Dynamic response of a blue phase to an applied field
V. Dolganov, G. Heppke, H.-S. Kitzerow

To cite this version:

HAL Id: jpa-00247768
https://hal.archives-ouvertes.fr/jpa-00247768
Submitted on 1 Jan 1992

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Dynamic response of a blue phase to an applied field

V. K. Dolganov (¹), G. Heppke (²) and H.-S. Kitzerow (²)

(¹) Institute of Solid State Physics Russian Academy of Sciences, 142432, Chernogolovka, Moscow Distr., Russia
(²) Iwan-N.-Stranski-Institut, Sekretariat ER 11, Technische Universität Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, Germany

(Received 7 May 1992, accepted 21 July 1992)

Résumé. — Nous avons étudié la dynamique des propriétés électro-optiques pour les mésophases cubiques Phase Bleue I (BPI) et Phase Bleue II (BPII) dans un mélange avec une anisotropie diélectrique négative. Le changement des intensités des réflexions de Bragg sous l’influence d’un champ alternatif modulé indique deux transformations différentes de la structure des phases bleues.

Abstract. — The dynamic response of the three-dimensionally ordered blue phases BPI and BPII to a step-function electric field was studied in a liquid crystal with negative dielectric anisotropy. A change of diffraction intensities, indicating the existence of two qualitatively different transformations of the structure, has been observed in a pulse electric field.

Introduction.

The local anisotropy of cubic blue phases (BP) gives rise to a number of nontrivial electrooptic effects [1]. The effects are associated with electrically induced reorientations which can occur either at a level of individual molecules and ordered regions inside a unit cell or at a macroscopic level, when a change of unit cell parameters or a unit cell reorientation takes place.

For the cholesteric structure, being less complex than the blue phase, the theory [2] predicts the existence of at least two relaxation times, caused by the local director rotation (τ₂ ≈ 10⁻⁴ 10⁻⁵ s) and by the change of the cholesteric pitch (τ₁ ≈ 1 s). In blue phases the analogue of the longer time τ₁ is the time of relaxation to an equilibrium value of the cell parameters. For the blue phases the appropriate time is well known [3], being τ₁ ≈ 10 s, which is close to the relaxation time calculated for a cholesteric liquid crystal. As far as the local transformation of the director is concerned, we should expect the shorter relaxation time. However the situation here may not be as simple as it is in the cholesteric liquid crystal because of the more complex structure.

At present, several electrooptical effects with relaxation times of 10⁻³ – 10⁻⁵ s have been observed in the BPI and BPII phases. The effects occur due to the field-induced change of the
refractive index [4-6], destruction of the blue phase in strong fields [7, 8], intensity change of the diffraction bands [9], shift of diffraction bands in the direction opposite to that of the electrostriction and with anomalously short relaxation time as compared to the electrostriction [9]. In the fog phase of liquid crystals orientational ordering is characterized by relaxation times of about $10^{-2}$ s [3]. In recent experiments [9] on BPI and BPII, an intensity change and a shift of diffraction bands were observed at a constant (« frozen ») size of the unit cell just as assumed for the model analyzed theoretically [2]. The diffraction measurements were performed [9] for the long-wave reflections of BPI and BPII in a material with positive dielectric anisotropy. At the same time it is known from « static » experiments that the effect of an electric field on blue phases depends on the sign of $\Delta \varepsilon$ and varies for different diffraction bands. Proceeding from this we studied the dynamics of the response to electric fields for materials with negative dielectric anisotropy. The measurements were carried out for different diffraction bands of BPI and BPII.

**Samples and measurement method.**

The mixture under investigation consists of the chiral material S811, Merck, F.R.G. (30 % by weight) and the nematic EN18, Chisso Corp., Japan with a large interval of nematic phase [3]. The mixture forms the three blue phases BPI, BPII and BPIII and possess a negative dielectric anisotropy. The investigated samples exhibit BPI in the thermal range 41.80-42.12 °C and BPII in the range 42.12-42.29 °C.

The diffraction lines in BPI ((200) and (110) reflections) and in BPII ((100) reflections) were measured in the transmission spectra. The spectra presented in the figures are the transmission spectra divided by the spectrum of incident light $I_0(\lambda)$. Repeating pulses of an on/off-modulated A.C. voltage (sine, 40 kHz) were applied to the sample. The period of 25 $\mu$s of the sine wave is smaller than the investigated relaxation times. The light intensities at different moments of time of sinusoidal voltages or pulse electric fields were recorded using a C115 oscillograph.

The 15 $\mu$m thick samples were placed between glass plates with an electrically conducting coating. The measurements were carried out for BPI samples with the orientations [100], [110] and BPII samples with the orientation [100] perpendicular to the plane of the cell. Temperature was maintained to within ± 0.01 °C by a thermostatic device.

