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HAL Id: jpa-00210937
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Electrostriction of BPI and BPII for blue phase systems with negative dielectric anisotropy (*)

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(Reçu le 27 septembre 1988, accepté le 21 novembre 1988)

Résumé. — La déformation des mésophases cubiques Phase Bleue I (BPI) et Phase Bleue II (BPII) sous l'influence d'un champ électrique faible est étudiée dans des mélanges avec une anisotropie diélectrique négative. Les pas du réseau en direction du champ électrique augmentent ou diminuent, selon l'orientation de la cellule élémentaire. Dans cet article, nous présentons des diagrammes de Kossel de ces structures déformées. Ces diagrammes permettent de déterminer complètement le tenseur d'électrostriction décrivant de petites distorsions du réseau dans un champ électrique. Pour deux mélanges, les valeurs des coefficients du tenseur d'électrostriction sont données.

Abstract. — The deformation of liquid crystalline blue phases BPI and BPII under the influence of a weak electric field is studied for systems with negative dielectric anisotropy. For the initially cubic structures of these materials, the interplanar spacings in the field direction were found to increase or to decrease in the field, depending on the orientation of the unit cell. In this paper, Kossel diagrams of the deformed structures are presented. By the reported experiments, the electrostriction tensor describing small distortions of the lattice in the electric field can be determined completely. For two mixtures, numerical values of the electrostriction coefficients are given.

1. Introduction.

During the last decade, cholesteric blue phases (BP), and especially the two cubic modifications BPI [body centered cubic, space group O\(^8\) (I\(4\_32\))] and BPII [simple cubic O\(^2\) (P\(4\_32\))], have been subjected to many investigations [1]. The most interesting feature of these phases is Bragg scattering of light in the visible wavelength range due to the size of the lattice constants (of the order 10\(^{-7}\) to 10\(^{-6}\) m).

Under the influence of an electric field, variations of the wavelengths $\lambda_{hkl}$ of the Bragg peaks have been observed [2] which can be explained by continuous deformation of the lattice [3], by reorientation [4], or by field-induced phase transitions between different blue phase modifications [2a, 5-8]. The electric field effects have been found to depend crucially on the sign of the dielectric anisotropy $\varepsilon_a = E_{ll} - E_{11}$ which indicates whether the molecules tend to align parallel ($\varepsilon_a > 0$) or perpendicular ($\varepsilon_a < 0$) to the field direction.

In this paper, we focus on small distortions of the cubic structure for materials with $\varepsilon_a < 0$. Earlier studies [9, 10] on one of the systems under investigation have shown that for BPI \([110] \parallel E\) and BPII \([100] \parallel E\) the interplanar spacing in the field direction can decrease with increasing field strength, whereas for materials with $\varepsilon_a > 0$ the inverse effect is observed. In another paper [11], we report on the first observation of a hexagonal blue phase in systems with negative dielectric anisotropy.

For small distortions, the deformation of a lattice can be described by the second rank strain tensor [12] which can be expanded in powers of the electric field strength $E$. Since ac-fields are used and since the effects of the electric field on the blue phase structure are independent of the field direction, the lowest order term to be considered is quadratic in $E$. Recently, F. Porsch and H. Stegemeyer [13] have shown that the quadratic term is adequate to describe the deformation of BPI in an electric field and that terms of higher order can be neglected. In this case, the dependence of the strain on $E$ is completely described by the fourth rank electrostriction tensor. Here, for the first time all coefficients of the electrostriction tensor will be given for BPI and BPII occurring in two mixtures with $\varepsilon_a < 0$.

2. The electrostriction tensor.

Homogeneous strain in a three dimensional lattice can be described by the symmetric strain tensor $\varepsilon_{ij}$, defined as

$$\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right),$$  \hspace{1cm} (1)

where the vector $(u_1, u_2, u_3)$ describes the displacement of a lattice point with coordinates $(x_1, x_2, x_3)$. The lattice displacements $u$ are not necessarily identical with the displacements of the molecules composing the liquid crystal; one can imagine a displacement of the lattice just by the reorientation of the molecules without any displacement of their mass centers. In the light diffraction experiments considered in the present paper, the deformation of the diffraction diagrams is sensitive only to the lattice deformation $u$.

