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NONLINEAR DIELECTRIC SUSCEPTIBILITY IN BLUE PHASES OF CHIRAL LIQUID CRYSTALS

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Abstract The deformation of the cubic blue phase I along the field changes from dilatation to compression or *vice versa* when the electric field vector is rotated from one crystallographic direction to another. This phenomenon is termed anomalous electrostriction and together with topology of phase diagrams of the blue phases awaits elucidation. Standard theory of blue phases is not able to explain these observations. Following the experiments of Pierański *et al.* we generalized the standard theory by incorporating a nonlinear dielectric susceptibility tensor (NDS). It is shown that the distortion of the cubic blue phase I in the presence of the NDS may display the anomalous electrostriction, in accordance with experiment. These results seem to indicate that nonlinear susceptibility tensor is a relevant order parameter for the blue phases.

INTRODUCTION

Blue phases of chiral liquid crystals have been studied intensively over the last decade. In the absence of an external field three types of the blue phases, also known as BPI, BPII and BPIII, have been found. Among them BPI and BPII are identified as a body-centered cubic structure with the space group symmetry $\mathcal{O}^8(\mathcal{I}4_132)$ and a simple cubic structure with the space group symmetry $\mathcal{O}^2(\mathcal{P}4_232)$, respectively. The structure of BPIII is still intensively studied. Recent measurements of the latent heat and of the dynamic light scattering for highly chiral materials[1] show continuous and noncritical evolution from the isotropic phase to BPIII. The most probable explanation of these observations, also known as an isotropic model[2–4], is to assume that both BPIII and the isotropic liquid are of the same macroscopic symmetry. This implies an existence of a critical point at intermediate chiralities, which, as far as we are aware of, has not been detected so far.

Another possibility that cannot be excluded - the so called cubic bond model[5,6] - assumes that BPIII structure is characterized by a nonvanishing cubic part of the nonlinear dielectric permittivity tensor. Within the frame of this model one could account for a tricritical point between BPIII and ISO phases[7] or for a weakly first order phase transition between these phases, with the latent heat proportional to $\frac{1}{\kappa^2}$, where κ is the chirality[8]. Perhaps it is worth to add that so far none of the two models is able to account for an experimentally observed topology of the phase diagrams.

Recently an additional support has been found that the nonlinear dielectric susceptibility could be a relevant order parameter for blue phases[9]. It comes from the studies of the effect of a weak electric field on the cubic blue phases. Namely, in the limit of the vanishing homogeneous field the monocrystals of BPI and BPII reorient themselves. Due to their cubic symmetry the reorientation process is governed by the cubic part $B^{(4)}_{\alpha\beta\gamma\delta}$ of the fourth rank nonlinear dielectric tensor $\chi_{\alpha\beta\gamma\delta}$[10]. The norm of this tensor is several orders of magnitude larger than in the case of molecular liquids and hence it is natural to expect that the $\boldsymbol{B}^{(4)}$ tensor may appear relevant, at least for the processes taking place in BPs subjected to the electric field.

One of such processes could be a deformation of the blue phase lattices by the weak electric field. These deformations are quantified by means of the ratios of the independent components $R_1 = R_{1111}$, $R_2 = R_{1122}$ and $R_3 = R_{2323}$ of the electrostriction tensor $\boldsymbol{R}$. Calculations carried out by Stark and Trebin[11] yield $R_1/R_2 = -2$, in agreement with experiments of Heppke[12] and Dolganov[13]. The ratio R_1/R_3 has been reproduced correctly for BPII, where experiments yielded values between 0.4 and 1.0 but not for BPI where the experimental values are *negative* (between -0.1 and -0.4). Theory gives in this case positive values similar to those obtained for BPII. The negative value of R_1/R_3 means dilatation along one crystallographic direction and compression along the other, and is known as an anomalous electrostriction. It remains one of the unsolved problems of chiral liquid crystal physics.

We show that the anomalous electrostriction could be explained by extending the original Landau- Ginzburg- deGennes theory to couplings that involve the $\boldsymbol{B}^{(4)}$ tensor[9]. The associated electrostriction tensor is expressed in terms of both the bond orientational tensor and the alignment tensor field of the undistorted system. The calculations generalize the work of Stark and Trebin[11]. Some details of the theory are given in the next two sections.

BEYOND STANDARD MODEL

A purpose of this section is to discuss a generalization of the standard theory of chiral liquid crystals. We start from the analysis of relevant order parameters.

The cholesteric phase and the blue phases of chiral liquid crystals are the structures for which the characteristic periodicity is of the order of 4000Å. Consequently, the mesoscopic level is an adequate starting point of the description.

