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Résumé. — On considère les effets du champ électrique sur les formes cristallines des Phases Bleues et de la Phase Hélicoïdale de cristaux liquides cholestériques. On démontre que l'énergie diélectrique de ces phases contribue à l'énergie β_{hkl} des marches sur les facettes (*hkl*) et, par conséquent, modifie les formes cristallines globales. On met en évidence : (1) l'apparition de facettes perpendiculaires à l'axe hélicoïdal de la Phase Hélicoïdale, (2) l'apparition de facettes (100) sur les monocristaux de la Phase Bleue II. On indique que les dimensions et les formes des facettes qui existaient sans champ sont modifiées par celui-ci.

Abstract. — Electric field effects on crystal shapes of Blue Phases and of the Helicoidal Phase of cholesteric liquid crystals are considered. We show that dielectric energy of these phases contributes to the energy β_{hkl} of steps on (*hkl*) facets and finally affects global crystal shapes : (1) facets perpendicular to the helix axis appear on droplets of the Helicoidal Phase, (2) (100) facets appear on monocrystals of the Blue Phase II. We point out that shapes and sizes of facets, existing without the field, should be modified by the field.

In recent theories [1-4], crystal shapes are considered in terms of a distribution of interacting steps on crystal surfaces. An isolated step on a surface perpendicular to an [*hkl*] direction (Fig. 1) is characterized by : its height, d_{hkl} ; a width, ζ_{hkl} ; and an energy per unit length, β_{hkl}. This last quantity is crucial in problems of facetting and growth. In equilibrium, the singularity of the surface energy, γ, in the vicinity of the [*hkl*] direction, required to form the [*hkl*] facet, is proportional to β_{hkl}. The growth rate of the facet decreases exponentially with the nucleation barrier, ΔE, also determined by $\beta_{hkl}(\Delta E \sim \beta)$. In the present letter we show that the step energy, β, of Blue Phases [4] and the helicoidal phase of cholesteric liquid crystals can be tuned by an external electric field. As a consequence, facets are created on droplets of the helicoidal phase and the shapes of monocrystals [4, 5] of Blue Phases drastically change in the presence of a field.

Blue Phases I and II (BPI, BPII) as well as the helicoidal phase (C) [6] are characterized by a spatial periodicity of the anisotropic part $\hat{\varepsilon}$ of the dielectric tensor $\hat{\varepsilon}^d$:

$$\hat{\varepsilon} = \hat{\varepsilon}^d - \frac{1}{3} \operatorname{tr}(\hat{\varepsilon}^d)\,\hat{\delta} = (\hat{\varepsilon}_0 + \sum_q \hat{\varepsilon}(\mathbf{q})\,e^{i\mathbf{q}\cdot\mathbf{r}} + \text{c.c.} \quad (1)$$

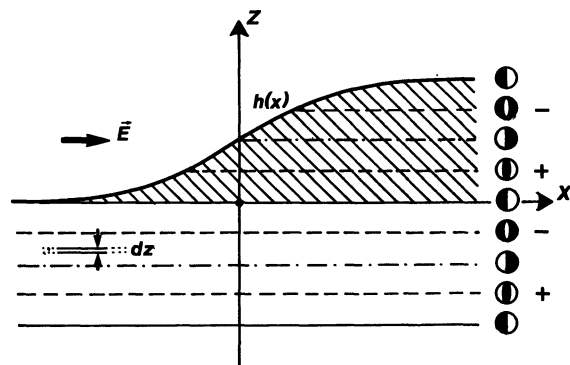For given conditions of temperature, pressure or

Fig. 1. — Action of the electric field on step formation due to the $m = 2$ [6] tensor wave $\hat{\varepsilon}_q$. The dielectric energy is modulated periodically along z (+ and − correspond to signs of the dielectric energy). The tensor wave is visualized schematically on the right (the symmetry of a sphere with black and white sections is that of the $m = 2$ spherical harmonic). The shape of step $h(x)$ results from competition between dielectric and surface energies.

composition, the order parameter, $\hat{\varepsilon}$, minimizes the bulk free energy $\int F_0(\hat{\varepsilon})\,dV$ of the system. In an electric field, **E**, the free energy density is modified as

follows [7] :

$$F(\hat{\varepsilon}) = F_0(\hat{\varepsilon}) - \frac{1}{8\pi} \mathbf{E}.\hat{\varepsilon}.\mathbf{E} = F_0(\hat{\varepsilon}) + F^{el}(\hat{\varepsilon}) . \quad (2)$$

