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Résumé. — Le comportement de la mésophase cholestérique phase bleue III (BPIII) sous l'influence d'un champ électrique est étudié dans un mélange, avec une anisotropie diélectrique négative ($\varepsilon_a < 0$), constitué du composé chiral S811 et du mélange nématique EN18. Comme dans un autre mélange avec $\varepsilon_a > 0$, qui a déjà été étudié auparavant, on observe une augmentation très forte de l'intensité de la réflexion sélective de BPIII. Cette augmentation n'a jamais été observée dans des systèmes avec une anisotropie diélectrique positive. L'effet est beaucoup plus rapide que le changement des longueurs d'onde de Bragg observé dans la phase bleue I et dans la phase bleue II sous l'effet de l'électrostriction.

Abstract. — The behaviour of blue phase III (BPIII) of chiral liquid crystals under the influence of an electric field has been studied for a mixture consisting of the chiral compound S811 and the nematic mixture EN18 exhibiting negative dielectric anisotropy $\varepsilon_a < 0$. As in one mixture with $\varepsilon_a < 0$ studied previously, a dramatic increase of the intensity of reflection is observed in the fog phase. This intensity increase, which has not been observed for systems with $\varepsilon_a > 0$, increases much more rapidly than the shift of the Bragg wavelengths which is observed in BPI and BPII due to electrostriction.

Introduction.

Blue phases, which occur in chiral liquid crystals in a narrow temperature interval close to the clearing temperature, have been intensively studied during the last decade [1]. The modifications BPI and BPII can be described by a chiral director field with body centered cubic O$^8$ (I 432) and simple cubic O$^2$ (P 432) symmetry, respectively. Since the lattice constants of these structures are several hundred nm, both BPI and BPII show sharp Bragg reflection bands in the visible wavelength range. However the third modification, called blue fog [2] or BPIII [3], shows only a broad, weak selective reflection [4-6] and its structure is still unknown [1]. Different models have been proposed in order to describe BPIII. According to the emulsion model [7], BPIII is considered as an emulsion of cholesteric droplets in an isotropic matrix, the double twist model [8, 9] consists of randomly oriented double twist...
cylinders, the cubic domain model [10, 11] contains small body centered cubic or simple cubic
domains or correlated regions, and the quasicrystal model [12-17] is characterized by a locally
icosahedral symmetry.

Under the influence of an electric field, phase transitions can be observed and further blue
phase modifications appear. For systems with positive dielectric anisotropy the observed
phases so far are a tetragonal (BPX), a three-dimensional hexagonal (BPH\textsuperscript{3D}) and a two-
dimensional hexagonal blue phase (BPH\textsuperscript{2D}) which are stable only in an electric field [1]. For
systems with negative dielectric anisotropy BPH\textsuperscript{3D} is the only observed field-induced
phase [18, 19]. Additionally, for BPI and BPII a continuous shift of the Bragg wavelengths
with increasing electric field strength occurs [20]. This behaviour causes interesting electrooptical
effects and indicates a continuous deformation of the lattice (electrostriction) [21-23]. The signs of the electrostriction coefficients depend on the sign of the dielectric anisotropy \(\varepsilon_a\) of the material.

The behaviour of BPIII in an electric field has been investigated for several systems with
positive dielectric anisotropy, namely mixtures of CE1, CE2 and K18 [6, 24], mixtures of
CE1, CE2 and M18 [6] and mixtures of CB15 with E9 or RO-TN 404 [25]. In all these
systems, the broad BPIII reflection band exhibits only a small change of the intensity and
wavelength, whereas for very high field strength (several V/\(\mu\)m), a field-induced transition
from BPIII to a blue phase modification showing sharp reflection bands occurs [24, 25].
However, for a system with negative dielectric anisotropy, a completely different behaviour
has recently been observed: in a mixture consisting of CE2, CE3 and CCN55 a large increase
of the intensity and a sharpening of the peak in BPIII was detected [26].

In this article, the results of investigations on another system exhibiting high chirality and
negative dielectric anisotropy are presented. The temperature-electric field phase diagram for
this mixture shows BPI, BPII and BPIII, as well as a field-induced phase transition from
BPIII to a blue phase exhibiting sharp Bragg peaks as observed previously [24-26]. This field
induced modification may be either BPII or BPH\textsuperscript{3D}. For values of the field strength below
the field-induced transition, both an increase of the integrated intensity (by one order of
magnitude) and a sharpening of the selective reflection peak are observed. Preliminary
investigations on the dynamics of the field effects observed in blue phases show that the
increase of the intensity for BPIII is very fast compared to the shift of the Bragg wavelengths
observed in BPI and BPII.