If the coordinate system is given by the unit vectors of the cubic lattice to be described, the diagonal components $\varepsilon_{ii}$ give the relative change of the lattice constants due to longitudinal strains, while the other components measure the shear strains.

For small deformations of the cubic structure which are independent of the sign of the electric field $E$ (piezoelectricity can be excluded), $\varepsilon_{ij}$ can be written as

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

In this relation, $\gamma_{ijkl}$ is the fourth rank electrostriction tensor. Due to the symmetry of $\gamma_{ijkl}$ in the first two and the last two suffixes equation (2) can be abbreviated using a matrix notation:
For cubic symmetry, only three coefficients of \( y_{ijkl} \) are independent and the matrix takes the form

\[
\begin{pmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
2 \varepsilon_{23} \\
2 \varepsilon_{13} \\
2 \varepsilon_{12}
\end{pmatrix}
= \begin{pmatrix}
\gamma_{1111} & \gamma_{1122} & \gamma_{1133} & 2 \gamma_{1123} & 2 \gamma_{1113} & 2 \gamma_{1112} \\
\gamma_{2211} & \gamma_{2222} & \gamma_{2233} & 2 \gamma_{2223} & 2 \gamma_{2213} & 2 \gamma_{2212} \\
\gamma_{3311} & \gamma_{3322} & \gamma_{3333} & 2 \gamma_{3323} & 2 \gamma_{3313} & 2 \gamma_{3312} \\
2 \gamma_{2311} & 2 \gamma_{2322} & 2 \gamma_{2333} & 4 \gamma_{2323} & 4 \gamma_{2313} & 4 \gamma_{2312} \\
2 \gamma_{1311} & 2 \gamma_{1322} & 2 \gamma_{1333} & 4 \gamma_{1323} & 4 \gamma_{1313} & 4 \gamma_{1312} \\
2 \gamma_{1211} & 2 \gamma_{1222} & 2 \gamma_{1233} & 4 \gamma_{1223} & 4 \gamma_{1213} & 4 \gamma_{1212}
\end{pmatrix}
\begin{pmatrix}
E_1 \\
E_2 \\
E_3 \\
E_2 \\
E_1 \\
E_2
\end{pmatrix}
\]  

(3)

For cubic symmetry, only three coefficients of \( y_{ijkl} \) are independent and the matrix takes the form

\[
\begin{pmatrix}
\varepsilon_{11} \\
\varepsilon_{22} \\
\varepsilon_{33} \\
2 \varepsilon_{23} \\
2 \varepsilon_{13} \\
2 \varepsilon_{12}
\end{pmatrix}
= \begin{pmatrix}
\gamma_{1111} & \gamma_{1122} & \gamma_{1122} & 0 & 0 & 0 \\
\gamma_{1122} & \gamma_{1111} & \gamma_{1112} & 0 & 0 & 0 \\
\gamma_{1122} & \gamma_{1112} & \gamma_{1111} & 0 & 0 & 0 \\
0 & 0 & 0 & 4 \gamma_{2323} & 0 & 0 \\
0 & 0 & 0 & 0 & 4 \gamma_{2323} & 0 \\
0 & 0 & 0 & 0 & 0 & 4 \gamma_{2323}
\end{pmatrix}
\begin{pmatrix}
E_1 \\
E_2 \\
E_3 \\
E_2 \\
E_1 \\
E_2
\end{pmatrix}
\]  

(4)

It will be shown in this paper that the coefficients \( \gamma_{1111} \), \( \gamma_{1122} \) and \( \gamma_{2323} \) can be determined experimentally.

3. Experimental conditions.

Kossel diagrams, which are due to Bragg scattering from blue phase monocrystals illuminated with convergent monochromatic light, have been described previously [8, 11].

Two separate mixtures have been investigated. The first is a mixture of the chiral compound S-(−)-4-((1-Methyl-heptyl)-oxybenzoyl)-4-hexyloxy-benzoate ("S 811", Merck, Germany)

(1) \[
\begin{array}{c}
\text{C}_6\text{H}_{13}\text{O} \\
\text{COO} \\
\text{COO} \\
\text{CH} - \text{C}_6\text{H}_{13}
\end{array}
\]

with the nematic mixture EN 18 (Chisso Corp., Japan) [14]. The second is a mixture of 1,4-Bis-<4-(2-methylbutyl)-benzoyloxy>-2-chloro-benzene

(2) \[
\begin{array}{c}
\text{C}_2\text{H}_5 \\
\text{CH} - \text{CH}_2 \\
\text{COO} \\
\text{OOC} \\
\text{CH} - \text{C}_2\text{H}_3 \\
\end{array}
\]

with the nematic mixture ZLI 2585 (Merck [14]). Both mixtures give similar results.