**Experimental results and discussion.**

The BPI spectrum beyond the fundamental absorption band is represented by a single band in the region of $\lambda \approx 432$ nm (Fig. 1). The band is the sum of one reflection (200) and four reflections equivalent to (110), coinciding in wavelengths for a body centered cubic structure $O^8\left(\lambda_{200} = \alpha n \sin \theta, \ \theta = 90^\circ; \ \lambda_{110} = \sqrt{2} \alpha n \sin \theta, \ \theta = 45^\circ; \ \lambda_{200} = \lambda_{110}\right)$. In the electric field the band splits into two bands: the reflection (200) is shifted to longer wavelengths, the reflections (110) to shorter wavelengths (Fig. 1). For the case of BPII the diffraction line (100) is at $\lambda \approx 520$ nm. The electrostriction leads to a shift of the reflection to shorter wavelengths. To investigate the dynamic effects spectral measurements were performed in the regions of diffraction bands (200) and (110) for BPI and (100) for BPII at different instants of sinusoidal voltages or pulses.

Figures 2a, c and d show the time-dependence of the intensity of light passing through the blue phase when an electric field $E(t)$ is applied to the sample (Fig. 2b). The measurements were performed at wavelengths corresponding to the maxima of the diffraction line. The light intensities $I(t)$ are modulated for all reflections with twice the frequency of the electric field. However the correlation between $I(t)$ and $E(t)$ is different. In the region of the (200) reflection
for BPI and (100) for BPII the minima $I(t)$ practically coincide with the extrema of the electric field. Modulation can be observed in electric fields with frequencies less than $10^3$ Hz. At higher frequencies modulation depth decreases and vanishes completely at $\nu > 10^4$ Hz. The opposite result was obtained for the reflections (110) in BPI (Fig. 1d) : the electric field led to an increase of the intensity of the light transmitted through the sample. The shift of maxima $I(t)$ is of the order of 0.6 ms with respect to maxima $E(t)$. The difference of $I(t)$ dependences indicates that different transformations of the structure can occur.

Figure 3 presents the spectrum in the region of (100) reflections in BPII when square pulses of 50 V are applied to the sample (hereafter mean quadratic values of the voltage will be
The modulation, shown in figure 2, stems from a change of reflection intensity and a slight wavelength shift of the reflection (Fig. 3). The same effect has been observed earlier in a material with positive dielectric anisotropy [9], but the sign of the intensity change and the direction of the wavelength shift are just opposite to those in [9]. The shift of the reflection [9] to shorter wavelengths was attributed to a change of the refractive index in an electric field. The shift, to longer wavelengths observed by us confirms this the interpretation, since the refractive index along the field direction increases in materials with $\Delta \varepsilon > 0$ ($\lambda = 2 \alpha n \sin \theta$).

Figure 4 shows the dependences on time for the intensity of light passing through a sample in the region of a diffraction peak. $I(t)$ can be described by one relaxation time ($\tau = 0.2 \text{ ms}$), electric field strength does not affect the shape of curves and $I(t)$ becomes a plateau at $t > 1 \text{ ms}$. A similar behavior is observed in BPI at $U < 43 \text{ V}$ for the (200) reflection (Fig. 5a).

At the same time the intensity of the (110) reflection remains constant. The intensity modulation of opposite sign at both sides from the center of the diffraction band (Figs. 5b, d) indicates its short wave shift in the electric field with a relaxation time $< 1 \text{ ms}$. The different direction of (200) (Fig. 3) and (110) reflection shifts (Fig. 5) is due to the fact that the (110) planes lie at the angle of $\sim 45^\circ$ to the direction of the electric field and the incident light. For the orientation (110)$// E$, the intensity of the (110) reflection increases and at $t \leq \tau_1$ it shifts to a long wave side, like the (200) reflection at [100]$// E$.

The similar changes of the (200) and (100) reflections in BPI and BPII reveal an analogous mechanism of these changes. A part of the sample, being orientationally disordered, may be reoriented by an electric field to [100]$// E$, corresponding to the energy minimum [10-12]. However at such a reorientation of the unit cells the intensity increase of both (200) and (110) reflections should have been expected, but this was not the case. Therefore another possibility

![Fig. 3](image-url)

**Fig. 3.** — The diffraction band (100), BPII. The duration of the electric pulses $A_1 = 1.1 \text{ ms}$, the repetition period $A_2 = 5 \text{ ms}$, $U = 50 \text{ V}$. (●) 1 ms after the pulse start, (×) between pulses. $T = 41.15 \degree C$.