From the data presented here, it can be concluded that the increase of the intensity of the
reflection in BPIII is not only characteristic for the mixture of CE2, CE3 and CCN55
investigated earlier [26], but for systems with negative dielectric anisotropy in general.
Moreover, the time dependence indicate that the mechanism for this effect is fundamentally
different from the electrostriction observed in BPI and BPII. The very slow shift of the Bragg
wavelengths connected with the electrostriction of BPI and BPII is possibly due to the motion
of defects, whereas the response of BPIII to the electric field might involve a reorientation of
small domains or of double twist cylinders.

Experimental setup.

The system under investigation is a mixture of 30.0 \% by weight of the chiral compound S-(–)-4-
\(\langle(1\text{-Methyl-heptyl})\text{-oxybenzoyl}\rangle\)-4-hexyloxybenzoate

\[
\begin{align*}
C_6H_{13}O- & \quad \bigcirc- COO- \quad \bigcirc- COO- \quad CH-C_6H_{13} \\
\quad \quad \quad CH_3 &
\end{align*}
\]
(S811, Merck, F.R.G.) with the wide temperature range nematic mixture EN18 (Chisso Corp., Japan) which exhibits a negative dielectric anisotropy \( (\varepsilon_a = -6 \) at 25 °C). The compounds were used as received without further purification. In order to investigate the behaviour in an electric field, the sample was contained between two glass slides coated with a transparent conducting layer (ITO) using mylar spacers of 12 |m thickness. No surface treatment for alignment of the director at the boundaries was used. The sample was investigated using a Zeiss Universal microscope in reflection.

The temperature of the sample was controlled by a modified Mettler hot stage allowing an accuracy of 3 mK. Sinusoidal voltages up to 100 V (rms) with a frequency of 1 kHz were utilized; reported voltages are rms values. The sample thickness was 12 |m. In order to investigate the reflection spectra, a Jarrel Ash spectrometer with a resolution of better than 1 nm was connected to the microscope tube and photon counting equipment was used to measure the intensity as a function of wavelength.

The dynamics of the electrooptical response was studied by applying a step modulation (on/off) to the applied AC voltage. The time dependence of the photomultiplier output for a fixed wavelength was registered by a multichannel analyzer (Canberra model 3100) in the multiscaling mode.

Results.

In the absence of an electric field, the investigated mixture shows the usual phase sequence Ch-BPI-BPII-BPIII-isotropic with increasing temperature. In mixtures exhibiting a concentration of less than 28% of the chiral component S811, only the blue phase modifications BPI and BPII were observed in agreement with earlier investigations [21]. Figure 1 shows the phase diagram for the 30% mixture in the electric field-temperature plane. Transition temperatures at constant voltage and transition voltages at constant temperature were determined by optical observation of the textures in the polarizing microscope. A direct field-induced transition from BPI to the cholesteric phase was observed for temperatures lower

![Phase diagram](image_url)

Fig. 1. — Phase diagram in the electric field, temperature plane for a mixture of 30.0% (by weight) S811 in EN18, sample thickness 12 |m. □: Transition temperatures determined for constant voltage. ○: Voltages of transition determined for constant temperature. Arrows indicate the temperatures for which the dependence of the respective Bragg wavelengths on the applied voltage are represented in figure 2 and figure 4.
than 43.670 °C. For higher temperatures in BPI a small change of the blue phase texture occurs for a field strength below the threshold to the cholesteric phase. The almost vertical line at about 58 V in the temperature range of BPIII represents a discontinuous increase of the intensity of the selective reflection leading to an unidentified blue phase modification BPE with sharp reflection bands appearing at wavelengths similar to those of BPII. No BPII-BPE discontinuity was observed, only the field-induced transition to the cholesteric phase. However, earlier investigations [18] have shown that in mixtures of the same components with only slightly lower concentration of the chiral compound S811, a continuous transition from BPII to a three dimensional hexagonal blue phase (BPH\textsuperscript{3D}) occurs. Thus, the BPE observed here in the temperature range of BPI and BPIII, respectively might be either BPII or BPH\textsuperscript{3D}. The threshold field strengths for the field-induced transitions from BPIII to BPE and from the blue phases to the cholesteric phase are of similar magnitude as for the BPII-BPH and for the BPH-Ch transition observed in other mixtures.

