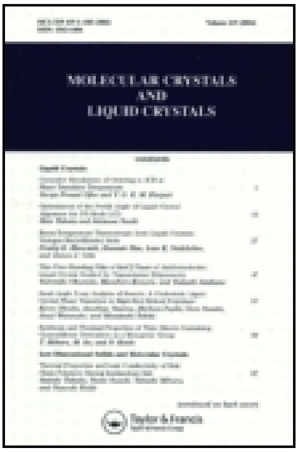

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# Interference Study of the Optical Anisotropy of the Cubic Blue Phase I

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# INTERFERENCE STUDY OF THE OPTICAL ANISOTROPY OF THE CUBIC BLUE PHASE I

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**Abstract** Anisotropy of the cubic blue phase I of two types is observed in a cholesteric-nematic mixture using optical interference. The anisotropy of the first type is independent on the polarization of light. The second kind of anisotropy means dependence of the refractive index on the direction of polarizer in the plane perpendicular to the (110) direction in defect free BPI samples. The last effect depends on the ratio of the wavelength of measurements to the Bragg wavelength.

The concept of spatial dispersion of the dielectric tensor takes into account the fact, that the polarization vector $\vec{\mathbf{P}}$ in a given point is determined by the electric field not only in the same point, but by some vicinity of it [1]. This leads to a dependence of the dielectric tensor on spatial coordinate (wave vector). The spatial dispersion contribution is determined by the ratio $a/\lambda$, where $a$ is a period of the system and $\lambda$ is the wavelength of light. In solid states spatial dispersion effects are small because $a \ll \lambda$, but there is some class of phenomena (girotropy), which can be explained only by taking into account spatial dispersion contribution. The ratio $(a/\lambda)$ in the case of liquid crystals is of the order of unity. Such a drastic change of the periodicity of the system gives qualitatively new possibilities for observation of spatial dispersion effects with respect to the solid state.

The blue phases possess the long-range orientational order , which is described by crystallographic cubic symmetry groups [5, 6]. On the other hand they are quite normal liquid-crystalline phases, because the material can flow through their three dimensionally periodical structure. These unique properties make the blue phases a suitable experimental object for investigation of the spatial disperison phenomena

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in liquid crystals, where the analogy between the optics of the blue phases and crystallooptics can be expected.

Investigations of the spatial dispersion in liquid crystals has been restricted only by optical activity of chiral phases (see for a review [2]), which is the spatial dispersion effect of the first order. In our recent investigations we have observed two new effects: an anomaly of the refractive index of chiral phases in the vicinity of the Bragg reflection wavelength [2] - [4] and optical anisotropy of the cubic blue phase I in the region of transmission of the substance [2]. In this work we have used quite new for the liquid crystals method of optical interferometry. To stimulate further theoretical and experimental investigations of the observed anomalies we give in this paper details of our measurements not published untill now.

## EXPERIMENTAL PART.

### Substances.

Mixture of 60.9 wt % of a highly chiral compound CB15 [4-cyano-4'-(2-methylbutyl)-biphenyl] (Merck) and a wide range nematic mixture E9 (Merck) with a large optical anisotropy.

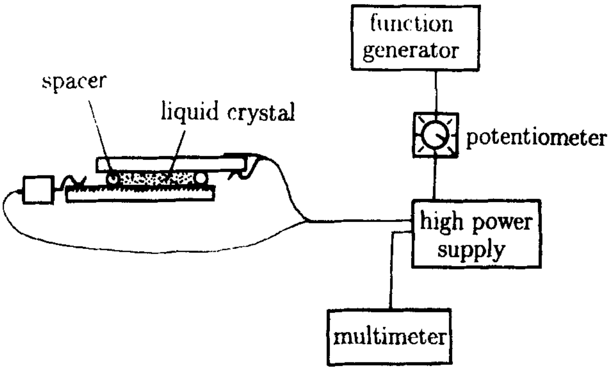


Figure 1. Scheme of the mirror cell.

