Blue phases in an electric field: phase transitions, electrostriction

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The behavior in an electric field of the blue phases BPI and BPII of liquid crystals having positive dielectric anisotropy was studied by optical methods. The temperature–electric-field phase diagram, which included BPI, BPII, cholesteric, and nematic phases, as well as three phases which are not realized in the liquid-crystalline state in the absence of a field, was obtained. The electrostriction constants in phases induced by an electric field were determined.

The blue phases of liquid crystals are of interest because of the nontrivial micro- and macroordering of their molecules, their physical and primarily optical properties, and the possibility of describing their phase transitions and structures quantitatively by means of general-physical theories[1,2] (for example, Landau's theory of phase transitions). The blue phases are unique because their three-dimensional crystallization is combined with the deformability characteristic of the liquid state; this is why the blue phases are also called crystalline liquids.[2] The blue phases contain structures with long-range translational order (BPI and BPII) as well as an amorphous phase (BPIII) having only short-range order.[3,4] The unit cell dimensions in the blue phases are three orders of magnitude larger than in normal crystals, and for this reason structural investigations are performed at optical wavelengths. In the materials studied, in spite of significant differences between their molecular structure and chirality, only two types of three-dimensional long-range order have been observed experimentally: the exchange-centered O^8 cubic lattice (the BPI phase) and the simple O^2 cubic lattice (the BPII phase). The cell parameters in all materials are proportional to the pitch of the cholesteric spiral.

The behavior of the blue phases in an electric field is much richer. An electric field can bring about reorientation,[5,6] changes in the cell dimensions,[7-9] and phase transitions into new structures.[8,10-14] Structural transformation is accompanied by significant changes in the macroscopic properties of the blue phases. However the available experimental results on phase diagrams and the functional dependence of the displacement of the Bragg reflections in a field are contradictory and there are no data on the electrostriction constants of field-induced blue phases.

In this work we measured the diffraction spectra of the blue phases of materials having a positive dielectric anisotropy. The temperature–electric-field phase diagram was reconstructed, the electrostriction constants of the electric-field-induced phases were determined, and the kinetics of the structural transformation accompanying the phase transition was traced.

The diffraction was recorded in the spectrum of light transmitted through single-crystalline samples of the blue phases (transmission spectra). A mixture of the chiral nematic 4-cyan-4(2-methyl)butyl-phenyl (52 wt. %) and the nematic liquid crystal 4-cyan-heptyloxydiphenyl with positive dielectric anisotropy was employed. The BPI and BPII phases occurred in the temperature intervals 27.30–27.67 °C and 27.67–27.82 °C, respectively. Diffraction was recorded from a part of the sample with transverse dimensions ~ 200 μm and the temperature was maintained with an accuracy of ± 0.005 °C. In order to suppress electrodynamic effects a 10^3 Hz electric field was employed. The measurements were performed in a variable electric field at a fixed temperature and with a variable temperature in a fixed electric field. Oriented single crystals were grown in flat cells with an electrically conducting coating by cooling the material from an isotropic liquid. Single crystals of blue phases with orientations [110] (in BPI) and [100] (in BPII) perpendicular to the planes of the cell were obtained.

Figure 1 shows the temperature–electric-field phase diagram. The diagram was constructed based on diffraction spectral measurements on structures with three-dimensional translational ordering (the regions 1, 2, BPI, and BPII of the phase diagram) and microscopic observations of the texture of structures which did not have three-dimensional translational order (the cholesteric *Ch* and nematic *N*). The phase transition into the cholesteric phase was identified based on the vanishing of reflections in the transmission spectrum (the axis of the spiral of the cholesteric was oriented perpendicular to the direction of the field) and the appearance of birefringence in the sample. The $Ch \rightarrow N$ transition was identified based on vanishing of macroscopic chirality and birefringence (homeotropic orientation of the nematic in an electric field) in the sample.