In order to study the behaviour in an electric field, alternating voltages of up to 60 V at frequencies between 1 kHz and 5 kHz have been applied to samples of 10-30 \(\mu\)m thickness. The liquid crystal itself is contained between the flat end of a glass cylinder coated with evaporated aluminium and a cover slide coated with a transparent conducting material. The
temperatures of the two surfaces have been separately controlled to an accuracy of ± 0.01 °C by Peltier elements. Kossel diagrams are observed in the focal plane of the objective of a polarizing microscope (type PME, Olympus) when the sample is illuminated with monochromatic convergent light.

In this case, the Bragg condition reads as

\[ 2d_{hkl} \cos \theta = \frac{\lambda}{\bar{n}}, \]

where \( d_{hkl} \) is the interplanar spacing of planes described by the Miller indices \((hkl)\), \( \lambda \) is the Bragg wavelength outside the crystal and \( \bar{n} = \bar{n}(\lambda) \) a mean refractive index. Monochromatic light of wavelength \( \lambda \) is scattered by a set of planes \((hkl)\) if the condition \( \lambda < \lambda_{hkl} \) is fulfilled, where \( \lambda_{hkl} = 2d_{hkl} \bar{n}(\lambda_{hkl}) \) is the Bragg wavelength for backscattering \((\theta = 0)\). The scattered light forms a cone with an apex angle \( \theta \) with respect to the normal to the planes, where

\[ \cos \theta = \frac{\lambda}{\lambda_{hkl}} \cdot \frac{\bar{n}(\lambda_{hkl})}{\bar{n}(\lambda)}. \]

Each of these Kossel cones leads to an ellipse in the Kossel diagram observed in the microscope. Planes perpendicular to the direction of observation are represented by a circle around the center of the Kossel diagram.

Investigations of the deformation of the blue phase structure under the influence of an electric field involve two quantities:

(i) The relative change of interplanar spacings \( d_{hkl} \) equals the relative change of the wavelength \( \lambda_{hkl} \) if the dispersion of the refractive index is neglected:

\[ \frac{d_{hkl}(E) - d_{hkl}(0)}{d_{hkl}(0)} \approx \frac{\lambda_{hkl}(E) - \lambda_{hkl}(0)}{\lambda_{hkl}(0)}. \]

The wavelength \( \lambda_{hkl} \) can be determined by variation of the wavelength \( \lambda \) of the monochromatic light used in the experiment. For \( \lambda = \lambda_{hkl} \) the angle of the Kossel cone becomes \( \theta = 0 \) and the respective Kossel line vanishes. (For \( \lambda > \lambda_{hkl} \) no Bragg reflection is observed).

(ii) The angle \( \theta \) between a wavevector \( q_{hkl} \) normal to the planes \((hkl)\) and the field direction (which is parallel to the viewing direction) is given by the ratio between the short axis \( r_1 \) and the long axis \( r_2 \) of the Kossel ellipse: \( \theta = \arccos \frac{r_1}{r_2} \).

A more convenient method to obtain the tilt angle \( \theta \) between a wavevector \( q_{hkl} \) and the field direction requires the determination of \( \lambda_1 = \lambda_{hkl} \) and a second characteristic wavelength \( \lambda_2 \) (Fig. 1): For \( \theta \neq 0 \) and \( \theta \neq 90° \) two ellipses corresponding to \( q_{hkl} \) and \( q_{hkl} \) can be observed in the Kossel diagram. For the wavelength \( \lambda \) where the two ellipses touch each other, the angle \( \theta \) is equal to the angle \( \theta \) of the Kossel cone and thus, according to equation (6):

\[ \theta \approx \arccos \left( \frac{\lambda_2}{\lambda_1} \right). \]