In the present paper we consider the low field limit for which the order parameter is only slightly perturbed by the field :

$$\hat{\varepsilon}(\mathbf{E}) = \hat{\varepsilon}(0) + \delta\hat{\varepsilon}(E^2) \quad \text{where} \quad \delta\hat{\varepsilon}(E^2) \ll \hat{\varepsilon}(0) . \quad (3)$$

In this limit, a volume average of the electric free energy

$$\langle F^{el} \rangle_V = \frac{1}{V} \int F^{el}(\hat{\varepsilon}(E = 0)) \, dV \quad \text{only has a contri-}$$

bution from the $\mathbf{q} = 0$ term, $\hat{\varepsilon}_0$ (Eq. (1)), which gives rise to a torque orientating the system in such a way as to minimize $\langle F^{el} \rangle_V$. On the other hand, dividing the crystal into layers of thickness $dz \ll q^{-1}$, perpendicular to a given $\mathbf{q}$ (Fig. 1), the surface average $\langle F^{el} \rangle_s = \frac{1}{S} \int F^{el}(\hat{\varepsilon}(E = 0)) \, dx \, dy$ varies periodically along $z /\!/ \mathbf{q}$.

For one component of the series (1) ($m = 2$ in Ref. [6]) :

$$\hat{\varepsilon} = \varepsilon_q \begin{pmatrix} -\sin qz, & \cos qz, & 0 \\ \cos qz, & \sin qz, & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (4)$$

and for $\mathbf{E} /\!/ x$ one has :

$$F_s^{el}(z) = \langle F^{el}(z) \rangle_s = \frac{1}{8\pi} \varepsilon_q E^2 \sin qz . \quad (5)$$

Although, as stated above, this energy averages to zero in the bulk, the energy of the last slab of thickness $2\pi q^{-1}$ (shadowed part in Fig. 1),

$$\Delta F^{el}/cm = \int dx \left(\int_0^{h(x)} F_s(z) \, dz \right) =$$

$$= \int \frac{1}{8\pi} \frac{\varepsilon_q E^2}{q} [1 - \cos qh(x)] \, dx, \quad (6)$$

depends on the detailed shape $h(x)$ of the step. This energy is lowest, $\Delta F^{el}/cm = 0$, for a sharp step : $h(x) = 0$ for $x < 0$, $h(x) = 2\pi q^{-1}$ for $x > 0$. For any other form $dh/dx > 0$ and $\Delta F^{el}/cm$ will be larger. The sharpening action of the field is opposed by an increase of the surface energy due to the elongation of the surface length in the x-direction :

$$\Delta F^s/cm = \frac{1}{2} \gamma \int \left(\frac{dh}{dx} \right)^2 dx, \quad (7)$$

γ is the surface tension. This elongation is greatest in the case of a sharp step and decreases as the step becomes smoother.

The shape $h(x)$ which minimizes the total energy $\Delta F^s/cm + \Delta F^{el}/cm$ is :

$$h(x) = 4 q^{-1} \operatorname{arctg} [\exp(x/\zeta)] . \quad (8)$$

where

$$\zeta = q^{-1} \sqrt{\frac{\gamma}{V_0(E)}} \quad \text{and} \quad V_0(E^2) = \frac{1}{8\pi} \frac{\varepsilon_q E^2}{q} .$$

The energy per unit length of such a step depends on the applied field as follows :

$$\beta = 8 q^{-1} \sqrt{V_0(E^2)} \, \gamma = \frac{d^{3/2}}{\pi^2} E \sqrt{\varepsilon_q \, \gamma} \sim d^{3/2} . \quad (9)$$

The action of the electric field on surface shape becomes significant when the quantity V_0 is the same order of magnitude as the surface tension. The amplitude ε_q of the Fourier component $\hat{\varepsilon}_q$ is the order of magnitude of the dielectric anisotropy $\varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp} \approx 10$ for the nematic phases (ZLI 1840 and E9) used to prepare the cholesteric mixtures. For a voltage of 30 V = 10^{-1} esu applied to a cell of thickness 100 μ = 10^{-2} cm one gets $V_0 \simeq 10^{-4}$ erg/cm², when $d = 2\pi q^{-1} = 0.2 \, \mu$m. The surface tension γ of Blue Phases in contact with the isotropic liquid or the Blue Fog, estimated previously in reference [4], is the order of 10^{-3}-10^{-4} erg/cm². The electric field can be increased by a factor of 10 but then Blue Phases and cholesterics lose their twisted structure [8, 9].

