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Electro-optic effects in blue phases

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A theory of electro-optic and elasto-optic effects in the blue phases of cholesteric liquid crystals is developed. The case of small structure deformations and a weak field is considered: $|\mathbf{E}| \ll E_c$, where E_c is the critical field for the cholesteric–nematic transition. The theory explains all of the main experimental facts: the field-induced birefringence and biaxiality, the distortion of the cubic structure (electrostriction) and the orientation of the blue phase monocrystals in an electric field.

1. Introduction

The structure of the blue phases (BPs) of cholesteric liquid crystals is now well understood [1–4] (except for the fog phase, BP III) whereas studies of their physical properties are still in their initial stage. Two of the BPs (BP I and BP II) have a periodic structure of the liquid-crystalline order parameter with cubic symmetry. The most probable space groups are I 4_132 for BP I and P 4_232 for BP II; the lattice constants are about equal to the cholesteric pitch (10^3–10^4 Å). At macroscopic distances the BPs have crystalline properties (their elastic moduli were measured in [5] and calculated in [6]; the faceting of BP monocrystals was observed in [4, 7]). At microscopic distances (much smaller than the lattice constant) the BPs look like an anisotropic liquid. The distribution of nematic-like order parameter of this anisotropic liquid inside the unit cell can be calculated from the Landau theory of phase transitions [1–3]. It is clear that the macroscopic properties of BPs are determined by the microscopic structure of the order parameter. In this paper the electro-optic and elasto-optic properties of BPs are discussed. Our theoretical results are compared with the observed field-induced effects in BPs such as the orientation of monocrystals [4, 7], the shifts of the Bragg reflections [4, 8, 9] and the birefringence [4, 10–12].

The influence of an electric field on the BPs is mainly connected with the distortions of the cubic double-twist structure. These distortions are analogous to the well-understood deformation of the cholesteric helix in external fields; their theoretical description can be obtained from the Landau theory [13]. However, in this approach the simple models of distortions were considered because of computational difficulties. In this paper a phenomenological approach is developed using the weak-field and small-strain expansion of the free energy ($|\mathbf{E}| \ll E_c$, $|u_{ik}| \ll 1$, where E_c is the critical field for unwinding the cholesteric helix [14] and u_{ik} is the strain tensor).

2. Phenomenological description

The free energy expansion is [15]

$$\Delta F = \frac{1}{2}\lambda_{iklm}u_{ik}u_{lm} - \frac{1}{16\pi}\chi_{iklm}E_iE_kE_lE_m - \frac{1}{8\pi}p_{iklm}E_iE_ku_{lm}, \qquad (1)$$

where summation over repeated indices is implied. The tensor coefficients $\hat{\lambda}$, $\hat{\chi}$ and $\hat{\mathbf{p}}$ are called the elastic constant tensor, the tensor of non-linear dielectric susceptibility

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and the elasto-optic tensor, respectively. The dependence of the dielectric susceptibility on $\mathbf{E}$ and u_{ik} may be obtained from equation (1) as

$$\Delta\varepsilon_{ik} = \chi_{iklm} E_l E_m + p_{iklm} u_{lm}. \tag{2}$$

The field-induced strain u_{ik}^{E} of free crystals is

$$u_{ik}^{\mathrm{E}} = \frac{1}{8\pi} s_{iklm} p_{nplm} E_n E_p \equiv R_{iknp} E_n E_p, \tag{3}$$

where the tensor $\hat{\mathbf{s}}$ is reciprocal to $\hat{\lambda}$; so

$$s_{iklm}\lambda_{lmnp} = (\delta_{in}\delta_{kp} + \delta_{ip}\delta_{kn})/2.$$

The tensor $\hat{\mathbf{R}}$ is called the electrostriction coefficient ($\hat{R} \approx E_c^{-2}$).

The deformation of the crystal lattice leads to changes of the reciprocal lattice vectors τ ($\Delta\tau_i = -u_{ik}^{\mathrm{E}}\tau_k$) and, hence, to shifts of the Bragg reflections. It should be noted that the electric field contributes to the energy of liquid crystals only in the combination $\chi_\alpha \mathbf{E}^2$, where χ_α is the anisotropy of the molecular polarizability. Therefore, the coefficient $\hat{\mathbf{p}}$ in equation (1) should be proportional to χ_α. The same result is also obvious from equation (2) directly: if the deformation u_{lm} is fixed (that is, the average molecular configuration is fixed), the sign of the deformation-induced $\Delta\varepsilon_{ik}$ is determined by the sign of the molecular dielectric anisotropy. These simple arguments explain the different signs of the shifts of the same reflections in the BPs with different signs of χ_α [4, 8, 9].