![Fig. 4](image-url)

**Fig. 4.** — Time dependence of the intensity measured at the (100) reflection peak of BPII, when an alternating voltage is switched on and off. a) $U = 36 \text{ V}$; b) $U = 50 \text{ V}$; a). b) $A_1 = 1.1 \text{ ms}$, $A_2 = 5 \text{ ms}$; c) $A_1 = 11 \text{ ms}$, $A_2 = 30 \text{ ms}$. 
should be considered: an electric field induces the reorientation of a local director inside a unit cell but not of the unit cells. This interpretation is in agreement with a short relaxation time: the changes of director orientations occur at microscopic level and therefore they must be characterized by short times. The structure of the blue phase is described by the set of Fourier harmonics $\mu_r$ [$13, 14$] ($\tau$-vector of a reciprocal lattice). Electric fields cause an increase of Fourier harmonics with $\tau/E$ in materials with $\Delta \varepsilon < 0$. This is, probably, associated with the fact that for the structures with a single harmonic (one-dimensional spiral) the $\tau/E$ orientation corresponds to an energy minimum.

The response of BPI to an electric field changes significantly at $U \approx 43$ V (Fig. 6). The transformation of the spectrum is the same as observed at $U < 43$ V (Fig. 5) (i.e. the intensity of the (200) reflection increases and the wavelength of reflection is shifted) but another type of changes appears which are characterized by longer relaxation times $\tau'$. When the duration of the electric pulses is increased the transformation of (110) reflections is determined by a longer process (Fig. 7). In the static electric field $E_0 = 2.8 \times 10^4$ V/cm ($U_0 = 43$ V) the transition to BPII or to the three-dimensional hexagonal structure BPH$_{3\text{D}}$ [3, 15] takes place. The size the of unit cell changes considerably (by a factor of about two) at the transition. In our case the unit cell of BPI retains at pulses being applied. The decrease of the (110) reflection intensity can not be explained by a phase transition into another structure in a part of the sample. Since in this case the intensities of both (110) and (200) reflections ought to change. Thus we conclude that a pulse field higher than $E_0$ causes a transformation of microordering which differs from that in the field $E < E_0$. At the BPI $\rightarrow$ BPII (or BPH$_{3\text{D}}$) transition the (200) reflection transforms into (100) of BPII ((1000) BP$_{3\text{D}}$), the (110) reflection converts into (110) of BPII ((1010) BP$_{3\text{D}}$) with a change of the Fourier harmonic values: $\mu_{\text{BPII}}(100) > \mu_{\text{BPI}}(200); \mu_{\text{BPII}}(110) \ll \mu_{\text{BPI}}(110)$ [16-18]. The sign of the change of (200) and (110) reflection intensities (Fig. 7) corresponds to the intensity changes occurring at the phase transition, that is the structure of the unit cell approaches the structural order of the phase, which would occur after the completed phase transition. The transformation of microordering in a pulse field occurs at the « frozen » parameters of unit cell.
Fig. 6. — The transmission spectrum of BPI (upper part of the figure). Time dependence of the intensity (the lower part of the figure). \( \Delta_1 = 2.5 \text{ ms}, \Delta_2 = 5.8 \text{ ms}, U = 50 \text{ V}, T = 42.06 \text{ °C} \). The arrows indicate the points where the time dependences of the intensity were measured.

Fig. 7. — Upper part of the figure: the transmission spectrum of BPI, 19 ms after the pulse start (●), between pulses (×), \( \Delta_1 = 20 \text{ ms}, \Delta_2 = 50 \text{ ms}, U = 50 \text{ V}, T = 42.06 \text{ °C} \). The lower part of the figure: Time dependence of the intensity. The arrows indicate the points where the time dependences of the intensity were measured.

Conclusions.

In agreement with earlier observations on liquid crystals with positive dielectric anisotropy [9] we have found that electric fields cause a fast spectral shift of the selective reflection band ((100) BPII) just in the opposite direction of the spectral shift caused by electrostriction. As
expected, the signs of the intensity changes and wavelength shift of the reflection bands are just opposite for different signs of the dielectric anisotropy. The relaxation times are $\tau_s \sim 2 \times 10^{-4}$ s when an alternating voltage is switched on and off. In addition to this effect another type of a diffraction intensity change was observed. Its characteristics are a threshold field strength and different relaxation times when an alternating voltage is switched on and off. Basing on the obtained experimental data it may be supposed that two qualitatively different transformations of the structure can occur in a pulse electric field at a « frozen » size of the unit cell: (1) Change of local order within the « old » unit cell, (2) Nonequilibrium reconstruction, connected with a phase transition. The second type of reconstruction can not be realized inside an « old » unit cell in a « static » experiment.

The changes of the structure may be presented as follows: the difference of relaxation times, which characterize the rotation of the director and the change of unit cell parameters, respectively, leads to an initial transformation inside a unit cell with « frozen » parameters. These changes in turn cause the variations of unit cell parameters. The general reconstruction, further on, may occur either in the manner of a continuous change of unit cell parameters or of the destruction of a unit cell and the formation of a new one.

References