The order parameter of the helicoidal phase is a linear combination of the $\mathbf{q} = 0$ component and of only one tensor wave :

$$\hat{\varepsilon}_c(\mathbf{r}) = \varepsilon_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} +$$

$$+ \varepsilon_q \begin{pmatrix} -\sin qz & \cos qz & 0 \\ \cos qz & \sin qz & 0 \\ 0 & 0 & 0 \end{pmatrix} . \quad (10)$$

In the low chirality limit [5], when the minimum of free energy is obtained for $\varepsilon_q/\varepsilon_0 = 3$, the order parameter can be written as :

$$\hat{\varepsilon}_c(\mathbf{r}) = \varepsilon_a \left(n_i \, n_j - \frac{1}{3} \delta_{ij} \right) \quad (11)$$

where

$$\mathbf{n} = \left[\cos \left(q_c \, z + \frac{\pi}{4} \right), \sin \left(q_c \, z + \frac{\pi}{4} \right), 0 \right]$$

$$q_c = q/2, \, \varepsilon_0 = \varepsilon_q/3 = \varepsilon_a/6, \, \varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp} .$$

In a mixture of 20 % CB15 in ZLI 1840, where the helicoidal phase was grown from the isotropic liquid, due to a positive sign of ε_a (≈ 10) the ε_0 term orients the helicoidal axis ($\mathbf{q} /\!/ z$) in a direction perpendicular to $\mathbf{E}(/\!/ x)$. The ε_q term introduces a modulation of free energy along z (Eq. (5)) and on surfaces parallel to $\mathbf{E}$ steps will have energy β (Eq. (9)).

In the experiment, the liquid crystal is contained between two parallel glass slides coated with transparent electrodes (Fig. 2a). In this geometry the field affects surfaces parallel to it. Let θ be an angle between a normal $\mathbf{m}$ to the surface of the crystal, and $\mathbf{q}$.

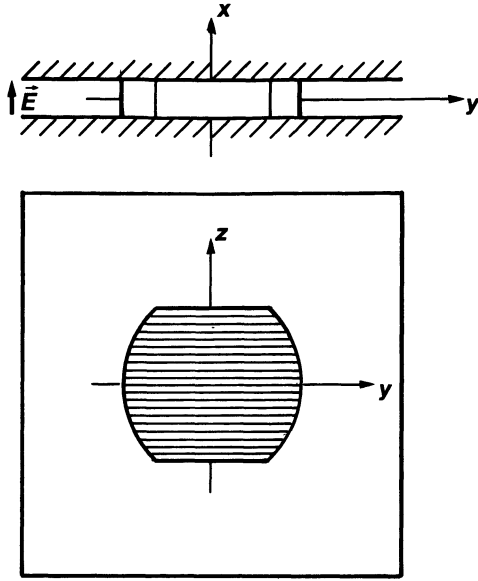The density of steps is $\left| \dfrac{\sin \theta}{d} \right|$ so that the surface

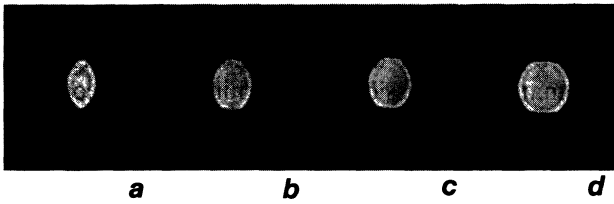Fig. 2(a). — Geometry of the experiment on the helicoidal phase.

Fig. 2(b). — Growth of a monocrystal of the helicoidal phase in electric field. The field is perpendicular to the plane of the page.

energy

$$\gamma(\theta) = \gamma_0 + \frac{\beta}{d}|\sin\theta| - 0(d\sin\theta)^3 \qquad (12)$$

has cups at $\theta = 0$ and $\theta = \pi$. In figure 2b we show a monocrystal of the helicoidal phase grown in an electric field and indeed, as expected from a Wulff plot generated using equation (12), it has two facets perpendicular to the helix axis.

An interesting feature of such a crystal shape is that rounded parts meet facets at a finite angle implying an effective attraction between steps so that the third order term in equation (12) must be negative. We discuss this effect in another article [10].

Blue Phases.

Blue Phases I and II have respectively the symmetry $0^8(I4_132)$ and $0^2(P4_232)$ [11]. In a first approximation one limits the series (1) to terms of lowest energy [6] which are $m = 2$ tensor plane waves (Eq. (4)) with wavenumbers $\frac{q \cdot a}{2\pi}$ (a is the dimension of the cubic unit

cell) : (110) and (200) for BPI and, (100) and (110) for BPII.

In the absence of the field, in ZLI 1840 mixtures, monocrystals of BPI and BPII show large (110) facets. In Blue Phase I (100) facets are inhibited by a fourfold screw symmetry, 4_1, parallel to [110]. In terms of surface energies, the distance between two equivalent crystal planes is $\frac{a}{4}$ and not $\frac{a}{2}$ [4]. In Blue Phase II the distance between two surfaces of the same energy in the [100] direction is $a/2$ and not a, due to the presence of a 4_2 axis.