This mixture exhibits following phase transitions between liquid-crystalline phases of interest (in degrees centigrade):

Chol 20.21 BPI 20.66 BPII 20.86 BPIII 21.36 Iso (60.9% CB15);
The optical anisotropy $\Delta n$ was measured in the cholesteric phase at the phase transition temperature Chol - BPI with an Abbe refractometer and was about 0.094 [3].

Mirror cell.

To compensate the optical rotation of the chiral phases a mirror cell was used [7] , which is shown on figure 1. The experimental cell consists of two glass plates with fiber spacers between them. The upper glass was covered with a thin transparent ITO film and the lower one was an aluminium mirror. Both glasses have been coated polyimide and uniaxialy rubbed. For our experiments it was important to have monodomain samples of the blue phases with a good quality. For this purpose we have oriented the vertical axes by application of the electric field and the asimuthal axes by the tangential boundary conditions. After the relaxation process we obtained perfect samples of the BPI without visualy observable defects and more than 200 $\mu$m in diameter. The structural wave vector [110] of the BPI unit cell is oriented by this method perpendicular to the substrate, $[1\bar{1}0]$ along the rubbing direction and [001] perpendicular to it in the plane of substrate.

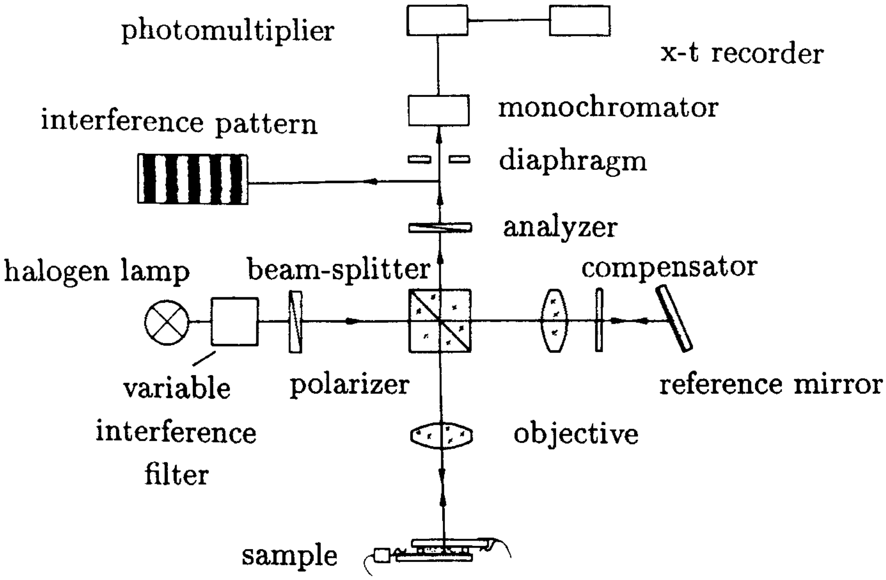


Figure 2. Experimental set up of the modified Linnik interferometer for measurements of the selective reflection and the refractive index dispersion.

Interference microscope.

Measurements of the refractive index dispersion have been carried out with a Leitz-Orthoplan microscope equipped with a Leitz interference reflection illuminator which realizes the Linnik interference scheme, and an automatized Jarrel Ash monochromator. Figure 2 shows the scheme of the experimental set up [2]-[4].

