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Spatial dispersion of the refractive index in cubic liquid-crystalline blue phases in the vicinity of optical Bragg reflection

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An anomaly in the refractive index is observed in the cubic liquid-crystalline blue phases (BP's) I and II of several cholesteric-nematic mixtures in the vicinity of optical Bragg reflection. Because the reflection wavelength is of the order of the BP lattice constant, this phenomenon can be explained by spatial dispersion of the dielectric tensor.

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In the short-pitch chiral liquid crystals, the three-dimensional director-field order of the blue phases (BP's) is energetically preferable with respect to the cholesteric spiral structure close below the clearing point [1–5]. From selective reflection measurements it follows that the BP I possesses a cubic-lattice structure of the space symmetry group O^8, while the BP II is characterized by O^2 and the BP III is an example of a thermodynamically stable amorphous phase [5–7]. Orientational order of the BP's with cubic symmetry is a matter of its anomalous optical properties, analogous to some extent to the optical properties of the solid cubic crystals. In the case of crystal optics, some phenomena can be explained only by taking into account a spatial dispersion (e.g., optical activity). The spatial dispersion exists because of the dependence of the dielectric tensor of the medium on the spatial coordinate or in terms of Fourier expansion on the light wave vector (wavelength) [8]. Spatial dispersion effects are determined by the ratio of the lattice parameter (a), characterizing the periodicity of the medium, to the wavelength of light (λ). In solid crystals the parameter a/λ is very small ($\approx 10^{-3}$). Therefore, these effects can be generally regarded as being small, with the exception of some special cases.

The blue phases and cholesterics possess only an orientational long-range order of the director field and no positional molecular long-range order. The analogs of the spatial dispersion are therefore effects, which exist because of the spatial inhomogeneity of the dielectric tensor at distances of about one light wavelength, which is the case in the BP lattices with $a/\lambda \approx 1$. Such a drastic change of the scale of the spatial periodicity can lead to the origin of a new class of optical phenomena. The chiral liquid crystals possess different refractive indexes and transmission coefficients for left and right circularly polarized light waves. This effect, as well as the mixing of a direct wave with diffracted light waves, changes the structure of the intrinsic optic waves of the medium in the vicinity of the Bragg reflection. The change of the structure of eigenwaves can be the reason for measurable optical effects combined with the change of optical characteristics of the medium.

In this article we report a direct measurement of the refractive index anomaly in the vicinity of selective reflection in the cubic blue phases I and II.

The measurements have been carried out in the BP I and BP II of mixtures of 60.9 and 53.7 wt % of the pure high chiral compound CB15 [4-cyano-4′-(2-methylbutyl)-biphenyl] (Merck) and a wide-range nematic-liquid-crystal mixture E9 (Merck), possessing a high birefringence $\Delta n = 0.257$ at $T = 20\,^{\circ}\mathrm{C}$, $\lambda = 589$ nm. These mixtures exhibit the following phase transitions between the high-temperature liquid-crystalline phases (in degrees centigrade): Chol 20.21 BP I 20.66 BP II 20.86 BP III 21.36 Iso (60.9% CB15); Chol 29.0 BP I 29.42 BP II 29.52 BP III 29.6 Iso (53.5% CB 15).

Measurements of the refractive index dispersion have been carried out with a Leitz-Orthoplan microscope equipped with a Leitz interference reflection illuminator, which realize the Linnik interference scheme, and a Jarrel Ash monochromator. The experimental cell consists of two coated glasses with 30-μm fiber spacers. The upper glass was covered with a thin transparent ITO (indium tin oxide) film and the lower one with an aluminum mirror coating. Figure 1 shows the scheme of the experimental setup [9]. In the microscope interferometer, the polarized or nonpolarized light beam from a halogen lamp is divided by a beam splitter into two coherent beams: a reference and a testing beam. The testing beam falls down perpendicularly to the upper glass surface; after transmission through the substance, it is reflected at the lower plate and interferes with reference beam, reflected from the reference mirror. The interference pattern is detected photographically or visually in the microscope. By this method there is no contribution to the optical path difference caused by the optical activity of the BP's [10]. The absolute refractive index n of a substance is determined by a simple formula [9]

$$n = m\lambda/2d \ ,$$

where m is the relative shift of the interference stripes in the substance, with respect to an empty cell, in units of the distance between neighboring stripes; λ is the wavelength of the light, determined by the position of the variable-interference filter; and d is the sample thickness.