On lateral surfaces parallel to E (Fig. 3), the modulation of the dielectric energy $\Delta F_s^{el}(z)$ (Eq. (5)) in the [110] direction has the same period as that of the field independent term F_0, i.e., $a/\sqrt{2}$. In the [100] direction the periodicity of ΔF_s^{el} is a in BPII and $a/2$ in BPI.
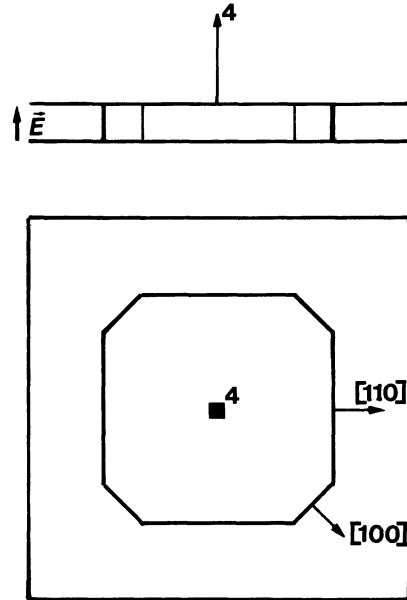

Fig. 3(a). — Geometry of experiment on Blue Phases. The electric field directed along the fourfold axis of the BPII crystal. (100) and (110) facets delimit the crystal perpendicular to E.
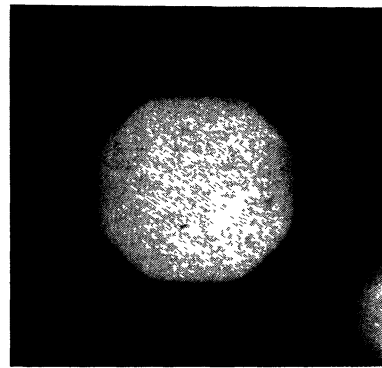

Fig. 3(b). — Photograph of a BPII crystal grown in the electric field.

Equation (9) shows that the step energy, β, is proportional to $d^{3/2}$ so that if $\varepsilon_{110}^{BPI} \simeq \varepsilon_{200}^{BPI}$ and $\varepsilon_{110}^{BPII} \simeq \varepsilon_{100}^{BPII}$, then,

$$\beta_{100} > \beta_{110} \quad \text{in} \quad \text{BPII} \qquad (13)$$

and

$$\beta_{200} < \beta_{110} \quad \text{in} \quad \text{BPI}.$$

Since the growth rates of facets decreases with β, the (100) facets grow more slowly than the (110) facets in BPII. In BPI, (110) facets are slower. This predicts that during growth in a field, (100) facets will increase in size in BPII monocrystals while in BPI monocrystals (110) facets persist. This theoretical prediction is observed experimentally. When the electrical field is applied in the geometry of figure 3, only (110) lateral facets limit the growth forms of BPI monocrystals. On growth forms of BPII (100) facets appear and coexist with (110) facets in low field. In large fields, the (110) facets disappear and the growth form is limited only by (100) facets.

The action of the electric field on facetting of Blue Phases can be far more complex than in the above examples. In fact, the modulation of the dielectric energy (Eq. (5)) due to the field is superposed on a modulation which existed without a field. In the simplest case when both modulations have the same period (e.g. the [110] direction in BPII) one still has to consider their phase relationship. The phase ϕ of $\Delta F_{el}(z) =$

$\dfrac{1}{8\pi}\,\varepsilon_q\,E^2 \sin(qz + \phi)$ changes continuously when $\mathbf{E}$ rotates around $\mathbf{q}$ ($\mathbf{E} \perp \mathbf{q}$). One expects, therefore, that for a particular direction of $\mathbf{E}$ the two modulations interfere destructively.

In the case where the field $\mathbf{E}$ does not coincide with a crystal symmetry axes (in Fig. 3 $\mathbf{E}$ is parallel to the fourfold axis), its action on each facet will be different and obviate the point symmetry (432) of the crystal habit.

In conclusion, in the present paper we have pointed out that a uniform electric film drastically affects the shapes of cholesteric phases. The effect is most striking in the case of the helicoidal phase in contact with the isotropic liquid where round shapes without field are replaced by a simple habit composed of two facets, perpendicular to the helicoidal axis, and of rounded parts which meet facets at a finite angle. In Blue Phases we roughly analysed the case of the field parallel to the fourfold symmetry axis. The appearance of (100) facets on BPII monocrystals in a field was accounted for.

Acknowledgments.

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