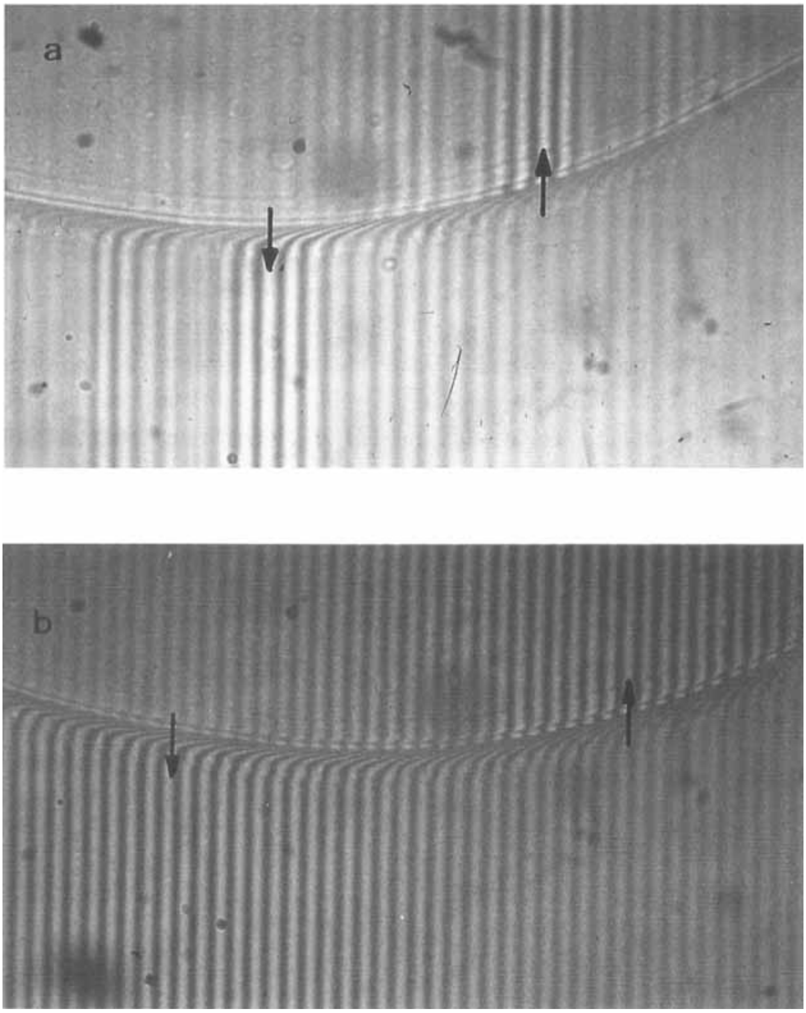


Figure 3. a) Interference pattern on the boundary between the isotropic phase of the mixure and the reference substance in the white light illumination. Sample thickness was 30 $\mu$m. Arrows shows the positions of the most intensive dark stripes , which should have zeroth number; b) the same with monochromatic light, as it was used in present work; arrows show the true positions of zeroth stripes found by the filter vibration method. See Color Plate I.

Because of application of the mirror cell a contribution to the optical path caused by the optical activity of the BPs is strongly equal to zero [7]. Using this experimental scheme it was possible to measure reflection spectra , to record interference patterns and visualize textures and phase transitions in liquid crystals photografically and with a video camera. The absolute refractive index n of some substance is determined by a simple formula [8]:

$$n = \frac{m\lambda}{2d} \qquad (1)$$

where

m is relative shift of interference stripes in the substance, with respect to the empty cell, in units of the distance between the neighbouring stripes,

$\lambda$ is the wavelength of light, determined by the position of the variable interference filter,

d is the sample thickness.

Because the shift of the stripes in the material with respect to the empty cell is very large, we have measured the distance between zeroth stripes in liquid crystal and a reference substance (cell glue Nordland UV Sealant, n = 1.50). Figure 3a shows the interference pattern on the boundary between the glue (upper part of the image) and the isotropic phase of the CB15/E9 mixure for the white light illumination. Such pattern gives only a qualitative information about the difference of refractive indexes. In approximation of small dispersion of the refractive index position of zeroth stripe does not depend on the wavelength , therefore it should be a black-white with the strongest intensity. The position of higher orders of interference do depend on the wavelength of illumination and corresponding stripes are colored. Because of the effect of color mixing a black-white stripe not obligatory corresponds to zeroth order of interference. The position of zeroth stripe in the material illuminated with white light on figure 3a can be determined wrongly, which demonstrates the next figure. Figure 3b shows the interference pattern in the monochromatic illumination, which was used in current work. The light beam was monochromatized by a variable interference filter with line width of 10 nm for the smallest splits of the collimating diaphragms. The position of zeroth stripe was found by a more accurate filter vibration method. The wavelength of illumination has been slightly varied by small vibrations of the variable optical filter. In this procedure zeroth stripe does not move for the reasons mentioned above,. whereas the higher order interfence stripes vibrate. One can see, that shift of zeroth stripes essentially differs from that of figure 3a.

