Diffraction of light in the blue phases of liquid crystals in an electric field

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Diffraction in three-dimensionally ordered BP I and BP II phases was measured at different times of alternating sinusoidal and pulsed electric fields. It was observed that the intensities of the diffraction fringes change, and these changes are characterized by relaxation times which are four orders of magnitude shorter than the times over which equilibrium cell parameters are established. The transformation of the diffraction spectrum indicates significant restructuring of the molecular ordering.

1. INTRODUCTION

The blue phases of liquid crystals with three-dimensional translational order have a cubic body-centered lattice O^8 (BP I phase) and a simple cubic lattice O^2 (BP II phase).[1,2] Investigations of the effect of an electric field on the blue phases led to the discovery of an entire series of nontrivial effects, such as, for example, a significant change ($\sim 10\%$) of the cell parameters (electrostriction),[3–6] phase transitions,[4,6–11] etc. In addition to changes of the cell parameters, restructuring of the orientational distribution of the molecules also occurs.[12–16] Local and macroscopic changes of structure should be characterized by significantly different relaxation times; this makes it possible to separate these processes experimentally. The characteristic times over which equilibrium cell parameters are established in the blue phases are equal to $\tau_1 \geqslant 1$ s.[17] Equilibrium cell parameters can be established in the specimen either by means of a continuous change or through the appearance and annihilation of defects (dislocations, disclinations). The large value of the relaxation time τ_1 is related with the fact that in the case when the cell parameters change continuously the reorientation of the molecules must occur in concert in the entire macroscopic volume and at the boundaries. The formation and annihilation of macroscopic defects also require macroscopic times.

In the diffraction experiments on translationally ordered blue phases, primarily physical phenomena associated with macroscopic relaxation times were studied. In the present work, in contrast to experiments performed thus far, diffraction was measured at different times of an alternating sinusoidal and pulsed electric fields. We observed that significant changes occur in the intensities of the diffraction fringes and these changes are characterized by relaxation times which are four orders of magnitude shorter than τ_1.

2. SPECIMENS AND MEASUREMENT PROCEDURE

The measurements were performed on a mixture of the chiral nematic 4-cyan-4(methyl)butyl-phenyl (52 wt.%) and the nematic liquid crystal 4-cyan-heptyloxydiphenyl. The BP I phase exists in the temperature range 27.3–27.67 °C and the BP II phase exists in the range 27.67–27.82 °C. The mixture exhibits positive dielectric anisotropy. The cell parameters of the cubic blue phases BP I and BP II are equal to $\sim 10^3$–10^4 Å, which makes it possible to investigate diffraction at optical wavelengths. The diffraction lines in the BP I phase [reflection (110)] and the BP II phase [reflection (100)] were measured in the transmission spectrum of naturally circularly polarized light. The spectra presented in this work consist of the transmission spectra $I(\lambda)$ normalized to the spectrum $I_0(\lambda)$ of the light incident on the specimen.

In order to prevent hydrodynamic phenomena in the specimens the measurements were performed in a sinusoidal electric field with frequency $\nu > 10^2$ Hz. In the pulsed measurements periodically repeating square pulses were employed. In order to prevent the formation of static charge on the electrodes the pulses were modulated with an alternating electric field with frequency $\nu_m = 4 \cdot 10^4$ Hz, greater than the inverse relaxation times of the processes of interest. The spectra were recorded at different times with the help of a model 165 boxcar integrator.

The thermostating apparatus made it possible to maintain the temperature with an accuracy of ± 0.01 °C. The specimens, which were 14 μm thick, were placed between two glass plates with transparent electrodes. The measurements were performed on oriented specimens in which the [110] direction in the BP I phase and the [100] direction in the BP II phase were perpendicular to the planes of the cell.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the transmission spectra of the BP II phase in an alternating electric field with frequency $\nu = 200$

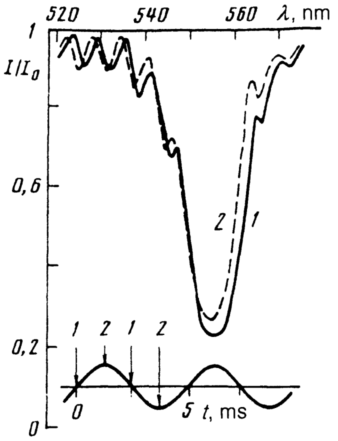

FIG. 1. (100) diffraction lines in the transmission spectrum of BP II at different times of the alternating electric field. $\nu = 200$ Hz and $T = 27.7$ °C. The times at which the measurements were performed are indicated at the bottom of the figure: $U_0 = 1$ (*1*) and 20 V (*2*).

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Hz in the region of the diffraction line (100); $U = 20$ V (here and below the amplitude values of the sinusoidal voltage applied to the specimen are presented). The measurements were performed at times when the electric field is equal to zero (*1*) and at the maximum of the electric field (*2*) (the "gate" width in the measurements was equal to 10^{-5} s). The maxima and minima on both sides of an intense diffraction fringe are related with the interference of light reflected from the boundaries of the specimen.[12] In an electric field the form of the spectrum does not depend on the polarization; this agrees with the centrosymmetric structure of the blue phases. At the same time, the diffraction spectra differ appreciably at different times of the alternating electric field. The difference consists of the fact that the intensity of diffraction changes and the diffraction fringe and the interference spectrum shift synchronously.