The relevant order parameters can be identified with the help of the permittivity tensors $\boldsymbol{\chi}^m(\boldsymbol{r})$, which enter expansion of the polarization $\boldsymbol{P}$ with respect to the applied electric field $\boldsymbol{E}$

$$\begin{aligned}\boldsymbol{P} &= \int \mathrm{d}^3\boldsymbol{r}[\boldsymbol{\chi}^1(\boldsymbol{r}) + \boldsymbol{\chi}^2(\boldsymbol{r}) \cdot \boldsymbol{E} + \boldsymbol{\chi}^3(\boldsymbol{r}) \cdot (\boldsymbol{E} \otimes \boldsymbol{E}) + \\ &\quad \boldsymbol{\chi}^4(\boldsymbol{r}) \cdot (\boldsymbol{E} \otimes \boldsymbol{E} \otimes \boldsymbol{E}) \ + \ \cdots].\end{aligned} \tag{1}$$

Local D_∞ or D_2 symmetries of majority of the liquid crystalline phases eliminate from the expansion (1) the odd rank susceptibilities $\boldsymbol{\chi}^{2n+1}$ $(n = 0, 1, ...)$. Hence, the primary order parameter, also known as the alignment tensor $\boldsymbol{Q}(\boldsymbol{r})$, could be associated with the anisotropic part of the second rank tensor $\boldsymbol{\chi}^2(\boldsymbol{r})$. It reads

$$Q_{\alpha\beta}(\boldsymbol{r}) = \chi^2_{\alpha\beta}(\boldsymbol{r}) - \frac{1}{3}\mathrm{Tr}(\boldsymbol{\chi}^2(\boldsymbol{r}))\delta_{\alpha\beta}. \tag{2}$$

The degeneracy of the tensor $\boldsymbol{Q}(\boldsymbol{r})$ is directly related to the local symmetry of liquid crystals: (a) the $\mathcal{SO}(3)$-symmetric state corresponds to the case when $\boldsymbol{Q}(\boldsymbol{r}) \equiv \boldsymbol{0}$; (b) for the $\mathcal{D}_\infty$- symmetric configuration two out of the three eigenvalues of $\boldsymbol{Q}(\boldsymbol{r})$ are equal; (c) for the $\mathcal{D}_2$- symmetric (biaxial) structure $\boldsymbol{Q}(\boldsymbol{r})$ all three eigenvalues are different.

The fourth rank tensor $\boldsymbol{\chi}^4(\boldsymbol{r})$ of components $\chi^4_{\alpha\beta\gamma\delta}(\boldsymbol{r})$ is the leading secondary order parameter. In the phenomenological description of liquid crystals $\boldsymbol{\chi}^4(\boldsymbol{r})$ usually is disregarded. But, as argued before, for the cubic Blue Phases such a procedure is questionable. In particular, the spatially averaged part $\boldsymbol{B}$ of $\boldsymbol{\chi}^4(\boldsymbol{r})$ seems to be relevant[10]. It is defined as

$$\boldsymbol{B} = \int \mathrm{d}^3\boldsymbol{r}\boldsymbol{\chi}^4(\boldsymbol{r}).$$

The tensor $\boldsymbol{B}$ can be divided into $\mathcal{SO}(3)$–irreducible tensors $\boldsymbol{B}^{(L)}$ of components $B^{(L)}_{\alpha\beta\gamma\delta}$ with momenta $L = 0, 2$ and 4. Clearly, for cubic blue phases, only the $L = 4$ hexadecupole part $\boldsymbol{B}^{(4)}$ of $\boldsymbol{B}$ should be retained.

Now we are ready to construct a generalized Landau- Ginzburg- deGennes expansion of the free energy density in terms of $Q_{\alpha\beta}(\boldsymbol{r})$ and $B^{(4)}_{\alpha\beta\gamma\delta}$. The expansion falls into three parts

$$\mathcal{F} = \mathcal{F}_{\mathrm{LGdG}}[\boldsymbol{Q}, \partial\boldsymbol{Q}] + \mathcal{F}_{\mathrm{coupl}}[\boldsymbol{Q}, \boldsymbol{B}^{(4)}] + \mathcal{F}_{\mathrm{bond}}[\boldsymbol{B}^{(4)}]. \tag{3}$$

The first part is the well known Landau- Ginzburg- deGennes free energy of chiral liquid crystals, also referred to as the standard theory. In terms of dimensionless units introduced by Grebel[14] it reads

$$\mathcal{F}_{\mathrm{LGdG}}[\boldsymbol{Q}(\boldsymbol{r})] = \mathcal{F}_{\mathrm{elastic}}[\boldsymbol{Q}(\boldsymbol{r}), \partial\boldsymbol{Q}(\boldsymbol{r})] + \mathcal{F}_{\mathrm{bulk}}[\boldsymbol{Q}(\boldsymbol{r})], \tag{4}$$

where

$$\mathcal{F}_{\mathrm{elastic}}[\boldsymbol{Q}(\boldsymbol{r}), \partial\boldsymbol{Q}(\boldsymbol{r})] = v^{-1}\int \mathrm{d}^3\boldsymbol{r}\left[\frac{1}{4}\kappa^2\left(\epsilon_{imn}Q_{nj,m} - Q_{ij}\right)^2 + \rho\left(Q_{ij,j}\right)^2\right], \tag{5}$$

and where

$$\mathcal{F}_{\text{bulk}}[\boldsymbol{Q}(\boldsymbol{r})] = v^{-1}\int \mathrm{d}^3\boldsymbol{r}\left[\tau \mathrm{Tr}\boldsymbol{Q}^2 - \sqrt{6}\mathrm{Tr}\boldsymbol{Q}^3 + \mathrm{Tr}(\boldsymbol{Q}^2)^2\right]. \tag{6}$$