The stripes shift has been measured to within one stripe, which gives an accuracy ±0.007 of the determination of the refractive index. The dispersion change of the refractive index of the glue was smaller than the accuracy of measurements. The temperature of the sample was controlled to 0.002 K.

## RESULTS.

Important feature of the observed interference pattern in chiral liquid crystals is its dependence on the proximity of the wavelength of measurements to the Bragg wavelength.

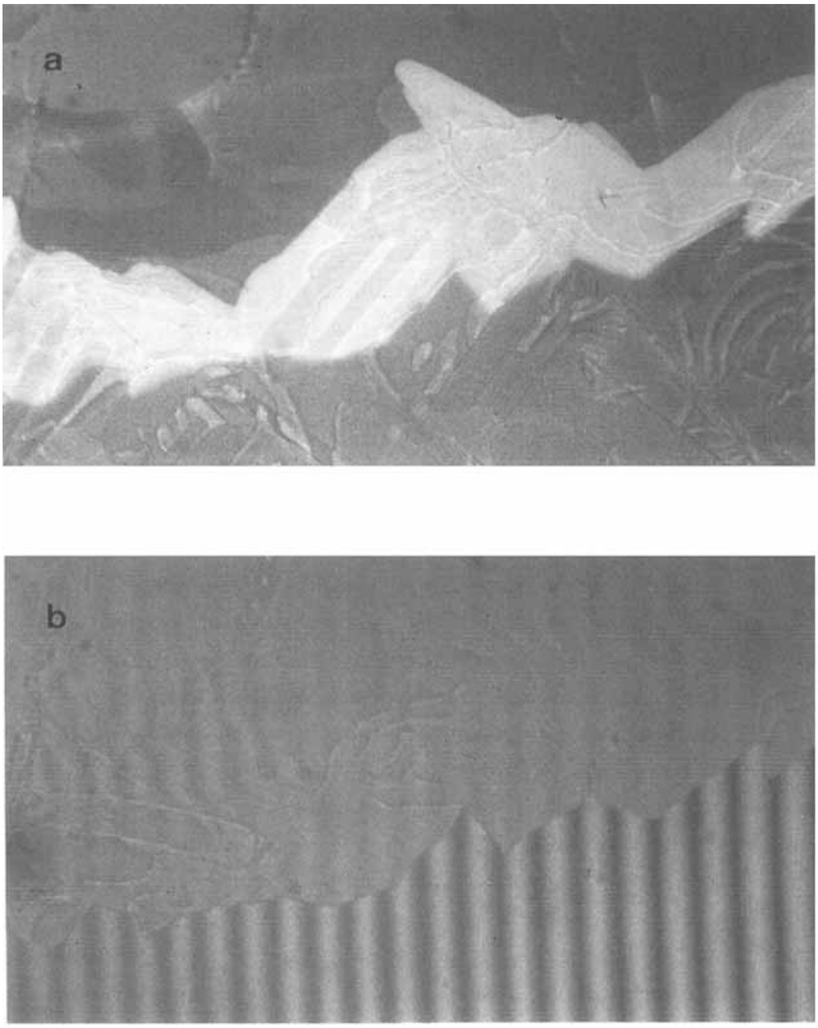
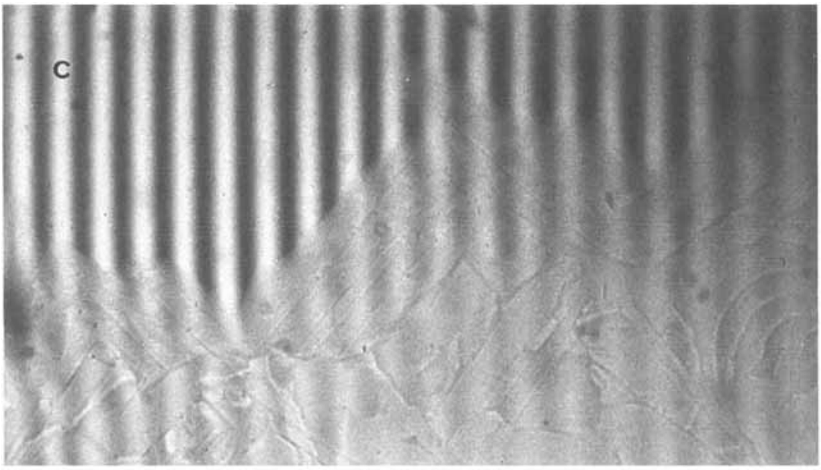
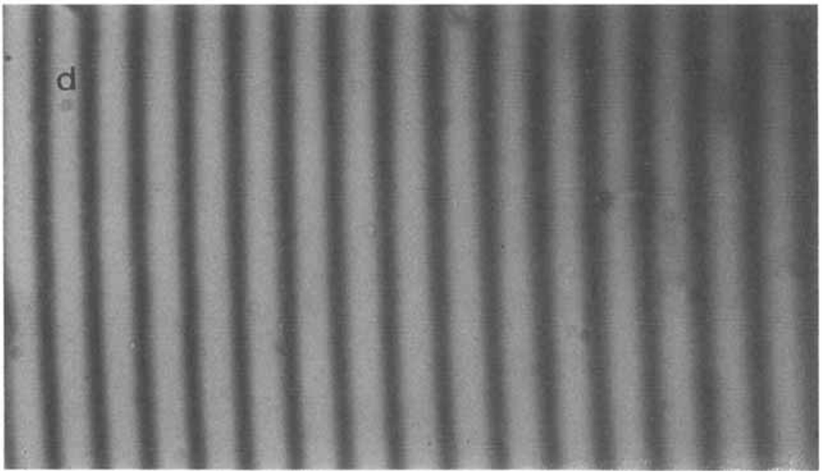