For substances with a positive dielectric anisotropy the unit cell of the BP II phase stretches along the direction of the field and, correspondingly, the reflection (100) shifts in the long-wavelength direction.[3-6,10] As one can see from Fig. 1, for $t \ll \tau_1$ we observe the reverse effect—short wavelength shift of the reflection. The shift of the diffraction fringe for $t \ll \tau_1$ can be explained by the change in the index of refraction n of the specimen in an electric field. The diffraction fringe lies in the spectrum at $\lambda = 2an\sin\theta$ (the Bragg–Yul'f condition), where a is the interplanar spacing and θ is the diffraction angle (in our case, $\theta = 90°$). The position of the interference maxima is determined by the relation $2dn = k\lambda$ (d is the thickness of the specimen). The shift of both types of spectral features is proportional to the change in the index of refraction $\delta\lambda/\lambda = \delta n/n$. For substances with positive dielectric anisotropy n decreases in the direction of the electric field[12] and this is what leads to the short-wavelength shift of the Bragg reflection (100).

Thus the effect of the electric field on the spectral position of a diffraction fringe leads to two opposite effects: on the one hand, a short-wavelength shift of the Bragg reflection without a change in the cell parameters for $t \ll \tau_1$ and, on the other hand, a larger shift of the reflection in the opposite direction owing to the change in the cell parameters at long times ($t \gg \tau_1$).[3-6,10]

The change in the intensity of a reflection (Fig. 1) is not related with the change in the interplanar spacings. In an alternating electric field with a "frozen" cell size the diffraction fringe "breathes" at double the frequency of the electric field. Two reasons for the observed effect must be considered: 1) partial reorientation of the structure in the electric field and 2) change of the diffraction intensity of the reflection. In order to determine the mechanism measurements were performed in the BP I phase and the relaxation times were determined. In the BP I phase the diffraction fringe is shifted and its intensity decreases, in a manner analogous to that described for the BP II phase, when an alternating electric voltage or pulses are applied to the specimen (Fig. 2). The effect is proportional to the square of the voltage (Fig. 3). The relaxation time is equal to $\sim 10^{-4}$ s (Fig. 4) both when an electric field is applied to the specimen and when the field is switched off. The successive change of the diffraction spectrum in a pulsed electric field is shown in Fig. 5. The superposition of the two effects (shift of the diffraction fringe and change in the intensity of the fringe) results in a complicated spectral dependence of the modulation of the light intensity in an electric field.

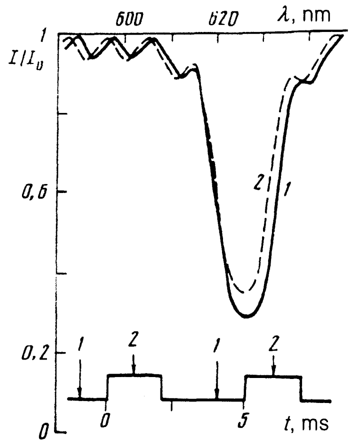

FIG. 2. (100) diffraction lines in the transmission spectrum of BP I in a pulsed electric field. $T = 27.6$ °C. The times at which the measurements were performed are indicated at the bottom of the figure.

On the basis of the available experimental data, the change in the intensity of the reflections cannot be explained by reorientation of part of the specimen in an electric field. It has been established experimentally and theoretically[18-21] that the preferred orientation of BP II in an electric field is $[100] \| \mathbf{E}$ (the four-fold axis is parallel to **E**). In the case of imperfect orientation of part of the specimen (different from $[100] \| \mathbf{E}$) the electric field should give rise to reorientation of this part of the specimen to a structure with $[100] \| \mathbf{E}$. Such a reorientation would result in an increase of the intensity of the reflection (100) in an electric field. The situation is analogous for the BP I phase. It has been shown experimentally[18] that the most stable orientation is $[110] \| \mathbf{E}$ and it does not change into other orientations. In our experiments the polycrystalline specimens, formed when BP I is prepared from the cholesteric phase, transformed in an electric field into a structure with the orientation $[110] \| \mathbf{E}$. All this taken together indicates that for both the (100) reflection of BP II and the (110) reflection of BP I in the case of reorientation

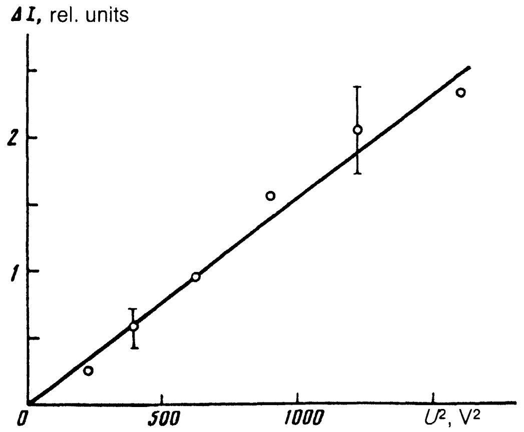

FIG. 3. Change in the intensity of the (100) diffraction line in the transmission spectrum of BP I as a function of U^2. $\Delta I = I(U_0) - I(U)$ (arbitrary units), $\nu = 200$ Hz, and $T = 27.6$ °C.