In our case we have measured the difference between the refractive indexes of a liquid crystal and a reference

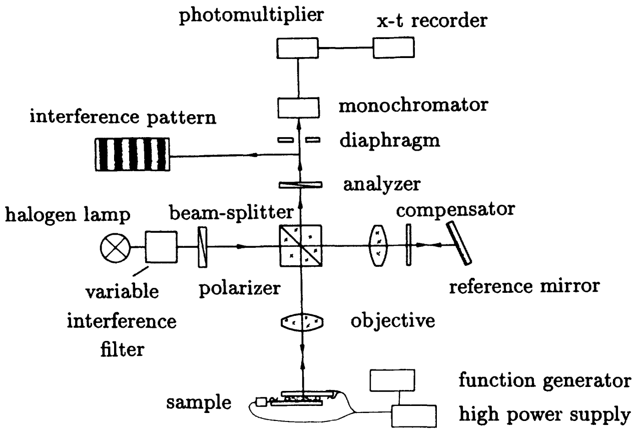

FIG. 1. Experimental setup of the modified Linnik interferometer for measurements of the selective reflection and refractive index dispersion.

substance with known refractive index (cell glue Nordland UV Sealant, $n=1.50$). The stripe shifts have been measured to within one stripe, which gives a ± 0.007 accuracy in determination of the refractive index. The dispersion change of the glue refraction index was smaller than the accuracy of the measurements. The measurements of the refractive index have been carried out on BP monodomain samples with monochromatic light, which have been obtained by means of a variable-interference filter with linewidth of 10 nm at the smallest diaphragms collimating the beam. The sample thickness has been determined by interference measurements of the empty cell to 30 ± 1 μm. The temperature of the sample was controlled to 0.002 K.

The BP I refractive index dispersion measurements have been carried out in the mixture with 60.9 wt % CB15. In the temperature range in which the BP I of this mixture is stable, the Bragg reflection wavelength is positioned between 518 and 550 nm. The BP II refractive index dispersion was measured in the mixture with 53.5 wt.% CB15, possessing a selective reflection in an interval from 527 to 538 nm. The homogeneous orientation of the BP I and BP II was obtained by applying an electric field to induce a phase transition to the nematic phase and a slow decrease of the electric field to zero. This procedure gives rise to the orientation of the wave vectors (110) in the case of BP I and (100) for the BP II perpendicularly to the glass surface. By this method no preferential orientation of the Fourier components of the order parameter parallel to the glass surface was obtained. Therefore, measurements in polarized and nonpolarized light give similar results. The dispersion of the refractive index was measured in the wavelength interval of 450–640 nm. The interference stripes disappear in the region of the strong diffractive reflection as a result of the loss of the coherency of testing and reference beams.

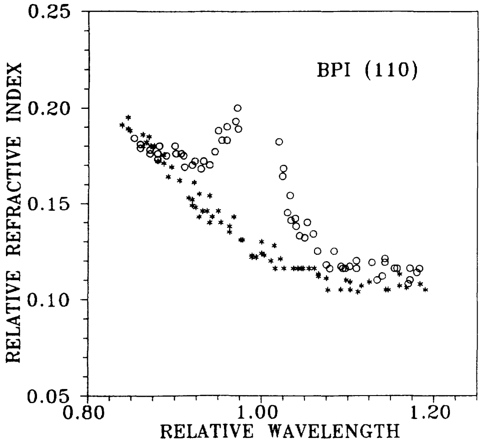

FIG. 2. Relative refractive index of the BP I (○) and the isotropic liquid (✱) with respect to the refractive index of the reference substance vs relative wavelength λ/λ_B. Liquid-crystal mixture: CB15/E9 with 60.9 wt % CB15. Temperature $T=20.35\,^{\circ}$C.

Figure 2 shows the dispersion of the average refractive indexes in the BP I and the isotropic liquid. The wavelengths are reduced to the BP I Bragg reflection wavelength $\lambda_B=541$ nm at $T=20.35\,^{\circ}$C. The refractive index of the isotropic liquid increases with decreasing wavelengths because of normal dispersion in the vicinity of the absorption edge ($\lambda=340$ nm). The measurements of the difference between the refractive indexes of the BP I and isotropic liquid far away from the selective reflection band are limited by the accuracy of our apparatus and can be estimated to be of the order of $\delta n=0.01$ at $\lambda/\lambda_B=1.1$. In the vicinity of the Bragg wavelength, a dramatic increase of the BP I refractive index from both sides of $\lambda/\lambda_B=1$ is observed: the BP I refractive index exceeds the corresponding values of the isotropic liquid by up to 4–5 %.

Figure 3 shows the dispersion of the BP II refractive index with respect to the isotropic liquid. The wavelengths are reduced to the BP II Bragg reflection wavelength $\lambda_B=530$ nm at $T=29.53\,^{\circ}$C. The difference between the BP II refraction index and that of the isotropic liquid far away from the selective reflection is, within our experimental accuracy, of the order of that between the BP I and isotropic liquid. The essential increase of the BP II refractive index is observed in the vicinity of the Bragg reflection. A comparison with the refractive index of the isotropic liquid shows that the peculiarity appears as a result of the selective reflection.