Figure 4. a) Texture of the BP I sample with three regions possessing different orientation of the crystallografic axes; interference patterns in blue ($\lambda \approx 470$ nm) (b); green ($\lambda \approx 530$ nm) (c) and red ($\lambda \approx 630$ nm) (d) illumination. See Color Plate II.

Figure 4a shows a part of blue phase I sample with three different orientations of domains. The asimuthal axes were not fixed in this case. The green domain corresponds to the orientation of the wave vector [110] perpendicular to the substrate. Changing the wavelength of monochromatic illumination one can obtain qualitatively different pictures.





The contrast of the pattern changes for the worse if the wavelength of illumination becomes equal to the Bragg wavelength in samples with free asimuthal orientation. Figure 4b shows the pattern for the wavelength corresponding to the blue color of the domain in the top part of the figure. Figure 4c present analogous image for the wavelength corresponding to the green color of the bottom domain.
See Color Plate III.

The domains with different orientations of the asimuthal axes are seen on the blue and green fields (figures 4b and 4c correspondingly).

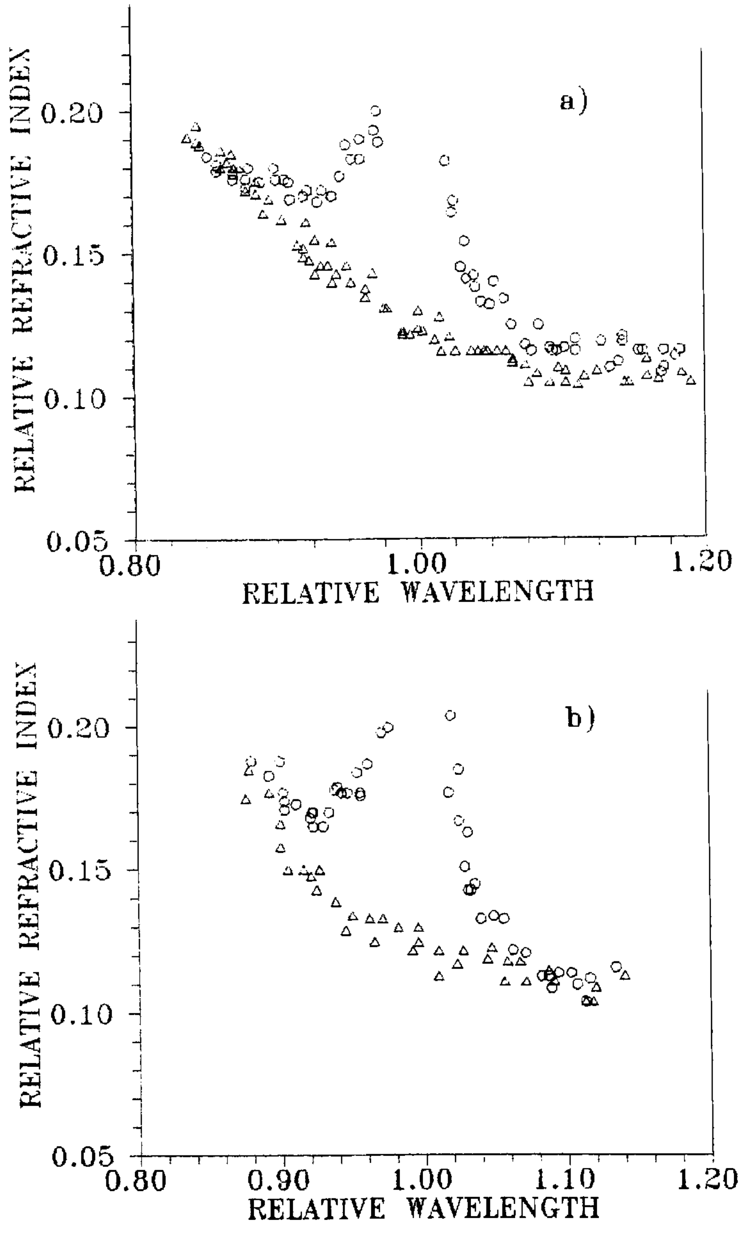