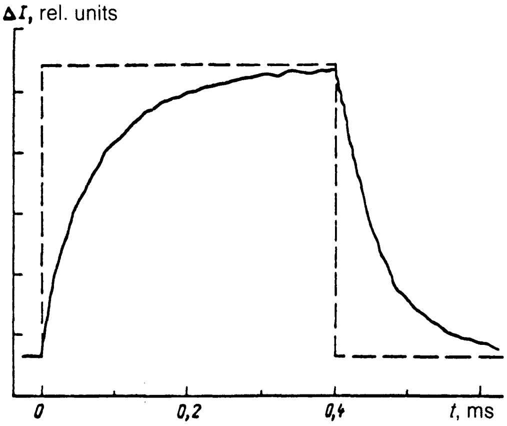

FIG. 4. Time of the change in the intensity of light transmitted through the specimen (arbitrary units) in the region of the maximum of the (100) diffraction fringe of the BP I phase. The dashed line is the electric field pulse. $U = 40$ V and $T = 27.6$ °C.

in an electric field the opposite effect should be expected—the intensity of the reflections should increase.

The diffraction intensity depends on the index of refraction.[22,23] However, the decrease in the index of refraction in the direction of the field is insignificant.[12,23] Estimates show[23] that the expected effect cannot bring about a significant change in the intensity of diffraction.

The intensity of the reflections is related directly with the structural ordering. In the blue phases the direction of the local "director" and the modulus of the orientational order parameter form, as they vary in space, a three-dimensional grating. The intensity of the reflections is determined by the moduli of the Fourier harmonics[23] ε_i of the permittivity tensor. The change in the absolute magnitude of the scalar order parameter ε as well as the relative contribution of different Fourier harmonics ε_i to the structural ordering can bring about a significant change in the intensity of the reflections. Transformation of the structure occurs within a unit cell without any change in the cell size and for this reason it is characterized by short relaxation times.

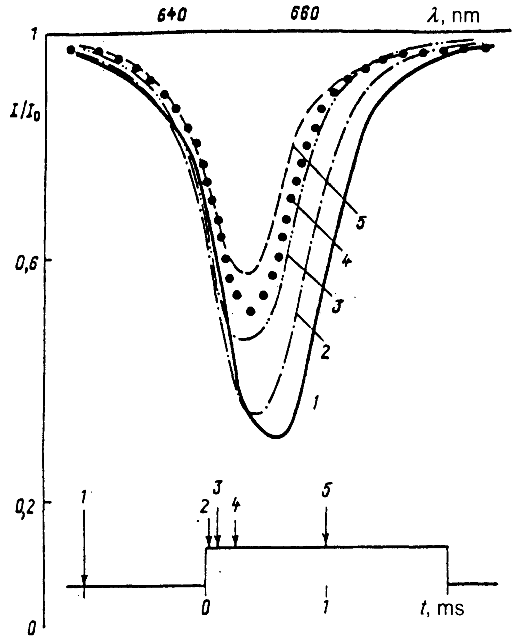

FIG. 5. (110) diffraction lines in the transmission spectrum of the BP I phase in a pulsed electric field. The pulse width is equal to 2 ms and the pulse repetition frequency is equal to 5 ms. $U_1 = 0$ (1), $U_2 = U_3 = U_4 = U_5 = 60$ V. The times at which the measurements were performed are indicated at the bottom of the figure: 0.04 ms (2), 0.1 ms (3), 0.25 ms (4), and 1 ms (5) after the start of the pulse. $T = 27.55$ °C.

Lubin and Hornreich[20] examined, with the help of Landau's theory, the effect of an electric field on structural ordering of the blue phases. For the BP II phase they studied the geometry realized in our experiment. It follows from their calculations that in an electric field, aside from deformation of the unit cell, the absolute values of the Fourier harmonics must change. In weak fields the effect is proportional to E^2, and the sign of the change in the intensity of the (100) reflection is the same as that observed in our experiment. However, the predicted change in the intensity is $\sim 10^{-2}$. It should be noted, however, that the electrostriction coefficients obtained in Ref. 20 are an order of magnitude smaller than the values observed experimentally in Refs. 3–6. In this connection it can be conjectured that the computed change in the Fourier harmonics is also too small. In this case the predicted effect[20] can make an appreciable contribution to the transformation, which we observed, of the diffraction spectrum.

An electric field gives rise in the blue phases to phase transitions at which both the structure and diffraction pattern change.[4,6–11] Since these transitions are weak first- or second-order phase transitions, the pretransitional transformation of the structure of the blue phases can make an additional contribution to the change of the diffraction spectrum.

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