Here κ is the chirality, t the reduced temperature, $\tau = \frac{1}{4}(t-\kappa^2)$ the renormalized reduced temperature, ρ the ratio of elastic constants, and v the volume.

We would like to mention that due to the presence of the chiral term in (5) the global minimization of (4) is very difficult and still unsolved. In practice we consider individually all relevant periodic and quasiperiodic structures by parametrizing $\boldsymbol{Q}(\boldsymbol{r})$ in terms of linear combinations of plane waves of helicity m. The expansion reads

$$\boldsymbol{Q}(\boldsymbol{r}) = \sum_{{}^*\boldsymbol{k}} \frac{1}{\sqrt{N_{{}^*\boldsymbol{k}}}}\left\{\sum_{\boldsymbol{k}\in{}^*\boldsymbol{k}}\left[\sum_{m=-2}^{2} Q_m(\boldsymbol{k})M_m(\boldsymbol{k})\right]e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\right\}. \tag{7}$$

Here the wave vectors $\boldsymbol{k}$ are taken from the reciprocal lattice of a space group $\mathcal{G}$, where ${}^*\boldsymbol{k} = \{\boldsymbol{k}' = \boldsymbol{S}\boldsymbol{k}; \{\boldsymbol{S}|\boldsymbol{t}\}\in\mathcal{G}\}$ is the star of $\boldsymbol{k}$ and $N_{{}^*\boldsymbol{k}}$ is the number of prongs of the star ${}^*\boldsymbol{k}$. Finally, $\boldsymbol{M}_m^{(2)}(\boldsymbol{k})$ is the basis of $L=2$ spin tensors, defined with respect to an orthonormal, right-handed local coordinate system $\left\{\hat{\boldsymbol{v}},\hat{\boldsymbol{w}},\hat{\boldsymbol{k}}\right\}$ with $\hat{\boldsymbol{k}} = \boldsymbol{k}/|\boldsymbol{k}|$ parallel to the z-axis. They read

$$\begin{aligned}
\boldsymbol{M}_0^{(2)}(\boldsymbol{k}) &= \frac{1}{\sqrt{6}}\left[3\hat{\boldsymbol{k}}\otimes\hat{\boldsymbol{k}} - \mathbf{1}\right]\\
\boldsymbol{M}_{\pm1}^{(2)}(\boldsymbol{k}) &= \pm\frac{1}{2}\left[(\hat{\boldsymbol{v}}\pm i\hat{\boldsymbol{w}})\otimes\hat{\boldsymbol{k}} + \hat{\boldsymbol{k}}\otimes(\hat{\boldsymbol{v}}\pm i\hat{\boldsymbol{w}})\right]\\
\boldsymbol{M}_{\pm2}^{(2)}(\boldsymbol{k}) &= \frac{1}{2}\left[(\hat{\boldsymbol{v}}\pm i\hat{\boldsymbol{w}})\otimes(\hat{\boldsymbol{v}}\pm i\hat{\boldsymbol{w}})\right]
\end{aligned} \tag{8}$$

The reality condition $\boldsymbol{Q}(\boldsymbol{r}) = [\boldsymbol{Q}(\boldsymbol{r})]^*$ additionally implies that

$$\boldsymbol{M}_m^{(2)}(-\boldsymbol{k}) = (-1)^m\left(\boldsymbol{M}_m^{(2)}(\boldsymbol{k})\right)^*. \tag{9}$$

After identifying all symmetry allowed values of wave vectors and helicity modes entering the summation in the formula (7) the free energy can now be calculated explicitely to yield