Figure 5. Relative refractive index of the BPI (o) and the isotropic liquid (Δ) with respect to the refractive index of the reference substance vs. relative wavelength $\lambda/\lambda_B$ in a liquid crystal mixture CB15/E9 with 60.9 weight % CB15. Sample thickness: a)30$\mu$m and b)16$\mu$m.

The second important feature is the shift of stripes between the green , blue bright and blue dark domains. Patterns of figures 4b-4d visualize the dependence of the refractive index on the ratio $\lambda/\lambda_B$. This means, that the blue phases are anisotropic , because for a given wavelength the refractive index depends on the orientation of the principal crystallografic axes with respect to the sample normal. This kind of anisotropy is seen in nonpolarized light , and we shall call it the anisotropy of the first type. Figure 4d shows the interference pattern on the same part of the sample with red illumination. The samples are optically isotropic, because no breaks of the stripes are seen. Hence, the concept of the optical isotropy of the cubic blue phases depends on the wavelength of measurements.

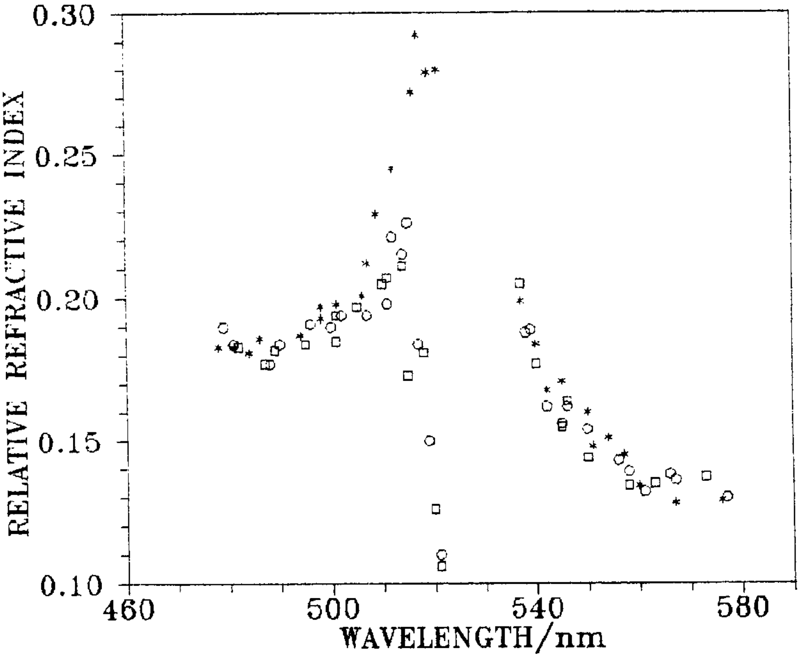


Figure 6. Refractive index dispersion curves of the BPI in a mixture with 60.9% CB15 in E9 for two directions of linear polirizer for the light beam propagating along [110] direction o - the polarizer parallel to the direction of rubbing, * - perpendicular to the rubbing direction.

