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Résumé. — L'électrostriction des Phases Bleues cubiques BPI et BPII est étudiée dans le mélange CB15/E9 ayant une anisotropie diélectrique positive. Dans la phase BPI de ce système, le pas du réseau dans la direction du champ électrique diminue sous l'influence de ce champ. Conformément aux prédictions théoriques, les composantes du tenseur d'électrostriction de ce mélange ont des signes opposés à celles trouvées dans les systèmes ayant une anisotropie diélectrique négative.

Abstract. — The electrostriction of the cubic blue phases was investigated in the well known mixture CB15/E9. The results for BPI prove that a decrease of the lattice constant in the field direction with increasing field strength can occur in a system with positive dielectric anisotropy. In agreement with recent theoretical considerations, all components of the electrostriction tensor for this mixture exhibit the opposite sign compared to systems with negative dielectric anisotropy.

Introduction.

The cholesteric blue phases BPI and BPII are known to exhibit a body centered cubic O₈ (I 4 132) and a simple cubic O² (P 4 32) structure respectively [1]. The lattice constants are in the range of the wavelength of visible light. Thus, Bragg scattering of visible light can be observed according to the relation

$$\lambda_{hkl} = 2 \cdot \bar{n}(\lambda_{hkl}) \cdot d_{hkl} \cdot \cos \theta$$

where $d_{hkl}$ is the interplanar spacing and $\theta$ is the angle between a wavevector normal to the planes $(hkl)$ and the direction of light incidence.

Due to deformations of the cubic lattice, the Bragg-wavelengths are shifted under the influence of an electric field [2]. The signs of these effects depend on the sign of the dielectric anisotropy $\epsilon_a = \epsilon_1 - \epsilon_\perp$ of the material and on the orientation of the cubic unit cell with respect to the field direction. For systems with positive dielectric anisotropy, it is known [2, 3] that red-shifts of the Bragg-peaks can occur under the influence of an electric field indicating that the interplanar spacing in the field direction increases with increasing field strength.
However, for systems with negative dielectric anisotropy, the Bragg-peaks can also be shifted to smaller wavelengths [4]. For BPI in systems with $\varepsilon_a < 0$, a decrease or an increase of the interplanar spacing in the field direction can be observed, depending on the orientation of the lattice [4].

The continuous deformation of the Blue Phase structure under the influence of alternating electric fields is determined by the electrostriction tensor $\gamma_{ijkl}$ describing the dependence of the deformation tensor $\varepsilon_{ij}$ on quadratic terms of the electric field strength:

$$\varepsilon_{ij} = \sum_{k=1}^{3} \sum_{l=1}^{3} \gamma_{ijkl} E_k E_l.$$  \hspace{1cm} (2)

Due to the cubic symmetry, the electrostriction tensor for the Blue Phases exhibits only three independent components. So far, the complete electrostriction tensor has been determined for BPII in a mixture with positive dielectric anisotropy [5] and for BPI and BPII in several mixtures with negative dielectric anisotropy [6], but not for BPI in systems with positive dielectric anisotropy.

In a recent paper by Dmitrienko [7], the different effects observed for BPI in systems with $\varepsilon_a < 0$ have been explained theoretically. Moreover, the considerations in this article predict that the signs of all electrostriction components are changed with the sign of $\varepsilon_a$. Consequently, a decrease of the lattice constant in the field direction should be expected in systems with $\varepsilon_a > 0$ for BPI oriented with a fourfold axis parallel to the field direction. This behaviour has not been demonstrated, so far.

In this paper, investigations on the electrostriction are presented for mixtures with positive dielectric anisotropy consisting of the chiral compound CB15 (BDH) and the nematic mixture E9 (BDH). Voltages with a frequency of 1 kHz were used up to an electric field strength of 2 V/\mu m (rms). For higher field strengths, field-induced phase transitions to non-cubic blue phase modifications, to the cholesteric phase and to the nematic state can occur. A review on these additional field effects observed in the investigated system has been given elsewhere [8].