$$\begin{aligned}
\mathcal{F}_{\text{deGL}} &= \frac{1}{2}\sum_{\sigma}\sum_{m}\left\{\frac{t}{2} - \kappa^2\left\{\frac{m}{2\sqrt{2}}r\sigma^{\frac{1}{2}} + \left[1+\frac{1}{6}\rho(4-m^2)\right]\frac{1}{4}r^2\sigma\right\}\right\}|Q_m(\boldsymbol{k})|^2\\
&+ -\sqrt{6}\sum_{\boldsymbol{k},\boldsymbol{k}',\boldsymbol{k}''}\sum_{m,m',m''} Q_m(\boldsymbol{k})Q_{m'}(\boldsymbol{k}')Q_{m''}(\boldsymbol{k}'')\\
&\qquad\times \mathrm{Tr}[\boldsymbol{M}_m^{(2)}(\boldsymbol{k})\boldsymbol{M}_{m'}^{(2)}(\boldsymbol{k}')\boldsymbol{M}_{m''}^{(2)}(\boldsymbol{k}'')]\delta_{\boldsymbol{k}+\boldsymbol{k}'+\boldsymbol{k}'',\boldsymbol{0}}\\
&+ \sum_{\substack{\boldsymbol{k},\boldsymbol{k}'\\ \boldsymbol{k}'',\boldsymbol{k}'''}}\sum_{\substack{m,m'\\ m'',m'''}} Q_m(\boldsymbol{k})\cdots Q_{m'''}(\boldsymbol{k}''')\\
&\qquad\times \mathrm{Tr}[\boldsymbol{M}_m^{(2)}(\boldsymbol{k})\boldsymbol{M}_{m'}^{(2)}(\boldsymbol{k}')]\ \mathrm{Tr}[\boldsymbol{M}_{m''}^{(2)}(\boldsymbol{k}'')\boldsymbol{M}_{m'''}^{(2)}(\boldsymbol{k}''')]\\
&\qquad\times\delta_{\boldsymbol{k}+\boldsymbol{k}'+\boldsymbol{k}''+\boldsymbol{k}''',\boldsymbol{0}},
\end{aligned}$$

where r is the absolute value of the wave vector $\boldsymbol{k}$ that minimizes the quadratic part of the free energy (10). Here $\sigma = n_1^2 + n_2^2 + n_3^2$ (n_i being the Miller indices).

Using symmetry-induced expansion of $\boldsymbol{Q}(\boldsymbol{r})$ the minimization of the free energy is thus reduced to a minimization over the real amplitudes $Q_m(|\boldsymbol{k}|)$. Due to numerical difficulties the most advanced calculations done so far were restricted up to four leading stars of the wave vectors and to the $m = 2$ modes. The latter correspond to the low-lying branch of the excitation spectrum of the quadratic part of the free energy (10). The last approximation makes the term proportional to ρ vanish and, consequently, a *universal* phase diagram is obtained in the (t, κ)-plane. As already discussed in the previous section the obtained phase diagram yields an incorrect identification of the structure of BPIII and cannot account for many trends observed experimentally[6].

The extended theory (3) includes additional two terms. The second term in (3), denoted $F_{\text{coupl}}[\boldsymbol{Q}, \boldsymbol{B}^{(4)}]$ is given by[5,6]

$$\mathcal{F}_{\text{coupl}} = -\frac{\lambda}{3} B^{(4)}_{\alpha\beta\gamma\delta} \int \mathrm{d}^3\boldsymbol{r}\, [Q_{\alpha\beta}(\boldsymbol{r})Q_{\gamma\delta}(\boldsymbol{r}) + Q_{\alpha\gamma}(\boldsymbol{r})Q_{\beta\delta}(\boldsymbol{r}) + Q_{\alpha\delta}(\boldsymbol{r})Q_{\gamma\beta}(\boldsymbol{r})]. \quad (11)$$

It describes the lowest order coupling between $\boldsymbol{Q}$ and $\boldsymbol{B}^{(4)}$.

The third term, $\mathcal{F}_{\text{bond}}$, is an arbitrary stable and $SO(3)$- symmetric polynomial in the components of $\boldsymbol{B}^{(4)}$. The simplest expansion for $\mathcal{F}_{\text{bond}}$ has been analysed by Jarić[7]. It reads

$$\begin{aligned} \mathcal{F}_{\text{bond}} \;=\; & \tfrac{1}{2}\overline{a}_2 B^{(4)}_{\alpha\beta\gamma\delta} B^{(4)}_{\alpha\beta\gamma\delta} + \tfrac{1}{3}\overline{a}_3 B^{(4)}_{\alpha\beta\gamma\delta} B^{(4)}_{\alpha\beta\mu\nu} B^{(4)}_{\gamma\delta\mu\nu} \\ & + \tfrac{1}{4}\overline{a}_{4,0} (B^{(4)}_{\alpha\beta\gamma\delta} B^{(4)}_{\alpha\beta\gamma\delta})^2 + \tfrac{1}{4}\overline{a}_{4,1} B^{(4)}_{\alpha\beta\gamma\delta} B^{(4)}_{\gamma\delta\mu\nu} B^{(4)}_{Q\nu\rho\sigma} B^{(4)}_{\rho\sigma\alpha\beta}. \end{aligned} \quad (12)$$

To obtain the global minima of the $\mathcal{F}_{\text{bond}}$ part one usually introduces a nine-dimensional spherical vector order parameter of components $B^{(4)}_m$ ($m = -4, \cdots, 4$), equivalent to the $L = 4$ irreducible part $\boldsymbol{B}^{(4)}$. Cartesian and spherical components are connected through the relation

$$B^{(4)}_{\alpha\beta\gamma\delta} = \sum_{m=-4}^{4} (-1)^m B^{(4)}_m M^{(4)}_{-m}(\hat{\boldsymbol{n}}), \quad (13)$$

where $\boldsymbol{M}^{(4)}(\hat{\boldsymbol{n}})$ are the irreducible basis tensors of spin $L = 4$. They are defined with respect to an orthonormal, right-handed triad $\{\hat{\boldsymbol{n}}_1, \hat{\boldsymbol{n}}_2, \hat{\boldsymbol{n}}_3 = \hat{\boldsymbol{n}}\}$ - the Goldstone mode of the system.