The dependence of the reflection positions on the electric field E is different in the BPI and BPII phases and depends significantly on the temperature in the BPII phase. In the BPII region of the phase diagram the spectral position $\lambda_{\rm BP}$ of the diffraction lines changes continuously as a function of the field strength without any change in the form of the functional dependence $\lambda_{\rm BP}(E)$. A quadratic dependence of the shift $\Delta\lambda = \lambda(E) - \lambda(0)$ of the long-wavelength reflection ([100] in O^2) is observed (Fig. 2) in the high-temperature part of BPII phase right up to the maximum field strength $E \sim 3.8 \cdot 10^4$ V/cm, above which there are no transmission reflections in the spectrum (transition into the region 3 of the phase diagram in Fig. 1). The absence of translational order in the direction of the field could be connected with the formation of a structure with two-dimensional ordering.[15,16] In the intermediate temperature range (below the BPII-1-2 triple point) there occurs in a field ($U \sim 41$ V, Figs. 3a and 4) a heretofore unobserved abrupt decrease of the cell parameter followed by further increase of $\lambda_{\rm BP}$ as the field increases. The phase transition $\text{BPII} \rightarrow 2$ occurs with

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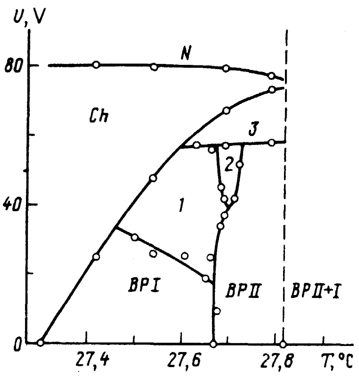

FIG. 1. Temperature–electric-field phase diagram. BPII + I—two-phase region BPII—isotropic liquid. The thickness of the sample is 15 μm.

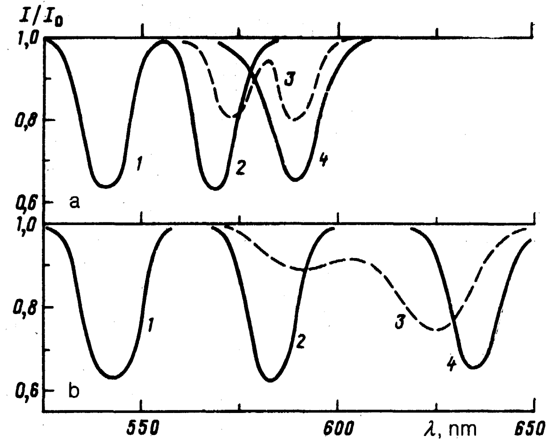

FIG. 3. The position of the diffraction lines of the transmission spectrum in an electric field: a—BPII, $T = 27.71$ °C [$U = 0$ (1), 32.3 V (2)]; the phase transition BPII → 2 [$U = 41$ V (3)], the region 2 of the phase diagram [$U = 47$ V (4)]; b—the phase transition BPII → 1, $T = 27.7$ °C [$U = 0$ (1), 38 V (2, 3, 4)]; the measurements 2, 3, and 4 were performed with an integral of 6 min, $d = 15$ μm.

significant hysteresis as a function of the field. The dependence $\lambda_{\rm BP}(E)$ is quadratic before and after the phase transition.

Two abrupt changes of the cell parameter are observed near the temperature of the BPII → BPI transition (Fig. 5). These changes correspond to the phase transitions BPII → 1 and 1 → 2 (Fig. 1). A similar behavior of the long-wavelength reflection was observed by Pievanski and Cladis[8] in BPII single crystals, located in the two-phase region BPII—isotropic liquid, as well as by Chen and Ho[13] (the mixture CB15:E9). Pievanski and Cladis[8] established, based on morphological observations and measurements of Kossel diagrams, the symmetry of the single crystals which are in equilibrium with the isotropic liquid. Comparison of these data with our measurements allows us to conclude that the region 1 of the phase diagram corresponds to the tetragonal phase BPX [Ref. 11] and the region 2 corresponds to the hexagonal phase BPH^{3D} [Ref. 8]. The BPII → BPX transition is accompanied by an abrupt change in the equilibrium values of the cell parameter (first order phase transition). In the process of the transition (Fig. 3b), however, the blue phase transforms through intermediate nonequilibrium structures: BPII cell extended in the direction of the field and compressed compared with the equilibrium cell in the BPX phase formed. The BPI–BPX transition (Fig. 1) occurs without a jump in the cell parameter (Fig. 6). The functional dependence of the interplanar distance on the square of the field changes. In the neighborhood of the transition $\Delta\lambda$ is a nonlinear function of E^2.