It was attempted to determine the structure of BPE by the investigation of Kossel diagrams. However, for our mixture only the central Kossel ring corresponding to the lattice vector along the field direction could be observed for BPE [27]. Kossel lines corresponding to other reciprocal lattice vectors, which would allow one to distinguish between BPH and a deformed BPII could not be seen since the lattice constants for this system are too small due to the high concentration of the chiral compound. Thus, it is of interest to apply the Kossel method to other systems in which BPIII occurs also for lower chirality.

In BPI and BPII, a continuous change of the Bragg wavelengths with increasing voltage is observed due to electrostriction (Fig. 2). The Bragg wavelengths corresponding to the (110) planes in BPI and to the (100) planes in BPII decrease with increasing field strength whereas the Bragg wavelength corresponding to the (200) planes of BPI increases. This behaviour indicates that for BPI the sign of the deformation depends not only on the sign of the dielectric anisotropy but also on the orientation of the lattice with respect to field direction. The effects represented in figure 2 confirm earlier investigations on systems with negative dielectric anisotropy [21].

![Fig. 2. Dependence of the Bragg wavelengths on the rms value of the applied alternating voltage (sine, frequency 1 kHz, sample thickness 12 μm) for the cholesteric phase (crosses), BPI (squares) and BPII (circles).]
For BPIII, a very broad selective reflection band is observed as in other systems. The intensity of this peak in the field off state is about two orders of magnitude smaller than that for BPI and BPII. However, under the influence of the electric field a dramatic increase of the reflected intensity occurs (Fig. 3). At the same time, the halfwidth of the BPIII reflection band decreases continuously from about 60 nm at 0 V to about 30 nm at 55 V (Fig. 4). The dashed line at 56 V in figure 4 indicates the transition from BPIII to BPE with sharp reflection bands which might be identical either to the deformed BPII structure or to the three dimensional hexagonal phase BPH\textsuperscript{3D}. The wavelength of selective reflection in BPIII changes slightly with increasing field strength and shows a very small change at the phase transition (Fig. 4).

![Graph showing reflection spectra for BPIII at different electric field strengths.](image1)

**Fig. 3.** — Reflection spectra of BPIII for different electric field strength (30 % S811 in EN18, \( T = 44.052 \, ^\circ C \)).

![Graph showing wavelength and linewidth of Bragg peaks for BPIII.](image2)

**Fig. 4.** — Wavelength of maximum intensity (circles) and linewidth (squares) of the Bragg peaks observed for BPIII versus the applied voltage (sample thickness 12 \( \mu m \), \( T = 44.052 \, ^\circ C \)).
The behaviour of BPIII in the system presented here is very similar to that of the mixture consisting of CE2, CE3 and CCN55 which has been investigated earlier [26].

In order to investigate the dynamic behaviour of the intensity increase in BPIII, an AC voltage of 50 V was applied to the 12 μm sample and switched on and off with a frequency of 2 Hz. The intensity of the reflected light measured at the wavelength of maximum intensity shows a fast response to the field (Fig. 5): from the time dependence of the intensity represented in figure 5 time constants of the order of several milliseconds can be estimated. Since the wavelength shift of the selective reflection is very small, the same curves were obtained for $\lambda = 461$ nm (wavelength of maximum reflection intensity at $E = 0$) and for $\lambda = 455$ nm (wavelength of maximum intensity at $E = 50$ V /12 μm).

In order to compare the dynamics of the electrooptical effect in BPIII to that of the electrostriction in BPI and BPII, the change of intensity at fixed wavelength due to the spectral shift of the Bragg peak was measured. The results (Fig. 6) indicate that the electrostriction of BPI and BPII is much slower than the electrooptical effect observed in BPIII. Figure 6 shows the spectrum of the (110) reflection band in BPI for 0 V and 40 V. The time dependence of the intensity when switching the voltage on and off was measured at 594 nm and 580 nm, respectively. At these wavelengths, the intensity varies almost linearly with the spectral position of the peak. From the curves given in figure 6, time constants of the order of several seconds can be estimated. This indicates that the electrooptical effect observed in BPIII is about three orders of magnitude faster than the electrostriction in BPI and BPII.