**Experimental results and discussion.**

For a mixture consisting of 49.2 % (by weight) CB15 and E9, the influence of an electric field on the Bragg reflection of BPI and BPII has been studied using a multielement-spectroradiometer PR-702A (Photo Research) as described earlier [9]. The results (Fig. 1) show that a decrease of the interplanar spacing in the field direction with increasing field strength can occur also in systems with $\varepsilon_a > 0$. This behaviour is observed for the (002)-planes of BPI if a fourfold axis [001] is parallel to the field direction.

From the results represented in figure 1, the electrostriction components for BPI and BPII can be determined [5, 6] by plotting the relative changes of the Bragg wavelengths versus the square of the electric field strength. For the two different orientations, straight lines are obtained exhibiting the slopes $\tilde{\gamma}_{[001]}$ and $\tilde{\gamma}_{[011]}$, respectively. Assuming a constant volume of the unit cell as found for systems with $\varepsilon_a < 0$, the electrostriction coefficients are given by the following relations [6].

$$\gamma_{iiii} = \tilde{\gamma}_{[001]}$$

$$\gamma_{iiij} = -\frac{1}{2} \tilde{\gamma}_{[001]}$$

$$\gamma_{iiij} = \tilde{\gamma}_{[011]} - \frac{1}{2} \tilde{\gamma}_{[001]}.$$  \hspace{1cm} (3)
Fig. 1. — Wavelength of the Bragg peaks (corresponding to planes \( (hkl) \)) versus applied field strength for BPI (34.1 °C) and BPII (34.3 °C) oriented with either a fourfold \([001]\) or a twofold axis \([011]\) parallel to the field direction (mixture of 49.2 % CB15 with E9). (\(\ast\)) Values observed for back reflection (\(\Theta = 5^\circ\)). (\(\bigcirc\)) Values observed for \(\Theta = 20^\circ\).

Using these equations, the components of the electrostriction tensor given in table I were obtained. The components of the electrostriction tensor for BPII exhibit the same order of magnitude as the values which have been determined by Porsch and Stegemeyer [5].

For single crystals of BPI exhibiting the orientation \([001] \parallel E\), the decrease of the lattice constant in the field direction with increasing field strength can also be observed by Kossel diagrams (Fig. 2). If BP monocrystals are illuminated with convergent monochromatic light in a polarizing microscope, the light scattered by planes \((hkl)\) forms a Kossel cone with apex angle \(2 \theta\) where \(\theta\) is given by equation (1). In the focal plane of the microscope objective, the

Table I. — Electrostriction components for a mixture of 49.2 % (by weight) CB15 in E9. The values are determined from the measurements of the selective reflection represented in figure 1. (Suffixes : \(i, j = x, y, z\); \(i \neq j\)).

<table>
<thead>
<tr>
<th>Blue phase</th>
<th>(\gamma_{iii})</th>
<th>(\gamma_{iij})</th>
<th>(\gamma_{ijj})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPI</td>
<td>(-3.2)</td>
<td>(+1.6)</td>
<td>(+22.1)</td>
</tr>
<tr>
<td>BPII</td>
<td>(+14.6)</td>
<td>(-7.3)</td>
<td>(+17.4)</td>
</tr>
</tbody>
</table>
Fig. 2. — Kossel diagrams for monocrystals of the deformed BPI in the electric field, oriented with a fourfold axis ([001]) parallel to the field direction (42.5 % CB15 in E9, $E \approx 21$ V/12 μm). a) $\lambda = 588$ nm, b) $\lambda = 550$ nm, c) $\lambda = 520$ nm. The theoretical diagrams are given (below) for $\alpha = 0.93$ which corresponds to a tetragonal structure with the ratio $a_z/a_x = 0.9$ for the lattice constants $a_z$ parallel and $a_x$ perpendicular to the field direction.