Substituting equation (3) into equations (2) and (1) we obtain the dielectric susceptibility and the free energy as functions of $\mathbf{E}$:

$$\Delta\varepsilon_{ik}^{\mathrm{E}} = \chi_{iklm}^{\mathrm{tot}} E_l E_m, \tag{4}$$

$$\Delta F^{\mathrm{E}} = -\frac{1}{16\pi} \chi_{iklm}^{\mathrm{tot}} E_i E_k E_l E_m, \tag{5}$$

where

$$\chi_{iklm}^{\mathrm{tot}} = \chi_{iklm} + \frac{1}{8\pi} p_{ikqr} s_{qrnp} p_{lmnp}.$$

Because of the cubic symmetry of BPs (the crystal class 432), each of the tensors $\hat{\lambda}$, $\hat{\chi}$ and $\hat{\mathbf{p}}$ can contain three independent constants; however, we can restrict the number of the constants using the liquid-crystalline nature of the BPs. For example, in the case of weak fields and small strains, the main contribution to $\Delta\varepsilon_{ik}$ results from the reorientation of molecules; hence, the average dielectric constant should be unchanged ($\Delta\varepsilon_{ii} = 0$). Thus, $\chi_{iilm} = 0$, $p_{iilm} = 0$ and each tensor contains only two independent constants. As a result $u_{ii}^{\mathrm{E}} = 0$ and the volume of the BP unit cell remains unchanged (in E^2 approximation only). Note that the tensor $\hat{\chi}$, used in the previous work [7, 13, 16], does not satisfy the condition $\chi_{iilm} = 0$ because in these papers only part of the tensor $\hat{\chi}$ (symmetrical over all indices) was considered.

3. Calculation of tensor coefficients

To obtain the explicit form of the tensors $\hat{\lambda}$, $\hat{\chi}$ and $\hat{\mathbf{p}}$, we explore the Landau theory (in the limit of weak fields and small strains). Being averaged over the unit cell, the Landau–de Gennes free energy [1–3] should give equation (1) where the

tensors $\hat{\lambda}$, $\hat{\chi}$ and $\hat{\mathbf{p}}$ should be some functionals of the order parameter of the undistorted BP structure. As the order parameter $\hat{\varepsilon}(\mathbf{r})$, we shall use the traceless part of the local dielectric susceptibility [1–3]. It is known that the dominant contribution to the Fourier harmonics of $\hat{\varepsilon}(\mathbf{r})$ is from the plane mode ($m = 2$ term) [1–4, 13, 17] (only these terms with amplitudes $\varepsilon(\tau, 2)$ will now be taken into account).

Rewriting equation (1) via the explicit small parameter $(\mathbf{E}/E_c)$, we can see that the new expansion coefficients ($\hat{\lambda}$, $\hat{\chi}E_c^4$ and $\hat{\mathbf{p}}E_c^2$) are of the same dimension (dyn cm^{-2}) and of the same order of magnitude: $\hat{\lambda} \approx \hat{\chi}E_c^4 \approx \hat{\mathbf{p}}E_c^2 \approx K_2 q_0^2$, where K_2 is the Frank constant [14], $q_0 = 2\pi/p_0$, p_0 being the undistorted cholesteric pitch. Near the transition to isotropic liquid (where BPs exist), K_2 is of the order of $c_1\hat{\varepsilon}^2$, where c_1 is the elastic constant in the Landau theory [1–3]. Thus, we can search for the tensors $\hat{\lambda}$, $\hat{\chi}E_c^4$ and $\hat{\mathbf{p}}E_c^2$ as quadratic functionals of $\hat{\varepsilon}(\mathbf{r})$ (and of its derivatives). The tensor functionals of $\hat{\varepsilon}(\mathbf{r})$ with proper dimension have two forms: $c_1\overline{(\partial\varepsilon_{ij}/\partial x_k)(\partial\varepsilon_{lm}/\partial x_n)}$ and $c_1 q_0 e_{ijk}\overline{\varepsilon_{lm}(\partial\varepsilon_{np}/\partial x_q)}$ (the overscores denote an average over the unit cell). These high rank tensor functionals should be convolved over some pairs of indices and then symmetrized to obtain the fourth-rank tensors with 432 symmetry [15].