Figure 5 gives a quantitative data on the anisotropy of the first type and shows the dependence of the refractive index of the mixture on the relative wavelength in the BPI for two sample thicknesses 30 $\mu$m (a) and 16 $\mu$m (b) for the light propagating along [110] direction. The samples were not oriented azimuthally and the illumination was not polarized. The refractive index of the isotropic liquid increases with decreasing wavelength because of the frequency dispersion in the vicinity of the absorption edge ($\lambda$ ≈340 nm). An anomaly of the refractive index of the BPI in the transmission region of the mixture in the vicinity of the Bragg wavelength of the BPI is observed. The recorded effect does not depend on the sample thickness and on polarization of light. The refractive index for the wavelengths far from the Bragg reflection band is independent on the orientation and coinsides with that of the isotropic liquid. The position of the refractive index anomaly always corresponds to the Bragg wavelength , which explains the images of the figures 4b-d.

Anisotropy of the second type was observed in defect-free samples with perfect orientation of the tangential ([110]) and asimuthal ([1$\bar{1}$0]) axes. Figure 6 shows dependence of the relative refractive index of the BPI on the wavelength for the directions of linear polarizator parallel to [001] and [1$\bar{1}$0] in 30$\mu$m thick samples. The refractive index dispersion curves for these two directions are qualitatively different. The [1$\bar{1}$0]-refractive index increases in the vicinity of $\lambda_B$, runs through a maximum and then decreases in the region of $\lambda/\lambda_B \leq 1$. The [001]- refractive index monotoneously increases on increasing wavelength for $\lambda \leq \lambda_B$. For $\lambda \geq \lambda_B$ the refractive index in both cases decreases with increasing wavelength. For $\lambda \leq \lambda_B$ an anisotropy of the cubic BPI with a positive sign of $\Delta n = n_{001} - n_{1\bar{1}0}$ has been observed.

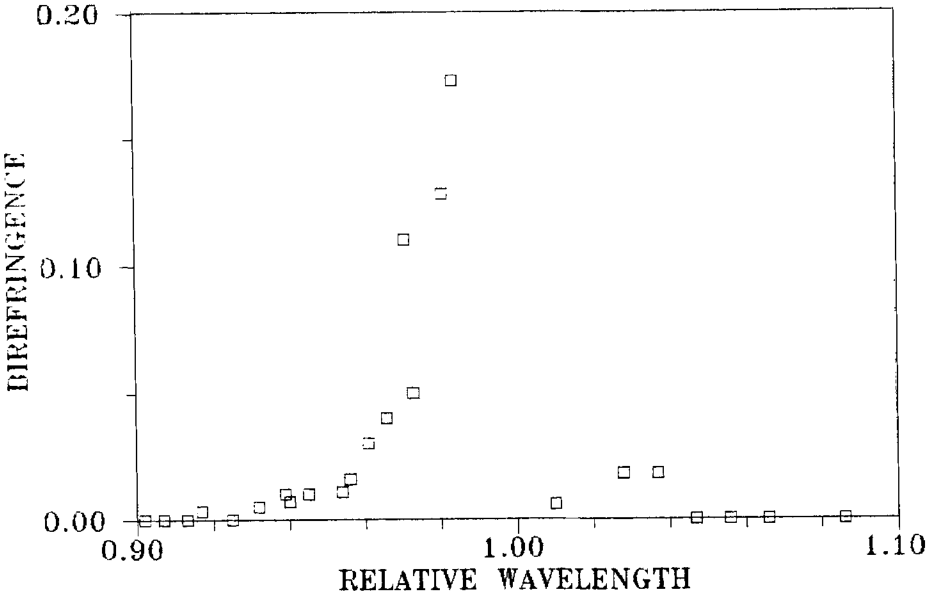


Figure 7. Birefringence of the BPI $\Delta n = n_{001} - n_{1\bar{1}0}$ vs the relative wavelength for the polarized light propagating along the [110] direction.