Global minima of $\mathcal{F}_{\text{bond}}$ are located in invariant subspaces of the nine-dimensional space $\{B^{(4)}_m\}$, corresponding to the subgroups of $\mathcal{SO}(3)$ as shown in Fig.(1)[7]. They are called isotropy groups of $B^{(4)}_m$.

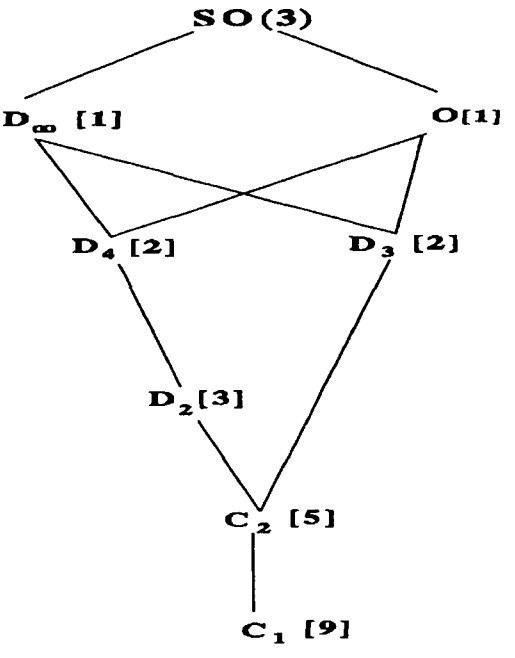

FIGURE 1 Isotropy groups of $B_m^{(4)}$. In square brackets additionally dimensions of the corresponding invariant subspaces are given.

Jarić proved that the lowest order theory (12) stabilizes structures with symmetries corresponding to the invariant subspaces of the lowest dimension: *(i)* an octahedral $\mathcal{O}$, *(ii)* an uniaxial $\mathcal{D}_\infty$ and *(iii)* a $\mathcal{D}_4$. The structure of $\mathcal{D}_4$ symmetry requires $\bar{a}_2 = \bar{a}_3 = 0$, which makes it much less probable than $\mathcal{D}_\infty$ and $\mathcal{O}$. Additionally, $\mathcal{D}_\infty$ and $\mathcal{O}$ symmetries are mutually exclusive in the parameter space.

A global minimization of the full free energy (3) can now proceed according to the scheme given in our recent publication. Since $\mathcal{D}_\infty$ symmetry has not been detected experimentally in BP's only $\mathcal{O}$ symmetry becomes relevant. Hence, we shall restrict $\boldsymbol{B}^{(4)}$ to the space of $\mathcal{O}$ symmetric hexadecupole tensors:

$$\boldsymbol{B}^{(4)} = B_0\sqrt{2\cdot 5\cdot 7}\left\{\sqrt{\frac{5}{14}}\left[M_4^{(4)}(\hat{\boldsymbol{n}}) + M_{-4}^{(4)}(\hat{\boldsymbol{n}})\right] + M_0^{(4)}(\hat{\boldsymbol{n}})\right\}. \tag{14}$$

Here B_0 is the norm of the tensor $\boldsymbol{B}^{(4)}$. Precise equilibrium forms of the tensors $\boldsymbol{Q}(\boldsymbol{r})$ and $\boldsymbol{B}^{(4)}$ may now be determined by minimizing $\mathcal{F}$ with respect to Q_m and B_0. In order to make calculations of the same accuracy as the ones carried out by Grebel, Hornreich and Shtrikman[14] one needs to take up to four leading stars of the wave vectors $\boldsymbol{k}$ for cubic space group symmetries. For each star the dominant contribution comes from $m = 2$ modes, which correspond to the low-lying branch of the excitation spectrum of the quadratic part of $\mathcal{F}_{\text{deGL}}$.