Kossel diagram can be observed which is a planar projection of the intersection lines of the Kossel cones with a sphere twice as large as the Ewald sphere [6, 8]. The experimental Kossel diagrams given in figure 2 show, that the wavelength $\lambda_{101}(\tilde{\theta})$ where the (101)- and the ($\overline{1}01$)-ring touch each other is larger (> 588 nm) than the wavelength $\lambda_{002}(0)$ (550 nm < $\lambda_{002}(0)$ < 588 nm) where the (002)-ring appears in the center of the diagram. For a tetragonal structure with the lattice constants $a_z$ parallel and $a_x$ perpendicular to the field direction, the angle $\tilde{\theta}$ is given by the relation

$$\tilde{\theta} = \arctan \frac{a_z}{a_x} \Leftrightarrow \cos \tilde{\theta} = \frac{1}{\sqrt{1 + \frac{1}{a_x^2} + \frac{1}{a_z^2}}}$$  \hspace{1cm} (4)

and the interplanar spacing $d_{101}$ by

$$d_{101} = \frac{1}{\sqrt{\frac{1}{a_z^2} + \frac{1}{a_x^2}}}$$  \hspace{1cm} (5)
According to equation (1), the values of the characteristic wavelengths $\lambda_{101}(\tilde{\theta})$ and $\lambda_{002}(0)$ can be obtained:

$$\lambda_{101}(\tilde{\theta}) = \frac{2na_z}{1 + \left(\frac{a_z}{a_x}\right)^2}, \quad (6)$$

$$\lambda_{002}(0) = \frac{na_z}{\bar{a}_x}. \quad (7)$$

Thus, the relation $\lambda_{101}(\tilde{\theta}) > \lambda_{002}(0)$ indicates a ratio $a_z/a_x < 1$ for the lattice constants. Since the diameters of the Kossel rings increase monotonically with decreasing wavelength, the ratio of the parameters $\xi_1$ and $\xi_2$ indicates also the relation $a_z < a_x$. For $E = 0$, the Kossel diagrams of the same crystals of BPI exhibit $\lambda_{101}(\tilde{\theta}) = \lambda_{002}(0)$ and $\xi_1 = \xi_2$ which is characteristic for a cubic structure.

The large effect represented in figure 2 was observed only for crystals of BPI which are grown from the isotropic phase in a mixture consisting of 42.5 wt.% CB15 in E9. For temperatures below the coexistence region of BPI and the isotropic phase, the effects are much smaller. The mixture containing 49.2% CB15 exhibits no coexistence of BPI and the isotropic phase, since BPII appears in the temperature range above BPI. As a consequence, the effect of the electric field on the lattice constant of BPI could not be detected by the Kossel technique (as expected from the relatively small change shown in Fig. 1).

In order to study the behaviour of the selective reflection for the latter mixture more precisely, the angular dependence has been investigated using cells with a reflecting second interface (Fig. 3). This technique allows to study also the interplanar spacings of planes which are not parallel to the sample surface [9]. For BPI oriented with a fourfold axis [001] parallel to the surface normal, not only a (002)-peak can be observed but also peaks corresponding to (101)- and (011)-planes (Fig. 4). For these planes, the angle $\theta$ between the reciprocal lattice vector $\mathbf{q}$ and the wavevector $\mathbf{k}$ of the incident light decreases with increasing angle $\theta$ between the wavevector $\mathbf{k}$ and the surface normal and according to the Bragg condition (Eq. (1)), the corresponding peaks are shifted to longer wavelengths with increasing angle $\theta$. When applying an electric field, the (101)- and (011)-reflection bands are