4. Results.

4.1 Deformation of BPI and BPII for two different orientations. — ([001] \parallel E and [011] \parallel E). Significant changes of the Kossel diagrams in an electric field have been observed
Fig. 1. — Principle of the determination of the tilt angle $\theta$ between a reciprocal lattice vector $q_{hk\ell}$ and the viewing direction (= field direction): The Kossel cones constructed in reciprocal space by means of a sphere twice as large as the Ewald sphere are shown (below) together with the corresponding Kossel diagrams (above) for different wavelength $\lambda$. According to the relations $|q_{hk\ell}| = 4 \pi n(\lambda)/\lambda_1$, $n(\lambda_1)/\lambda_1$, and $n(\lambda_2)/\lambda_2$, the tilt angle $\theta$ is given by $\cos \theta = \lambda_2 n(\lambda_1)/(\lambda_1 n(\lambda_2)) = \lambda_2/\lambda_1$.

for monocrystals of BPI and BPII. The effects observed for fixed incident wavelength are represented in figure 2.

The change of the interplanar spacing in field direction can be studied either by observation of the diameter of the central Kossel ring [corresponding to (002)- or (011)-planes for BPI and to (001) and (011) for BPII respectively] for constant wavelength $\lambda$ (Fig. 2) or by determination of the wavelength $\lambda_{hk\ell}$ where the central ring vanishes. Figure 3 shows the dependence of $\lambda_{hk\ell}$ on field strength for the two longest periodicities observed in BPI and BPII. An increasing interplanar spacing $d_{002}$ in field direction is observed for BPI, while both $d_{001}$ for BPII and $d_{011}$ for BPI and BPII decrease if the respective planes are perpendicular to the field direction.
Fig. 2. — Changes of Kossel diagrams due to the deformation in the electric field for materials with $\varepsilon_a < 0$. The parameter $\delta$ is the relative variation of the periodicity in field direction. The diagrams are calculated assuming a constant volume of the unit cell.

Moreover the experimental Kossel diagrams indicate lack of cubic symmetry for the structures continuously deformed in the field. The symmetry breaking is most obvious for two cases (Fig. 4):

(i) for BPI, oriented with [001] $\parallel$ $\vec{E}$, (Fig. 4a) the diameter $\xi_1$ of the (002)-ring is larger than the distance $\xi_2$ between the intersection points for the two ellipses corresponding to the (101) and the (101)-line. The ratio $\xi_1/\xi_2$ is related to the ratio of the lattice constants parallel and perpendicular to the field direction;

(ii) for BPII, oriented with [011] $\parallel$ $\vec{E}$, (Fig. 4b) the diameter $\tilde{\xi}_1$ of the central (011)-ring is smaller than the distance $\tilde{\xi}_2$ between the two intersection points of the (001) and the (010)-line. For the undeformed structure, $\tilde{\xi}_1 = \tilde{\xi}_2$ is obtained as expected for cubic symmetry.
Fig. 3. — Change of the wavelengths $\lambda_{\text{eff}}$ in the electric field $E$ for BPI and BPII oriented with a twofold and fourfold axis parallel to the field direction. Mixture of 37.0 % of compound 2 in ZLI 2585.

Fig. 4. — Experimental Kossel diagrams for the deformed structures: a) BPI, [001] $\parallel$ E (25.5 % compound 1 in EN 18, $E = 35$ V/18 $\mu$m, $\lambda = 431$ nm); b) BPII, [011] $\parallel$ E (37.0 % compound 2 in ZLI 2585, $E = 30$ V/13 $\mu$m, $\lambda = 412$ nm).
For the structures obtained by continuous deformation of the cubic unit cell, the same symmetry arguments are valid as those considered for materials with \( \varepsilon_a > 0 \) [3, 7, 8], although the signs of the effects are different. If the field is applied along the [001] direction of BPI or BPII, the influence of the electric field is described by different changes of the lattice constants parallel and perpendicular to the field direction while the vectors representing the unit cell preserve their directions. Consequently, the deformed structures exhibit the tetragonal space groups \( D_{4h}^0(1 4 2 2) \) and \( D_4^5(P 4 2 2 2) \), respectively.