Detailed calculations[6] show that the BPI and the BPII space group structures found earlier within de Gennes' theory (4) are also recovered here. Furthermore,

the relative orientation of the $\boldsymbol{B}^{(4)}$ and $\boldsymbol{Q}(\boldsymbol{r})$ fields (Goldstone mode), which is exclusively determined by a minimization of the coupling term (11), can be fixed along the [100] direction, in agreement with the experiments of Pierański. The calculations also preserve the symmetries of BPI and BPII and improve the phase diagram, although the experimentally observed limited stability of BPII cannot be reproduced. The model may destabilize the artificial $\mathcal{O}^5$ structure but unfortunately BPI is also destabilized in this case. Finally, the model (3) predicts a new structure with cubic symmetry with $\boldsymbol{B}^{(4)} \neq \boldsymbol{0}$ and $\boldsymbol{Q}(\boldsymbol{x}) \equiv \boldsymbol{0}$ which can be made stable in that place of the phase diagram where BPIII is localized.

Though currently available experimental data are indicating that the isotropic model may be more relevant for the structure of BPIII the cubic bond order also seems relevant for the description of the blue phases. The question to be answered experimentally is whether it can form long range ordering in BPIII or whether it only exists locally. Unfortunately at theoretical level a direct comparison of the free energies of the isotropic model and of the cubic bond model is not possible at present.

ELECTROSTRICTION OF CUBIC BLUE PHASES

The deformation of the cubic lattices of blue phases by an electric field depends on the field strength. In a weak field, both BPI and BPII crystals are oriented with their [100] axis parallel to the field $\boldsymbol{E}$ [10]. The reorientation process of the BPI and BPII crystals is governed by the nonlinear dielectric susceptibility $\boldsymbol{\chi}^{(4)}$ and matches the bond orientational order parameter $\boldsymbol{B}^{(4)}$.

In stronger fields, the phenomenon of electrostriction[13,14], *i.e.* the continous deformation of the structure, occurs. In particular, BPI shows the so called *anomalous electrostriction.* It means that the sample is dilated or compressed along the field direction, depending on the orientation of the field with respect to the crystallographic axes. In this paper we look for the explanation of this phenomenon incorporating $\boldsymbol{B}^{(4)}$ tensor into the standard description of the electrostriction of the BPs.

Before going to details of the calculations let us start with the introduction of the electrostriction tensor. One may view electrostriction as a competition between elastic and electric forces which results in an equilibrium deformation of the structure. The deformation is described by the symmetric deformation tensor $\boldsymbol{\varepsilon}$:

$$\varepsilon_{ij} = \frac{1}{2}(\nabla_i v_j + \nabla_j v_i) \tag{15}$$

where the vector of components v_i characterizes a deviation of the mean molecular orientations from their equilibrium positions. Using notation of Stark and Trebin[11] the free energy for a distorted blue phase in an external electric field $\boldsymbol{E}$ is given by

$$\mathcal{F}_{\text{distorsion}} = \frac{1}{2}\boldsymbol{C} \cdot (\boldsymbol{\varepsilon} \otimes \boldsymbol{\varepsilon}) - \frac{\delta'}{8\pi}\boldsymbol{\chi}(\boldsymbol{r}) \cdot (\boldsymbol{E} \otimes \boldsymbol{E}), \tag{16}$$

where the first term represents the elastic free energy with $\boldsymbol{C}$ being the matrix of the elastic constants; δ' is a constant which takes into account the difference

between the internal and external electric field. Expansion of the dielectric tensor $\boldsymbol{\chi}(\boldsymbol{r})$ of the distorted structure with respect to the deformation tensor $\boldsymbol{\epsilon}$ yields

$$\boldsymbol{\chi} = \chi_0 \mathbf{1} + \boldsymbol{b}\boldsymbol{\epsilon} + \boldsymbol{\chi}^4(\boldsymbol{E} \otimes \boldsymbol{E}) + \cdots \tag{17}$$

where χ_0 is the isotropic term, $\boldsymbol{b}$ the elastooptic tensor and $\boldsymbol{\chi}^4$ the nonlinear dielectric susceptibility defined by Eq.(1). As usual, the equilibrium value of the deformation tensor $\boldsymbol{\epsilon}$ is found by minimizing $\mathcal{F}_{\text{distorsion}}$

$$\frac{\partial \mathcal{F}_{\text{distorsion}}}{\partial \boldsymbol{\epsilon}} = 0 = \boldsymbol{C}\boldsymbol{\epsilon} - \frac{\delta'}{8\pi}\boldsymbol{b}^t(\boldsymbol{E} \otimes \boldsymbol{E}), \tag{18}$$

where

$$\boldsymbol{\epsilon} = \boldsymbol{R}(\boldsymbol{E} \otimes \boldsymbol{E}), \tag{19}$$

and where

$$\boldsymbol{R} = \frac{\delta'}{8\pi}\boldsymbol{C}^{-1}\boldsymbol{b}^t. \tag{20}$$

For the cubic structures the matrix of elastic constants can be written using the Voigt notation as

$$\boldsymbol{C} = \begin{pmatrix} C_1 & C_2 & C_2 & 0 & 0 & 0 \\ C_2 & C_1 & C_2 & 0 & 0 & 0 \\ C_2 & C_2 & C_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & C_3 & 0 & 0 \\ 0 & 0 & 0 & 0 & C_3 & 0 \\ 0 & 0 & 0 & 0 & 0 & C_3 \end{pmatrix},$$

where $C_1 = C_{1111}$, $C_2 = C_{1122}$, $C_3 = C_{1212}$. This implies that the electrostriction tensor $\boldsymbol{R}$ also has only three independent components: $R_1 = R_{1111}$; $R_2 = R_{1122}$; $R_3 = R_{2323}$.