Fig. 5. — Time dependence of the intensity of the light reflected by BPIII at $\lambda = 461$ nm, when an alternating voltage of 50 V (rms, sample thickness 12 μm) is switched on and off with a frequency of $\approx 2$ Hz. (Mixture of 30.0 % S811 in EN18, $T = 44.060 \, ^\circ C$).

Discussion.

Comparing the behaviour of the BPIII reflection peak in systems with positive and negative dielectric anisotropy, we note that for both systems the wavelength shift of the peaks is smaller than in BPI and BPII. In BPIII, therefore, the electric field causes little change in the spatial periodicity of the director field, while in BPI and BPII there is a significant electrostriction effect. The most striking difference between the behaviour of BPIII and BPI/BPII is the large increase of selective reflection intensity under the influence of an electric field observed for BPIII in mixtures with $\varepsilon_a < 0$. We conclude that the structure of the BPIII domain is fundamentally different from the structure of the BPI and the BPII lattice. These results argue against the cubic domain model for BPIII.
Fig. 6. — a) Reflection spectra corresponding to the (110) planes in BPI \( (T = 43.761 \, ^\circ C) \) for \( E = 0 \) \( (\lambda_{\text{max}} = 591.5 \, \text{nm}) \) and \( E = 40 \, \text{V/12 \, \mu m} \) \( (\lambda_{\text{max}} = 583 \, \text{nm}) \). b) and c) Time dependence of the intensity of the reflected light measured at b) \( \lambda = 594 \, \text{nm} \) and c) at \( \lambda = 580 \, \text{nm} \), when an alternating voltage of 50 V (rms, sample thickness 12 \, \mu m) is switched on and off with a frequency of less than \( 2 \times 10^{-3} \, \text{Hz} \).

Another argument against the cubic domain model in the case of body centered cubic (O\( ^5 \)) is that an increase of the reflection intensity would indicate an orientation of the (110) planes perpendicular to the field direction since for the (200) and (111) planes of an O\( ^5 \) structure only very weak intensities (if any) are expected. The circularly polarized modes of the selective reflection are forbidden for the respective reciprocal lattice vectors (200) and (111) according to the optical selection rules [28] which follow from the symmetry of the dielectric tensor. However, it follows from very general symmetry considerations [29] that only the orientation with either a threefold or a fourfold axis parallel to the field can be stable. Thus, the selection rules dictate against the structure O\( ^5 \) but since these rules have been found to be violated in some experiments, this argument is not conclusive.
If BPII-like cubic domains (simple cubic O$^3$) are considered for BPIII, the same behaviour observed for systems with $\varepsilon_a < 0$ should also be expected for systems with $\varepsilon_a > 0$, since for BPII in materials with either sign of $\varepsilon_a$ the same orientation [100] $\parallel E$ was observed to be stable in the electric field [21, 29]. This expectation is also in contradiction to the experimental results for BPIII.

The behaviour of the intensity of the BPIII reflection peak depends markedly on the sign of the dielectric anisotropy. Whereas mixtures with $\varepsilon_a > 0$ show little change [25] or even a small decrease [24] in the Bragg intensity with increasing field, systems with $\varepsilon_a < 0$ show a dramatic increase. This behaviour appears qualitatively compatible with the double twist model of BPIII. In this model the $q$-vectors ($|q| = 2\pi$/pitch) characterizing the twist in a double-twist cylinder are everywhere radial. Application of a field to such a cylinder made of $\varepsilon_a > 0$ material causes the cylinder axis to align parallel to the field and the vector $q$ to be perpendicular to the scattering vector for backscattered light. Consequently, the BPIII scattering peak should decrease as is observed [24]. For $\varepsilon_a < 0$, however, the cylinders align perpendicular to the field, thereby bringing the vector $q$ into coincidence with the scattering vector and increasing the reflectivity. Furthermore, the decrease in the BPIII linewidth with increasing field means the dimension of the double twist cylinder along the direction of the scattering vector has increased, thereby increasing the reflected intensity further. Finally, we speculate that there may be an additional stacking of the cylinders which leads to pretransitional formation of BPE regions within the BPIII region. Thus the wavelengths of the BPIII and BPE are essentially the same (Fig. 4) but since the transition is first order, there are small discontinuities in the intensity (not shown) and the linewidth (Fig. 4).