However, if one of the twofold axes of a blue phase crystal is parallel to the field direction, different deformations of the lattice in the [100] and [011] directions (Fig. 5) have to be considered [8]. If the field is applied along the [011] direction of the body centered cubic [simple cubic] lattice, the face centered \( D_2^4(F 2 2 2) \) [C-centered \( D_5^6(C 2 2 2) \)] orthorhombic unit cell describing the deformed structure is represented by three vectors \( x'(E), y'(E), z'(E) \) being parallel to the [100], [011] and [011] directions of the undeformed cubic lattice (Fig. 5). For the case of absent field, this unit cell provides for an equivalent representation of the cubic structure and exhibits the lattice constant \( |x'(0)| = |x| = a \) and \( |y'(0)| = |y| = |z'(0)| = |z| = \sqrt{2} a \), where \( a \) is the cubic lattice constant.

**Fig. 5.** Transformation of the unit cell in order to describe the deformation of the cubic lattice if an electric field is applied along a twofold axis ([011]). The Miller indices \([hkl]\) designate the respective directions in the cubic lattice. The basis vectors \( x, y, z \) of the new unit cell change their lengths under the influence of the electric field leading to an orthorhombic unit cell described by the vectors \( x', y', z' \).

For BPI, the ratio \( |x'| / |y'| = \tan \xi \), can easily be determined from the Kossel diagrams [8]. For the systems under investigation with \( \varepsilon_a < 0 \), a value of \( \xi_4 = 34^\circ - 36^\circ \) has been found being independent of the field strength within experimental accuracy. This behaviour is different from mixtures of CB15 with E9 exhibiting positive dielectric anisotropy, where the parameter \( \tan \xi \), was found to vary continuously from \( 1 / \sqrt{2} \) to 1 with increasing field strength corresponding to a continuous transition from the deformed BPI structure to the tetragonal BPX [8]. For the mixtures reported here, the occurrence of an additional tetragonal phase BPX in the electric field has not been observed.

### 4.2 Dependence of the Interplanar Spacing of (001)-Planes on the Orientation at Constant Field Strength

For monocrystals of BPII, the influence of the electric field on the wavelength \( \lambda_{001} \) has been found to depend considerably on the orientation (Fig. 6a).
Fig. 6. — Dependence of the wavelength $\lambda_{001}$ on the angle $\vartheta$ between the [001]-axis and the field direction for a mixture of 40.0% of compound 2 in ZLI 2585. a) $\lambda_{001}$ versus field strength for monocrystals of different orientation $[hkl] \parallel E$. b) $\lambda_{001}$ versus angle $\vartheta$ at constant field strength (40 V/17 $\mu$m) : □ : Values obtained for crystals of random orientation ; ○ : Values obtained during reorientation of an initially [112]-oriented crystal around the twofold axis $\perp E$.

This wavelength is given by the value where the corresponding Kossel line disappears with increasing wavelength. $\lambda_{001}$ measures the interplanar spacing $d_{001}$ (Eq. 5). By comparing the curves represented in figure 6a, one can see that the influence of the field on the (001) interplanar spacing decreases with increasing angle $\vartheta$ between the [001]-axis and the field direction ([112] : $\vartheta = 35.3^\circ$, [011] : $\vartheta = 45^\circ$, [111] : $\vartheta = 54.7^\circ$).

This behaviour has been studied in more detail by observation of [112]-oriented crystals anchored at the surface. These are found to reorient very slowly under the influence of the electric field (Fig. 7). During their rotation around the [110]-axis at constant field strength, the wavelength $\lambda_{001}$ and the tilt angle have been determined one after the other by applying the methods described in section 3, and a continuous variation has been found (Fig. 6b).

It should be noted that for crystals with the orientation [011] $\parallel E$ the rotational axis perpendicular to the [001]-axis and the field direction is [100] (instead of [110] as for crystals with orientation [112] or [111] $\parallel E$) and consequently a different dependence of $\lambda_{001}$ on $\vartheta$ might be expected: If the electric field is described using spherical polar coordinates $E$, $\vartheta$, $\varphi$ which are related to the orthogonal axes of the crystal lattice as usual, the influence of
the field direction on the stretching of the (001) interplanar spacing should be expected to depend on both $\theta$ and $\varphi$. However, within experimental accuracy no influence of an additional parameter $\varphi$ could be detected, and [112]-, [111]- and [011]-oriented monocrystals as well as slightly tilted crystals with random values of the parameter $\varphi$ could be fit by the same curve (Fig. 6b).