Let us now calculate the free energy of the field induced deformation as a function of the undistorted order parameters $\boldsymbol{Q}(\boldsymbol{r})$ and $\boldsymbol{B}^{(4)}$. If $\boldsymbol{r}$ is a vector describing the position of the lattice points before the deformation then, to lowest order, the position $\tilde{\boldsymbol{r}}$ of the distorted structure is

$$\tilde{\boldsymbol{r}} = (\mathbf{1} + \boldsymbol{\epsilon})\boldsymbol{r}. \tag{21}$$

The wave vectors $\tilde{\boldsymbol{k}}$ of the distorted reciprocal lattice transform inversely

$$\tilde{\boldsymbol{k}} = (\mathbf{1} + \boldsymbol{\epsilon})^{-1}\boldsymbol{k} \approx (\mathbf{1} - \boldsymbol{\epsilon})\boldsymbol{k}. \tag{22}$$

The deformation of the $\boldsymbol{k}$ vectors rotates the tensors $\boldsymbol{M}_2^{(2)}(\boldsymbol{k})$. Additionally, $\boldsymbol{Q}(\boldsymbol{k})$ and $\boldsymbol{B}^{(4)}$ acquire the homogeneous parts $\boldsymbol{b}\boldsymbol{\epsilon}$ and $\tilde{\boldsymbol{b}}\boldsymbol{\epsilon}$, respectively.

All the calculations are carried out within the model of rigid helices. By this scheme we imply that the deformation of the amplitudes $Q_2(\boldsymbol{k})$ and of the secondary order parameter $\boldsymbol{B}^{(4)}$ is disregarded. More specifically

$$\boldsymbol{Q}(\boldsymbol{r}) = \sum_{\boldsymbol{k}} Q_2(\boldsymbol{k})\boldsymbol{M}_2^{(2)}(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \xrightarrow{\boldsymbol{\epsilon}} \widetilde{\boldsymbol{Q}}(\boldsymbol{r}) = \boldsymbol{b}\boldsymbol{\epsilon} + \sum_{\boldsymbol{k}} Q_2(\boldsymbol{k})\boldsymbol{M}_2^{(2)}(\tilde{\boldsymbol{k}})e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

and

$$\boldsymbol{B}^{(4)} \xrightarrow{\boldsymbol{\varepsilon}} \widetilde{\boldsymbol{B}^{(4)}} = \boldsymbol{B}^{(4)}.$$

The distorted tensors $\boldsymbol{M}_2^{(2)}(\tilde{\boldsymbol{k}})$ can be expanded with respect to the deformation tensor $\boldsymbol{\varepsilon}$. The corresponding formulae have been derived by Stark and Trebin[11].

Now, the excess free energy resulting from the distortion of the cubic ground state reads

$$\mathcal{F}_{\text{distorsion}} = \Delta\mathcal{F}_{\text{Q}} + \Delta\mathcal{F}_{\text{coupl}} + \Delta\mathcal{F}_{\text{bond}}, \tag{23}$$

where

$$\Delta\mathcal{F}_{\text{Q}} = \mathcal{F}_{\text{LGdG}}[\widetilde{\boldsymbol{Q}}] - \mathcal{F}_{\text{LGdG}}[\boldsymbol{Q}], \tag{24}$$

$$\Delta\mathcal{F}_{\text{coupl}} = \mathcal{F}_{\text{coupl}}[\widetilde{\boldsymbol{Q}}] - \mathcal{F}_{\text{coupl}}[\boldsymbol{Q}]. \tag{25}$$

Due to the approximation of the rigid helices the $\Delta\mathcal{F}_{\text{bond}}$ vanishes and we are effectively left with the coupling term. To perform the calculations of the $\Delta\mathcal{F}_{\text{coupl}}$ part the Goldstone mode is fixed parallel to $[n00]$ directions of the $\mathcal{O}^2$ and $\mathcal{O}^8$ structures.

Using the scheme presented previously, and also minimizing the free energy $\mathcal{F}_{\text{distorsion}}$ with respect to the elastooptic tensor $\boldsymbol{b}$, we arrive to the formulas for independent components of the electrostriction tensor $\boldsymbol{R}$

$$R_1 = \frac{\delta'}{8\pi}\frac{b_1}{C_1 - C_2} = -2R_2, \tag{26}$$

and

$$R_3 = \frac{\delta'}{8\pi}\frac{b_3}{C_3}. \tag{27}$$

They obey an additional condition $R_1 = -2R_2$. This is the consequence of our approximation in which the density is conserved. The numerical values of the electrostriction tensor depend on the order parameters $\boldsymbol{Q}$ and $\boldsymbol{B}^{(4)}$ that minimize the free energy (3) of the unperturbed states. Under the approximation of rigid helices the minimization considerably simplifies as the purely bond order part does not enter directly the electrostriction tensor calculations. Consequently it is sufficient to minimize de Gennes part (4) of the total free energy (3) together with the coupling part (11) and treat the product λB_0 as a free parameter.