The arguments given for the double twist model are also valid for the emulsion model. Reorientation of cholesteric droplets would also cause an increase of the reflected intensity for systems with negative dielectric anisotropy since the director tends to align perpendicular to the field direction, thereby orienting the cholesteric helix axis in the field direction. For systems with positive dielectric anisotropy, an orientation of the helix axis perpendicular to the field direction would be expected and thus a slight decrease of the intensity should occur. This effect is also in agreement with previous experimental data [24].

Concerning the quasicrystal model, no theory predicting the behaviour in an electric field has been published so far. Thus we are not able to discuss our results with respect to this model in detail. However, the dramatic increase of the intensity seems to argue against this model. Icosahedral domains, like cubic domains, do not exhibit dielectric anisotropy. In order to see any field effect, dielectric anisotropy has to be induced by the electric field which means that the lowest order term describing the dependence of the free energy on the electric field strength is proportional to $E^4$. Moreover, the icosahedron exhibits many equivalent reciprocal lattice vectors, so that it is hard to believe that just a reorientation can cause an increase of the reflection intensity by one order of magnitude. It is much more reasonable that BPIII consists of small anisotropic domains (such as double twist tubes or cholesteric droplets) which are reoriented by the field as described above. In the latter case, the lowest order term in the free energy is proportional to $E^2$ which agrees with the experimental observation that relatively small field strengths can cause an increase of the intensity. The assumption that the increase of intensity is due to a reorientation of double twist tubes or cholesteric droplets can be proved by investigating the reflection perpendicular to the field direction which has not been done yet. For systems with positive dielectric anisotropy, a slight increase of the reflection intensity perpendicular to the field direction would be expected.

Finally we review the implication of the rapid response of the BPIII peak ($\approx$ ms) as compared to the much slower response of the BPI/BPII peaks ($\approx$ s). In the former case, the spatial periodicity of the structure is only changed slightly (which is indicated by the almost
constant Bragg wavelength) whereas in the latter case the response is due to a change of interplanar spacings in the lattice. Since the structure of BPI and BPII is described by a regular lattice of disclination tubes, this change involve the motion of disclination tubes which might be connected to some flow of material. On the other hand, a reorientation of double twist cylinders or cholesteric droplets dispersed in an isotropic matrix can be considered to be much faster.

Another example indicating that an electrooptical effect which does not require the change of the spatial periodicity of the blue phase structure can be much faster than the electrostriction has been found earlier: it has been shown [30] that in BPI and BPII not only a change of the lattice constants but also a change of the refractive index occurs when an electric field is applied. The time constants for this effect have been found to be several orders of magnitude lower than the time constants for the shift of the Bragg wavelengths [30]. This behaviour indicates also that a change of the average molecular orientation, i.e. a change of amplitudes of the modes of the tensor order parameter in blue phases can be much faster than a change of the spatial periodicity of the structure. It might be interesting to note that the time constants for this variation of the refractive index are of the same order of magnitude as those for the intensity change observed here for BPIII.

Recent investigations on the dynamics of the field-induced phase transitions [31] have shown that the response of blue phase systems to an electric field due to these field-induced transitions is also quite fast compared to the dynamic behaviour of the electrostriction observed here.

Conclusions.

The experimental results on BPIII presented in this article show a large increase of the intensity and sharpening of the selective reflection band under the influence of an alternating electric field. By comparison with earlier experimental results on other mixtures [24-26] it can be concluded that this behaviour is due to the negative sign of the dielectric anisotropy. The experimental data of this work and earlier papers [24-26] can be qualitatively explained by the double twist model or by the emulsion model for BPIII.

As in other materials with positive and negative dielectric anisotropy, a field-induced phase transition from BPIII to the high-field blue phase BPE was observed, which shows a sharp reflection band at almost the same wavelength as the weaker peak of BPIII. This field-induced phase might be identical either to the deformed BPII phase (P 4222) or to the three dimensional hexagonal phase BPH$^{3D}$ (P 6222). The determination of the space group of this phase would be helpful to understand the mechanism of this field-induced phase transition.

Investigations on the dynamics of the electrooptic effects in blue phases show that the increase of the reflection intensity in BPIII is much faster than the electrostriction in BPI and BPII. This indicates that the time dependence of the electrostriction is determined by one or more slow processes (for example the motion of disclinations or flow of material) which do not occur in BPIII under the influence of the electric field. This behaviour also fits in the BPIII model of randomly oriented, independent double twist cylinders or cholesteric droplets which are reoriented in the electric field. A more detailed study on the dynamics of the electrooptic effects observed in BPI, BPII and BPIII is in progress [32].

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