The observed effect can be explained by taking into account the spatial dispersion correction of the dielectric constant of the chiral liquid crystal. The tensor of the dielectric constants of a substance is determined as the coefficient of proportionality between the vectors of electric induction **D** and the electric field **E** [11]:

$$\mathbf{D}=\overleftrightarrow{\epsilon}\mathbf{E}\ . \tag{1}$$

As a result of selective reflection, the electric-field vector in the vicinity of the Bragg reflection can be described as a sum of Bloch waves [12–14]:

$$\mathbf{E}(\mathbf{r},t)=\mathbf{E}_0\sum_{\tau\neq 0}\mathbf{E}_\tau\exp(i\mathbf{k}_\tau\cdot\mathbf{r}-i\omega t)\ , \tag{2}$$

where $\mathbf{E}_0$ is the amplitude of the direct wave with wave vector $k_0=2\pi n/\lambda$, $\mathbf{E}_\tau$ is the partial amplitude of the diffracted light waves with the wave vectors $\mathbf{k}_\tau$ satisfying

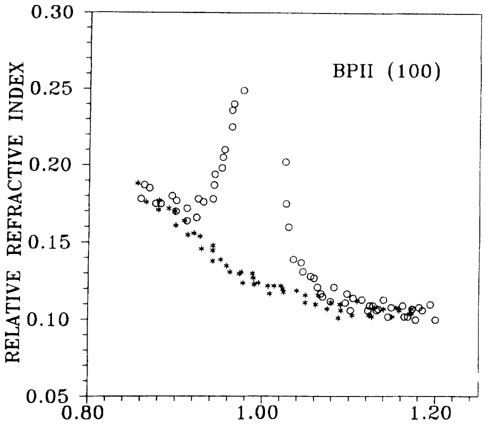

FIG. 3. Relative refractive index of the BP II (○) and isotrope liquid (∗) with respect to the refractive index of the reference substance vs relative wavelength λ/λ_B. Liquid-crystal mixture: CB15/E9 with 53.5 wt % CB15. Temperature $T=29.53\,^{\circ}\mathrm{C}$.

the Bragg equation $\mathbf{k}_\tau=\mathbf{k}_0+\tau$, $k_0=k_\tau$, and τ is the wave vector of the reciprocal space of the blue phases, $\tau=4\pi n/\lambda_B$.

The effective change of the electric-field amplitude leads to a change of the dielectric permittivity of the substance in the region of Bragg reflection. The amplitudes $\mathbf{E}_\tau$ have been calculated as the solutions of Maxwell's equations in [13] in the framework of perturbation theory outside the region of strong Bragg reflection. For our geometry with the light wave vector $\mathbf{k}_0 \| \tau_{110}$ for the BP I and $\mathbf{k}_0 \| \tau_{100}$ for the BP II, an equation for the determination of ϵ_{eff} can be obtained:

$$\epsilon_{\text{eff}}\mathbf{E}_0=\epsilon_0\mathbf{E}_0 + \sum_{\tau\neq 0} \epsilon^2(\tau,2)\mathbf{k}_0^2\mathbf{m}_\tau^*(\mathbf{m}_\tau\mathbf{E}_0)/\epsilon_0[\tau^2+2(\mathbf{k}_0\tau)] \,, \tag{3}$$

where $\epsilon_0=n^2$ is the average dielectric constant, $\epsilon(\tau,2)$ is the modulus of the planar-mode component of the Fourier harmonic with the wave vector τ, $\mathbf{m}_\tau=2^{-1/2}(\mathbf{m}_1-i\mathbf{m}_2)$, and $\mathbf{m}_\tau^*$ is the complex conjugate of $\mathbf{m}_\tau$.

The unit vectors $\mathbf{m}_1$, $\mathbf{m}_2$, and τ/τ form a right-handed local coordinate system, in which the basic matrices determining the chiral structure of the ϵ_τ component of the order parameter are defined [2,3], for example, in the case of the BP I for $\tau_{110}, \mathbf{m}_1 \| (001)$.

The refractive index n of the substance is determined by the formula [11]

$$n=\{\tfrac{1}{2}[\epsilon'+(\epsilon'^2+\epsilon''^2)^{1/2}]\}^{1/2} \,, \tag{4}$$

where ϵ' and ϵ'' are the real and imaginary parts of the dielectric permeability.

In our case we measure the average refractive index between the two circular polarizations and over the possible orientations of the structural Fourier components parallel to the glass surface. The averaging of the formula (3) in the region, where the experimental measurements are available, gives the correct qualitative description of the experimental data. Theoretical estimations show, however, that the change of the sign of the spatial dispersion contribution takes place in a narrow region around the Bragg wavelength. Equation (3) is valid for the case in which the intrinsic polarizations are close to circular. For the region of strong Bragg reflection near $\lambda=\lambda_B$, Eq. (3) is not applicable, because the second term runs to infinity. In this case the intensity of the diffracting wave in transmission decreases and the polarizations of the eigenwaves are elliptic. From our measurements it follows that this effect should be observable in other chiral liquid-crystalline phases possessing Bragg reflection in a suitable spectral region. These measurements are planned to be reported elsewhere.

In conclusion, the anomaly of the refractive index is observed in the vicinity of the selective reflection of light far away from the absorption band in the cubic liquid-crystalline blue phases I and II. This phenomenon is explained by spatial dispersion of the dielectric tensor in the BP's director-field structure with three-dimensional spiral order.

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