Being aware of the fact that the free energy (4) does not reproduce the relative stability of BPI and BPII structures we used a minimization procedure consisting of two parts. First of all only the stability of BPI with respect to the isotropic phase was considered. Secondly the same minimization was carried out by assuming that only BPII and the isotropic phase are present. Thus we searched for the regions on the phase diagram where the particular cubic blue phase had lower free energy than the isotropic phase. More specifically, for fixed values of the parameters κ, λB_0 and of the temperature we found the values of the scalar amplitudes $Q_2(\boldsymbol{k})$ corresponding to a minimum of the free energy up to three stars of symmetry allowed $\boldsymbol{k}$-vectors. Taking into account that the amplitude of the fourth star is negligible this makes our calculations consistent with those of Grebel[14].

The results are presented in Fig.(2), see also[9]. It shows the areas in $(\lambda B_0, \kappa)$-plane, where the anomalous electrostriction can occur irrespectively of the value of

the temperature. Five regions can be distinguished. In the first area, denoted O^8, only BPI behaves anomalously. Then follows the area ($O^8 + O^2$) where R_1/R_3 is negative for both structures. For still higher coupling strength only BPII behaves anomalously (O^2). In the remaining two areas, the ratio R_1/R_3 is positive for BPI and BPII.

The results show that the anomalous electrostriction of the BPI is explained with the help of the bond-order tensor. However, for certain values of the parameter λB_0, such an anomalous behaviour may also be induced in the BPII phase, which is not observed experimentally. The values of the coupling constant λB_0 for which the anomalous behaviour is induced in BPI but not in the BPII give hints as regarding models proposed for the structure of the BP III.

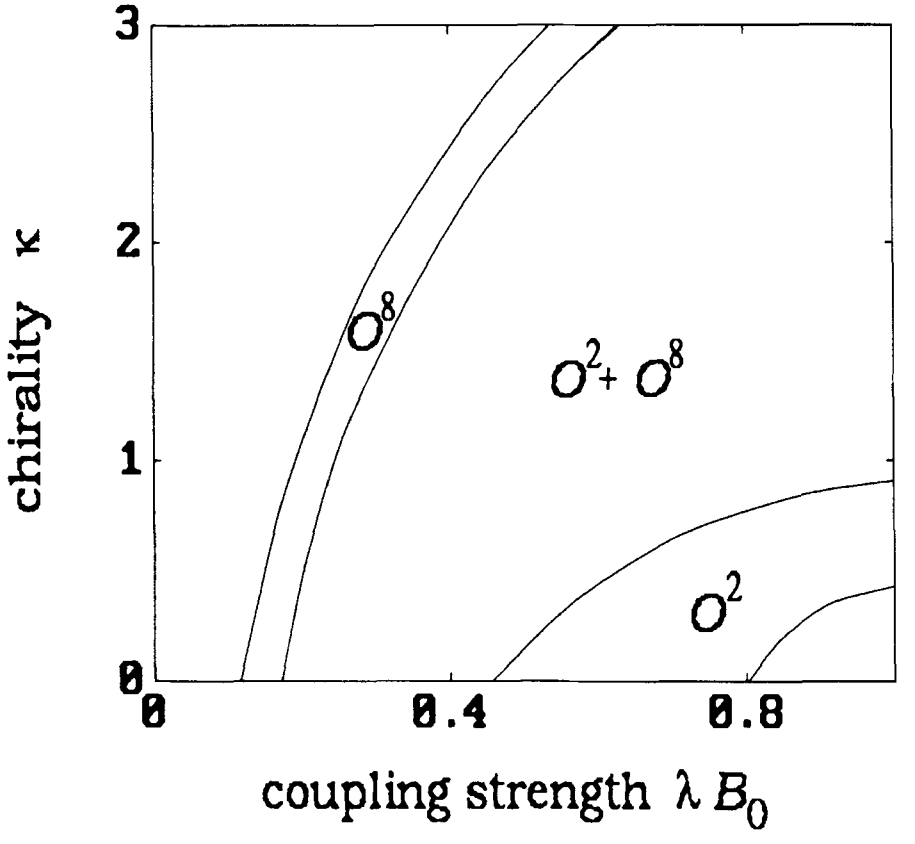

FIGURE 2 The dependance of the electrostriction on the coupling strength λB_0. The symbol of the phase indicates that in the particular area the given structure shows an anomalous behaviour.

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