Figure 7 shows the dependence of the birefringence of the BPI on the relative wavelength for the previous figure. The value of the anisotropy of the refractive index increases with increasing wavelength for $\lambda \leq \lambda_B$ and reaches values of the order of 0.2 in the vicinity of the Bragg wavelength. Interesting feature is , that the birefringence for the wavelengths larger , than the Bragg wavelength, is zero with accuracy of our measurements.

## DISCUSSION.

The observation of the effect of optical anisotropy of nongirotropic cubic crystals of silicon (Si) and gallium arsenide (GaAS) with low dislocation density has been reported in [9, 10]. This effect was theoretically considered as spatial dispersion of higher orders in $(a/\lambda)$ in [1]. We shall try to understand the main features of our results in analogy with these findings using theory developed for the case of solid state by Ginsburg and Agranovich.

In [1] authors have described the spatial dispersion using reciprocal tensor of the dielectric constants $\epsilon_{ij}^{-1}$:

$$(\mathbf{E}(\omega, \mathbf{k}) = \hat{\epsilon}^{-1}(\omega, \mathbf{k})\mathbf{D}(\omega, \mathbf{k})), \tag{2}$$

where $\mathbf{E}$ is the electric field ; $\mathbf{D}$ is the electric induction; $\mathbf{k}$ is the wave vector of light; $\omega$ is its frequency.

In our case spatial dispersion effects of first order are equal to zero and we take into account second order terms in the development of the reciprocal dielectric constant in powers of $(a/\lambda)$. We take:

$$\epsilon_{ij}^{-1} = \delta_{ij}\epsilon_0^{-1}(\omega) + \beta_{ijlm}k_l k_m, \tag{3}$$

where $\epsilon_0(\omega)$ is frequency dependent part of the reciprocal tensor of dielectric constants; $k_l$ are components of the wave vector of light. The solution of the Maxwell equations shows, that the refractive index of a cubic phase depends on the polarization of light beam. Optical birefringence in the plane perpendicular to the direction [110] can be expressed in the following:

$$\Delta n = n_{1\bar{1}0} - n_{001} = \frac{1}{2}[\beta_3 + \frac{1}{2}(\beta_2 - \beta_1)]n^5\frac{4\pi^2}{\lambda^2}, \tag{4}$$

where $\beta_1, \beta_2, \beta_3$ are three independent components of the fourth rank tensor $\beta_{ijlm}$, which follows from the cubic symmetry of the blue phases (crystallographic class O (BPI and BPII)):

$$\beta_{iiii} = \beta_1,\ \beta_{iijj} = \beta_2,\ \beta_{ijij} = \beta_3. \tag{5}$$

Other components are equal to zero.

For the birefringence of the nongyrotropic solid crystal silicon, investigated in [9] was obtained $\Delta n \approx 5 \times 10^{-5}$. This is approximatelly by four orders of magnitude smaller, than the effect observed in our work for the BPI, which only qualitatively corresponds with (4).

The anisotropy of the blue phases depends on symmetry of the direction of the propagation of light. In the experimentally accessible geometry of the experiment with the BPI the wave vector of light is parallel to [110] direction of the reciprocal space. This direction has two fold symmetry axis (the BPI possesses the symmetry group $I4_132$) and the observation of anisotropy of the refractive index in this orientation correlates with symmetry arguments. In analogous experiments with the BPII (symmetry group $P4_232$) the light beam propagates parallel to the [100] direction, which possesses a four fould symmetry axis. As it was shown in [2] the refractive index is isotropic in plane perpendicular to [100].

This consideration of spatial dispersion effects, based on the theory developed for solid crystals can be regarded only as a first illustrative step , because $\lambda/\lambda_B$ can not be taken as a small parameter for the chiral liquid crystals. The other possibility is to take into account m=1 components of the order parameter (conical structure mode) in equations describing the diffraction optics of the blue phases in [11]. This is not realised untill now and deserves further attention.

**Acknowledgements.**
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