5. Conclusions.

We have shown that electrostriction for blue phases can be studied for arbitrary orientation with respect to the field direction if monocrystals are anchored at the surface. However, only the orientation [001] $\parallel \mathbf{E}$ is stable in the electric field.

In order to interpret the experimental data presented in section 4 within the framework of equation (4), three special cases have to be considered concerning the components of the electric field in the coordinate system of the cubic lattice.

(i) Variation of the lattice constant in the field direction if the field is applied along the $z$-axis of the cubic lattice ([001] $\parallel \mathbf{E}$):

the components of the field vector $\mathbf{E}$ in the coordinate system of the crystal are $E_1 = 0$, $E_2 = 0$, $E_3 = |\mathbf{E}| = E$ and the relative change of the lattice constant in field direction is given by

$$\frac{\lambda_{001}(E) - \lambda_{001}(0)}{\lambda_{001}(0)} = \varepsilon_{33} = \gamma_{1111} E^2 = \tilde{\gamma}_{[001]} E^2. \quad (9)$$

The stretching of the lattice perpendicular to $\mathbf{E}$ for this case is given by $\varepsilon_{11} = \varepsilon_{22} = \gamma_{1122} E^2$ and the dilatation of the unit cell volume is

$$\Delta = (1 + \varepsilon_{11})(1 + \varepsilon_{22})(1 + \varepsilon_{33}) - 1 \approx \varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33} = (\gamma_{1111} + 2 \gamma_{1122}) E^2. \quad (10)$$

(ii) Variation of the periodicity in field direction if the field is applied along the [011]-axis of the cubic lattice:

the components of the field are $E_1 = 0$ and $E_2 = E_3 = E/\sqrt{2}$.

The strain tensor $\varepsilon_{ij}$ which is obtained with these components can be transformed in its diagonal form by rotation of 45° around the x-axis and the stretching in field direction is given by

$$\frac{\lambda_{011}(E) - \lambda_{011}(0)}{\lambda_{011}(0)} = \frac{1}{2} (\varepsilon_{22} + 2 \varepsilon_{23} + \varepsilon_{33})$$

$$= \frac{1}{2} (\gamma_{1111} + \gamma_{1122} + 2 \gamma_{2323}) E^2 = \tilde{\gamma}_{[011]} E^2. \quad (11)$$

(iii) Variation of the lattice constant along the $z$-axis for arbitrary field direction:

the vector $\mathbf{E}$ can be described in polar coordinates defined as usual: $E_1 = E \sin \theta \cos \varphi$, $E_2 = \sin \theta \sin \varphi$, $E_3 = \cos \theta$, where $\theta$ is the angle between the [001]-axis of the crystal and the field direction. The relative change of the lattice constant along [001] is given by

$$\varepsilon_{33} = (\gamma_{1122} \sin^2 \theta \cos^2 \varphi + \gamma_{1122} \sin^2 \theta \sin^2 \varphi + \gamma_{1111} \cos^2 \theta) E^2$$

$$= (\gamma_{1122} \sin^2 \theta + \gamma_{1111} \cos^2 \theta) E^2. \quad (12)$$

Note, that this expression is independent on the value of $\varphi$ in agreement with the experimental results described in section 4.2.
Fig. 7. — Kossel diagrams of a BPII-monocrystal during reorientation at constant field strength \( E = 40 \text{ V/17 \mu m} \). The initially [112]-oriented crystal anchored at the surface rotates slowly around the [110]-axis until the fourfold [001]-axis is parallel to the field direction.
From the experimental data of figure 3, the values $\tilde{\gamma}_{[001]}$ and $\tilde{\gamma}_{[011]}$ can be determined by a linear regression of the relative changes of the wavelength as a function of the square of the field strength.

Additionally, in the experiment reported in section 4.2 the relative change $\varepsilon_{33}$ of the (001) interplanar spacing was found to become zero for the orientation $[111] \parallel E (\theta = 54.7^\circ)$. For this case equation (12) reads as

$$\varepsilon_{33} = \frac{2}{3} \gamma_{1122} + \frac{1}{3} \gamma_{1111} = 0$$

and consequently the relation

$$\gamma_{1122} = -\frac{1}{2} \gamma_{1111}$$

is obtained. The same result is obtained generally by assuming a constant volume of the unit cell (i.e. by setting $\Delta = 0$ in equation (10)). Taking into account the agreement of the Kossel diagrams observed experimentally (Fig. 4) with the theoretical Kossel diagrams calculated for a constant unit cell volume, we conclude that this relation (Eq. 13) is valid generally for small deformations of the cubic blue phases by an electric field.