The tensor functionals contribute to $\hat{\lambda}$, $\hat{\chi}E_c^4$ and $\hat{\mathbf{p}}E_c^2$ with independent numerical coefficients, which are the same both for BPs and for the cholesteric phase because equation (1) for all phases results from the Landau–de Gennes free energy (different phases have different sets of $\varepsilon(\tau, 2)$). Thus, we can determine most of the numerical coefficients requiring the validity of the functionals for $\hat{\lambda}$, $\hat{\chi}E_c^4$ and $\hat{\mathbf{p}}E_c^2$ in the case of cholesterics. We note that in cholesterics the tensor $\hat{\lambda}$ has only one non-zero component:

$$\lambda_{zzzz} = c_1 \sum_{\tau} \tau^2 |\varepsilon(\tau, 2)|^2$$

(the z axis is along the helix axis). Tensors $\hat{\mathbf{p}}$ and $\hat{\chi}$ can be evaluated from the de Gennes–Meyer theory of cholesteric distortion [14] in the $\mathbf{E}^2$ approximation: $p_{iklm} = 0$ because the field-induced changes of the pitch are of the order of $\mathbf{E}^4$ and the $\mathbf{E}^2$ term is absent; then

$$\begin{aligned}\chi_{xxxx} &= \chi_{yyyy} = \chi_{xyxy} = \chi_{yxyx} = \chi_{yxxy} = \chi_{xyyx} \\ &= -\chi_{xxyy} = -\chi_{yyxx} = (\pi^5/256)E_c^{-4} c_1 \sum_{\tau} \tau^2 |\varepsilon(\tau, 2)|^2\end{aligned}$$

and for the rest $\chi_{iklm} = 0$.

Taking into account all of these restrictions we can obtain for BPs:

$$\lambda_{iklm} = c_1 \sum_{\tau} \tau^2 |\varepsilon(\tau, 2)|^2 T_{iklm}, \tag{6a}$$

$$\chi_{iklm} = (\pi^5/768)E_c^{-4} c_1 \sum_{\tau} \tau^2 |\varepsilon(\tau, 2)|^2 (3T_{iklm} + \delta_{il}\delta_{km} + \delta_{kl}\delta_{im} - \delta_{ik}\delta_{lm}), \tag{6b}$$

$$p_{iklm} = Bc_1 E_c^{-2} \sum_{\tau} \tau(\tau - 2q_0) T_{iklm} |\varepsilon(\tau, 2)|^2, \tag{6c}$$

where

$$T_{iklm} = \tau_i \tau_k \tau_l \tau_m / \tau^4$$

and B is the numerical coefficient remaining undetermined by this procedure. Note that equation (6 a) for $\hat{\lambda}$ is slightly different from that derived in [6] by another method (the bulk moduli given by both expressions are equal). It should also be emphasized

that equation (6*b*) is not applied to cholesterics because in its calculation the cubic symmetry of BPs has been used.

4. Discussion

We can compare equations (6) quantitatively with the available experimental results because the values of $|\varepsilon(\tau, 2)|^2$ have been determined both theoretically and experimentally [2–4, 17]. Let us discuss first the temperature and pitch dependence of $\hat{\boldsymbol{\lambda}}$, $\hat{\boldsymbol{\chi}}$ and $\hat{\mathbf{p}}$. The temperature dependence is due mainly to the temperature dependence of ε, where ε is the typical value of the order parameter ($\varepsilon^2 \approx \Sigma_\tau |\varepsilon(\tau, 2)|^2$). Taking into account that

$$E_c^2 \approx q_0^2 K_2/\varepsilon \approx c_1 q_0^2 \varepsilon,$$

we can obtain

$$\hat{\boldsymbol{\lambda}} \approx c_1 q_0^2 \varepsilon^2, \qquad \hat{\boldsymbol{\chi}} \approx (c_1 q_0^2)^{-1}, \qquad \hat{\mathbf{p}} \approx \boldsymbol{\varepsilon}$$

and

$$\hat{R} \approx (c_1 q_0^2 \varepsilon)^{-1}.$$

Note that $\hat{\boldsymbol{\chi}}$ is independent of temperature and $\hat{\mathbf{R}}$ increases with increasing temperature; the last is in accord with experiment [8].