The electrostriction constants $\gamma(\Delta\lambda/\lambda = \gamma E^2)$ for the long-wavelength reflections differ significantly (Fig. 5) in the BPII ($\gamma = 13.5\cdot 10^{-15}$ m^{2}V^{-2}) and tetragonal BPX ($\gamma = 20\cdot 10^{-15}$ m^{2}V^{-2}) phases. In the BPII phase γ is close in magnitude to the electrostriction constant in the system CB15:E9 (Ref. 9). The displacement of the reflection at the phase transition BPII → BPH^{3D} (Fig. 4) is not accompanied by a change in the electrostriction constant. The electrostriction is determined by the magnitudes of the Fourier harmonics of the order parameter of the blue phases.[17] Based on the dependence $\Delta\lambda(E)$ in BPII and BPH^{3D} as well as the virtu-

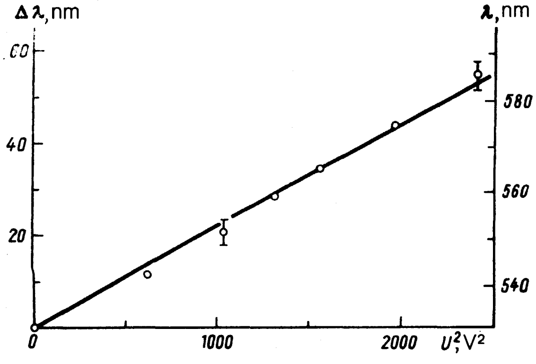

FIG. 2. The displacement of the diffraction lines of BPII versus U^2; $T = 27.79$ °C, $d = 15$ μm.

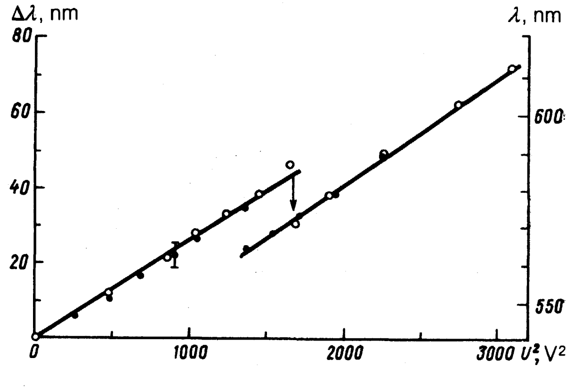

FIG. 4. The displacement of the diffraction lines versus U^2 at the phase transition BPII → 2. ○—increasing field, ●—decreasing field; $T = 27.71$ °C, $d = 15$ μm.

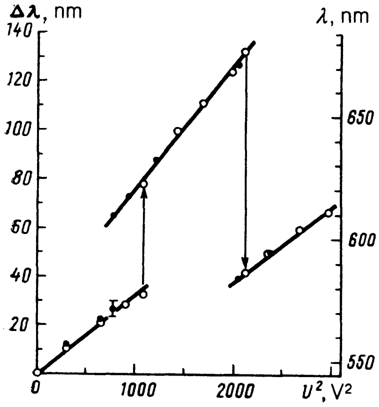

FIG. 5. The displacement of the diffraction lines versus U^2 at the phase transitions BPII → 1-2. ○—increasing field, ●—decreasing field; $T = 27.685$ °C, $d = 15$ μm.

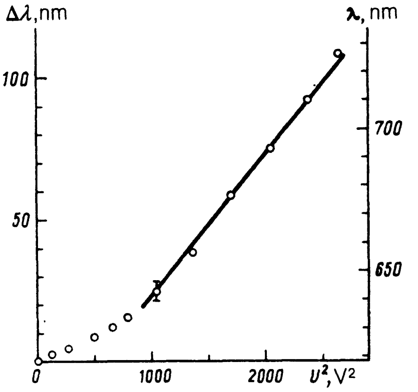

FIG. 6. The displacement of the diffraction line versus U^2 at the phase transition BPI-1; $T = 27.59$ °C, $d = 15$μm.

ally identical intensity of the long-wavelength reflections of these phases, it can be concluded that the local molecular ordering and the spatial ordering of the director in the cell do not change significantly at the phase transition BPII → BPH^{3D}.

Thus we have obtained, for the first time, the temperature–electric-field phase diagram which contains three phases that are not realized in the liquid-crystalline state in the absence of a field. The form of the phase diagram is not described by existing theoretical models of blue phases. It was observed that in a field the cell parameter for BPII changes abruptly and that in the BPI phase the $\Delta\lambda$ is a nonlinear function of E^2. It was established that in the BPII and field-induced phases the quadratic dependence of $\Delta\lambda$ on E holds right up to the critical fields giving rise to phase transitions. The electrostriction constants in field-induced phases were determined for the first time.

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