By plotting the relative changes of the wavelengths versus the square of the electric field strength for [001] and [011]-oriented crystals, the electrostriction components (table I) have been obtained according to

$$\gamma_{1111} = \tilde{\gamma}_{[001]}$$
$$\gamma_{1122} = -\frac{1}{2} \tilde{\gamma}_{[001]}$$
$$\gamma_{2323} = \tilde{\gamma}_{[011]} - \frac{1}{4} \tilde{\gamma}_{[001]}.$$  

It should be noted that the values given in table I describe the deformation more qualitatively: due to the experimental error of the sample thickness the accuracy of the values in table I is ± 10 % to ± 15 % depending on the absolute value of the thickness. Moreover, the

<table>
<thead>
<tr>
<th>Table I. — Electrostriction components for the mixtures under investigation.</th>
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<tbody>
<tr>
<td>Chiral compound</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Nematic component</td>
</tr>
<tr>
<td>Concentration of the chiral compound (% by weight)</td>
</tr>
<tr>
<td>$\gamma_{1111}/(10^{-15} \text{ m}^2 \text{ V}^{-2})$</td>
</tr>
<tr>
<td>$\gamma_{1122}/(10^{-15} \text{ m}^2 \text{ V}^{-2})$</td>
</tr>
<tr>
<td>$\gamma_{2323}/(10^{-15} \text{ m}^2 \text{ V}^{-2})$</td>
</tr>
</tbody>
</table>
approximation of equation (2) is valid only for small distortions (only values for $E < 2 \text{ V/\mu m}$ have been taken into account). In order to describe the behaviour close to the transition to the hexagonal or cholesteric phase, higher order terms have to be considered if the strain tensor is expanded in powers of $E$.

The values obtained for the electrostriction coefficients are in agreement with the experimental observation (Sect. 4.1) that for monocrystals of BPI and BPII oriented with one of their twofold axes parallel to the electric field the ratio of the two lattice constants $|x'|$ and $|y'|$ perpendicular to $E$ does not change significantly. For the change of the parameter $\xi_4 = \arctan(|x'|/|y'|)$ calculated from the data of table I using $E = 2 \times 10^{-6} \text{ V/m}$, a maximum value of $|\Delta \xi_4| = 1.7^\circ$ is obtained which is close to the limit of experimental accuracy. However, larger effects due to the occurrence of a tetragonal phase BPX for mixtures with higher chirality (as observed for materials with $\varepsilon_a > 0$ [8]) can not be excluded.

Recently, the effect of a weak electric field on the blue phase structure of materials with $\varepsilon_a > 0$ has been considered basing on a Landau theory by Lubin and Hornreich [3]. In agreement with experiments, an increase of the interplanar spacing in the field direction has been predicted for most of the space groups which were taken into account. However, it has been shown for a structure with the space group $O^g$ — referred to as $O_4^g$ — that in principle the inverse effect can also be expected. The aim of our paper is to report experimental data for materials with $\varepsilon_a < 0$ which had not been subject to theoretical considerations so far.

Acknowledgments.

The authors thank Michaela Wolff for preparation of the chiral compound 2. G. Heppke and H. Hitzerow would like to thank the Laboratoire de Physique des Solides in Orsay for their kind hospitality. Grateful acknowledgments are dedicated to Prof. Peter Crooker for his critical revision of the manuscript. This work has been supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 335, « Anisotrope Fluide »). The company E. Merck (Darmstadt) kindly supplied us with the nematic mixture ZLI 2585.

References

[14] EN 18 (Chisso Corp.) is a commercially available nematic mixture exhibiting a dielectric anisotropy of $\varepsilon_s \approx -6$ for $T = 298$ K, $f = 1$ kHz. ZLI 2585 (Merck) consists of Bicyclohexylcarbonitriles with the Cyano-group in axial position ($\varepsilon_s \approx -8$ for $T = 298$ K, $f = 5$ kHz).