To discuss the field-induced shifts of the Bragg reflections we suppose that in equation (6*c*) $B > 0$. It follows from equations (3) and (6) that the 110 reflection in BP I and the 100 reflection in BP II have red (blue) shifts if $\chi_\alpha > 0$ ($\chi_\alpha < 0$), and the 200 reflection in BP I is shifted in the direction opposite to 110 (the field is assumed to be parallel to the reflections). In BP I the ratio of the shifts is given by $(\Delta\tau/\tau)_{110}/(\Delta\tau/\tau)_{200} \approx -0{\cdot}6$, in close agreement with experimental results [8]. Equations (3) and (6) may be also used for the quantitative description of the Kossel diagram distortions observed in an electric field [18]. Note that due to the coefficient $(\tau - 2q)$ in equation (6*c*), the electrostriction effects should be small in any phases where $\tau \simeq 2q_0$ for all harmonics with large $\varepsilon(\tau, 2)$; this result is also evident from a sum rule [2]. Indeed, a very small field-induced shift is observed in BP III where $\tau \simeq 2q_0$ [19].

The field-induced dielectric tensor (equation (4)) contains two contributions: the first from the non-linear susceptibility $\hat{\boldsymbol{\chi}}$ and the second from electrostriction. These contributions can be measured separately because of their different response times: $t_\chi \gtrsim 10^{-4}$ s and $t_p \gtrsim 10^{-2}$ s [9–12]. It is rather difficult to estimate the second contribution quantitatively because the absolute value of B is unknown. However, this contribution seems to be small compared with the first one because $(\tau - 2q_0)^2 \ll \tau^2$ for harmonics with large $\varepsilon(\tau, 2)$. It should be emphasized that equations (4) and (6) describe the birefringence induced both parallel and perpendicular to the field direction (numerical calculations have been made for the latter case only [13]). For example, if $\mathbf{E} \parallel [110]$, all characteristic values of $\Delta\hat{\varepsilon}^E$ are different and, neglecting electrostriction, we obtain from equations (4) and (6) that $(\Delta\varepsilon^E_{\parallel 110}) : (\Delta\varepsilon^E_{\parallel 001}) : (\Delta\varepsilon^E_{\parallel 1\bar{1}0}) \approx 1 : (-0{\cdot}73) : (-0{\cdot}27)$ (orientation $[110] \parallel \mathbf{E}$ can be stabilized by wall anchoring). If the strain u_{ik} is caused by external mechanical distortion and $\mathbf{E} = \mathbf{0}$, equations (2) and (6) describe the elasto-optic effects.

The stable orientation of free BP monocrystals is that which minimizes the free energy (equation (5)) [7, 16]. The relevant part of χ^{tot}_{iklm} has the form $A\Sigma^3_{\alpha=1} n_i^\alpha n_k^\alpha n_l^\alpha n_m^\alpha$ [7],

where $\mathbf{n}^{\alpha}$ ($\alpha = 1, 2, 3$) are unit vectors parallel to the four-fold cubic axes. Neglecting again the electrostriction contribution to $\hat{\chi}^{\text{tot}}$ we obtain for A

$$A = \frac{\pi^5}{256} E_c^{-4} c_1 \sum_{|\tau|} \tau^2 |\varepsilon(\tau, 2)|^2 C(\tau)),$$

where for the strongest harmonics $C(100) = C(200) = 2$, $C(110) = -1$, $C(211) = -2$. Thus, the $\{100\}$ and $\{200\}$ harmonics are favourable for the orientation $[100] \parallel \mathbf{E}$ ($A > 0$), whereas the $\{110\}$ and $\{211\}$ harmonics are favourable for the orientation $[111] \parallel \mathbf{E}$ ($A < 0$). Using experimental (or theoretical) values of $\|\varepsilon(\tau, 2)|^2$, we obtain both for BP I and for BP II that $A > 0$ and the orientation $[100] \parallel \mathbf{E}$ should be stable, in agreement with observations [7]. In the I 432 phase, where the $\{110\}$ harmonics are dominant, the orientation $[111] \parallel \mathbf{E}$ should be stable in accord with numerical results [13].

So far we have not distinguished between the values of the dielectric anisotropy for the different frequencies of the electric fields and those of the light beams; the generalization to the case of different values and to magnetic fields are trivial. Note, in conclusion, that the flexoelectric effects are also possible in BPs due to the presence of gradients of the order parameter. The spontaneous polarization is allowed by symmetry at any points of the unit cell except those with 23 or 432 point symmetry (certainly, the average spontaneous polarization should be zero for the 432 crystal class). The presence of spontaneous polarization may be very important for the electro-optical properties of BPs.

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