text{ esu} = \frac{15 \text{ kV}}{\text{cm}}$  is smaller by several orders of magnitude than typical molecular field involved in nonlinear susceptibilities of molecular liquids ( $\approx 10^8 \frac{\text{V}}{\text{cm}}$ ). Obviously, the microscopic mechanism of the nonlinear susceptibility  $\chi_{\alpha\beta\gamma\delta}$  must be fundamentally different in Blue Phases than in usual molecular liquids. Indeed, in Blue Phases these are not individual molecules but giant unit cells (containing about  $10^7$  molecules) which are deformed by the field. This collective mechanism is analogous to the well understood deformation of a cholesteric helix in an external magnetic (or electric) field [8]. In Blue Phases, the dielectric constant tensor  $\epsilon_{\alpha\beta}(\mathbf{r})$  is a 3D periodic function of position  $\mathbf{r}$ . The electric field exerts local torques  $\Gamma(\mathbf{r}) = (\epsilon \cdot \mathbf{E}) \times \mathbf{E}$ , which are functions of position  $\mathbf{r}$  in the unit cell, and deforms the whole pattern  $\epsilon_{\alpha\beta}(\mathbf{r})$ . The deformation  $\delta\epsilon_{\alpha\beta}(\mathbf{r})$  has a nonzero volume average  $\frac{1}{V} \int \delta\epsilon_{\alpha\beta}(\mathbf{r}) d^3r$  which can be written as

$$\overline{\delta\epsilon_{\alpha\beta}} = \chi_{\alpha\beta\gamma\delta} E_\gamma E_\delta. \quad (14)$$

Obviously, as the deformation of the crystal of Blue Phases results from the equilibrium between the electric ( $\sim \epsilon_a E^2$ ) and elastic torques ( $\sim Kq^2$ ),  $\chi_{\alpha\beta\gamma\delta}$  must be the order of  $\epsilon_a/Kq^2$ .

With  $K \approx 10^{-7}$  dynes and  $q \approx 10^5 \text{ cm}^{-1}$  one gets  $E_c = \sqrt{Kq^2} \approx 30 \text{ esu}$  which is the same order of magnitude as the field  $E_c = A^{-1/2}$  introduced above. A detailed calculation of the field induced deformation of Blue Phases is postponed to another article [9].

## 6. Discussion.

The action of the electric field on the Blue Phases has been reported recently by Stegemeyer *et al.* [10] and by Porsch *et al.* [11]. In the reference [11], devoted mainly to a field-induced birefringence of the Blue Phases, a polycrystalline texture of the Blue Phase II was found to turn to a new one at field  $E = 1.8 \times 10^4 \text{ V/cm}$ . As the sample was polycrystalline, in order to determine the orientation of this new texture, the authors considered a lack of the field-induced birefringence and concluded that it must be aligned with an axis of an order higher than two ( $C_4$ ) parallel to  $\mathbf{E}$ . This observation, not explained, concerning the Blue Phase II is in agreement with our results.

The nonlinear dielectric susceptibility tensor  $\chi_{\alpha\beta\gamma\delta}$ , which has been shown in the present article to be the origin of orientation of Blue Phases in the electric field, should be possible to detect by conventional measures of dielectric polarization. It is important to emphasize that in this kind of experiment, the response of Blue Phases will depend crucially on the frequency of the

field. For  $f < f_c \approx \frac{Kq^2}{\mu} \approx 10^2-10^3$  Hz the polarization  $\mathbf{P}$  will have a component  $3f$ . For frequencies larger than  $f_c$  the generation of the third harmonics will be suppressed but the measured dielectric constant will increase quadratically with the intensity of the applied field.

Let us mention finally a striking similarity between  $\lambda_{\alpha\beta\gamma\delta}$  and the order parameter of cubic liquid crystals introduced by Nelson and Toner [12]. In fact, if one neglects spatial periodicity of  $\varepsilon_{\alpha\beta}(\mathbf{r})$  and considers only average correlations of orientations of molecules in Blue Phases, then the order parameter will be precisely :

$$\lambda_{\alpha\beta\gamma\delta} = \lambda \left[ \sum_{i=1}^3 n_{\alpha}^i n_{\beta}^i n_{\gamma}^i n_{\delta}^i - \frac{1}{5} (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) \right]. \quad (15)$$

The coupling of  $\lambda_{\alpha\beta\gamma\delta}$  with the electric field has been considered in detail by Saidachmetov [13]. The orientation of cubic liquid crystals predicted in reference [13] is precisely the same as that which we have pointed out here for the case of Blue Phases. The main difference consists in orders of magnitude of quantities involved in the coupling with the field. Due to the

smallness of the lattice constant of smectic D considered in reference [13] the characteristic field  $E_c = A^{-1/2}$  should in these materials be much larger than in Blue Phases. Also, the possibility of Fredericks transition discussed in reference [13] has to be examined critically. The three-dimensional crystal periodicity of Blue Phases does not allow a continuous deformation of the type involved in the usual Fredericks transitions in nematics. This is the main difference between true cubic liquid crystals and Blue Phases.

## 7. Conclusions.

We found experimentally in mixtures of CB15 in E9 or ZLI1840 that electric torques preferentially orient blue phase crystals with their four-fold axis parallel to the field direction. We argue that this effect is a cooperative one and not a single molecular one. We predict that reorientation times should scale as  $E^4$ . Since large fields tend to destroy cubic blue phases the appropriate range of voltages may be quite small.

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