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Fig. 3. — Schematic drawings of the pass of light in our experimental set up: the reflection spectra are determined for $\Theta_1 = \Theta_2$. Due to reflection at the second interface (a) Bragg-peaks can be observed also for planes being not parallel to the surface [9]. For these planes, the Bragg wavelength depends not only on the angle $\Theta$ but also on the azimuthal angle $\varphi$ describing the orientation of the lattice (b).
shifted to larger wavelength (Fig. 4) which can be explained by a decrease of the angle $\theta$ due to the decrease of the lattice constant in the field direction: if the lattice constant along the [001]-direction ($a$) is changed by the factor $\alpha$ ($a_z = a \cdot \alpha$) and the volume of the unit cell is preserved ($a_x = a_z = a/\sqrt{\alpha}$), the interplanar spacings and the angle $\theta$ in equation (1) are given by

$$d_{\text{101}} = d_{\text{011}} = \frac{\alpha}{\sqrt{1 + \alpha^3}} \cdot a$$

\[ \text{(8)} \]
and

\[ \cos \theta = \frac{-h \sqrt{\alpha} \sin \Theta \cos \varphi - k \sqrt{\alpha} \sin \Theta \sin \varphi + l \alpha^{-2} \cos \Theta'}{\sqrt{h^2 \alpha + k^2 \alpha + l^2 \alpha^{-2}}} \]  \hspace{1cm} (9) 

where \( \varphi \) is the azimuthal angle shown in figure 3b. According to this relation, the Bragg-wavelengths of the (101)- and (011)-planes are expected to increase with decreasing \( \alpha \), as found in the experiment.

The influence of an electric field on BPI for the orientation [001] \( \parallel \) \( E \) has been studied earlier for a similar system (CB15/M18) by Porsch and Stegemeyer [3]. The authors reported on a splitting of the respective reflection band (Fig. 1a in Ref. [3]) and showed that the mean value for the two wavelengths of maximum intensity increases slightly with increasing field strength (Fig. 2a of Ref. [3]). The splitting observed by Porsch and Stegemeyer in transmission is similar to the behaviour of the system studied here in back reflection. For the mixture CB15/E9, this splitting can be explained by a blue shift of the (002)-peak and by red-shifts of the (011)- and (101)-peaks. Both effects indicate a decrease of the lattice constant in the field direction, as explained above.

For BPII, our observations of the selective reflection are in agreement with the results given in references [3, 5]. According to our considerations presented here, the triplet of the blue reflection band at \( \lambda_{011}(0) \) shown in figure 1b of reference [3] can be explained by a contribution of the (010)- and (001)-planes to the scattering of [011]-oriented monocrystals of BPII, if the cubic structure is slightly deformed or if the [011] axis is not exactly parallel to the direction of light incidence.

Conclusions.

It has been demonstrated for the first time that the influence of an electric field can lead to a decrease of the lattice constant in the field direction for BPI in a system with positive dielectric anisotropy. A comparison of the results presented here and the results of earlier investigations [6] shows (Fig. 5, Tab. II) that the components of the electrostriction tensor for the system with \( \varepsilon_a > 0 \) exhibit just the opposite signs compared to systems with \( \varepsilon_a < 0 \). This behaviour is in agreement with the theoretical considerations by Dmitrienko [7]. For free single crystals of BPI surrounded by the isotropic phase, the effect of the electric field was found to be larger than for temperatures below the coexistence region of BPI and the

![Fig. 5. — Schematic representation of the deformation of the unit cell due to electrostriction for materials with positive and negative dielectric anisotropy \( \varepsilon_a \) if the field direction is parallel either to a fourfold or to a twofold axis.](image-url)
Table II. — Sign of the electrostriction components depending on the dielectric anisotropy.

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon_a &gt; 0$</th>
<th></th>
<th>$\varepsilon_a &lt; 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BPI</td>
<td>BPII</td>
<td>BPI</td>
</tr>
<tr>
<td>$\gamma_{iii}$</td>
<td>$-$</td>
<td>$+$</td>
<td>$+$</td>
</tr>
<tr>
<td>$\gamma_{ijj}$</td>
<td>$+$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
<tr>
<td>$\gamma_{ijj}$</td>
<td>$+$</td>
<td>$+$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

isotropic phase. It should be interesting to study the influence of these conditions as well as the influence of the chirality more precisely.

Acknowledgments.

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References