

## Selective optical reflection in the fog phase

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The optical scattering spectrum of the fog phase of a liquid crystal has been measured. This spectrum is found to be wavelength-selective. The half-width of the diffraction peak exceeds the diffraction half-width in the *BPI* and *BP II* quasicrystalline phases. The wide-band nature of the spectrum is evidence that there is no long-range order in the fog phase.

The so-called blue phases of chiral liquid crystals have recently attracted considerable experimental<sup>1-5</sup> and theoretical<sup>6-10</sup> interest. Up to three intermediate blue phases (*BPI*, *BP II*, *BP III*) have been detected experimentally in a narrow temperature interval ( $\sim 0.1-1^\circ$ ) between the liquid phase and the phase of a cholesteric liquid crystal. It has been shown that *BPI* and *BP II* have a cubic structure, and several characteristics of this structure have been determined. The experimental progress has made it possible to construct a theory<sup>8-10</sup> to describe the *BPI* and *BP II* cubic phases of the

liquid crystals. As for *BP III*, known as the "fog phase," its nature is not clear; the experimental data are extremely scanty,<sup>1,5</sup> and there has been no theoretical prediction of its appearance. An experimental study of the characteristics of *BP III* is accordingly the subject of greatest interest in research on the blue phases of liquid crystals. The fog phase in short-pitch cholesterics precedes the appearance of the *BPI* and *BP II* phases during cooling from the isotropic liquid phase with pronounced fluctuations near the point of an absolute instability of the liquid. A study of *BP III* is accordingly important not only for determining the nature of this phase but also, more generally, for reaching an understanding of the nature of phase transitions in liquid crystals.

In the present letter we report measurements of optical scattering in the *BP III* phase. A comparison with the data on *BPI* and *BP II* leads to a conclusion regarding the nature of the translational order in the fog phase.

For the measurements we used the liquid crystal cholesteryl nonanoate and a mixture of cholesteryl nonanoate and cholesteryl chloride. The transmission spectra and the scattering spectra ( $2\theta = 170^\circ$ ) are measured in the same region of the sample,  $0.5 \times 0.5$  mm in size. The thickness of the quartz cell is 0.5 mm; the temperature is regulated within  $\sim 0.01^\circ\text{C}$ . Since it is not possible to synthesize single-domain oriented samples of the *BP III* phase, the spectra of the *BP III* phase are compared with the spectra of polycrystalline samples of the *BPI* and *BP II* phases. To obtain polycrystalline samples, we heat the cholesteryl nonanoate to the phase of an isotropic liquid, cool it into the cholesteric phase, and hold it there for 1 h. The blue phases in the samples are obtained by heating from the cholesteric phase. The polydomain nature of the *BPI* and *BP II* samples is monitored by measuring the transmission spectra; the data on the transmission spectra of *BP III* agree with the results found by Meiboom and Sammon,<sup>1</sup> and we use this agreement as the criterion for concluding that the fog phase has been produced. The measurements are carried out in the interval 630–230 nm with the help of a hydrogen lamp. The spectra reported here are the experimental scattering spectra divided by the spectrum of the lamp.

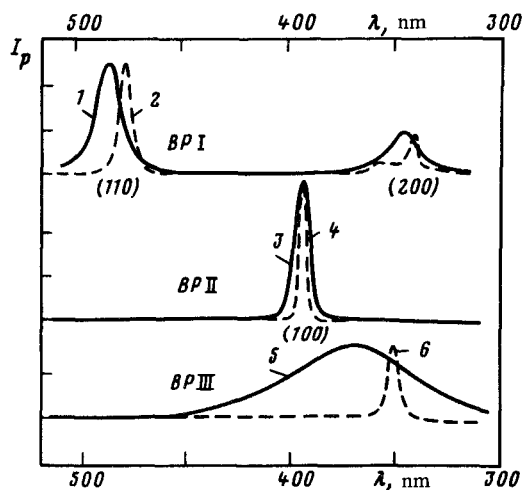


FIG. 1. Optical diffraction ( $I_p$ ) spectra in cholesteryl nonanoate. 1—*BPI* phase,  $T = 90.63^\circ\text{C}$ ; 2—*BPI*,  $T = 90.7^\circ\text{C}$ ; 3,4—*BP II*,  $T = 90.95^\circ\text{C}$ ; 5—*BP III*,  $T = 91.0^\circ\text{C}$ ; 6—cholesteric,  $T = 90.4^\circ\text{C}$ . Spectra 2 and 4 were measured 2 h after the corresponding phases were produced. The ordinate scale for the diffraction spectrum of *BP III* is six times larger than that for *BP II* (3).

The spectra of the *BP I* and *BP II* phases (Fig. 1) are represented by (110) and (200) reflections of the  $O^8$  body-centered lattice and the (100) reflection of the  $O^2$  simple cubic lattice. The structure near the (200) diffraction peak stems from double reflections by (110) planes.<sup>1)</sup> The half-width of the reflections is determined by the polydomain nature of the sample. Immediately after the *BP I* phase is obtained, the width of the reflection can reach 20 nm, even if the transition occurs from the cholesteric phase with narrow reflections. Holding the sample in the *BP I* phase causes a narrowing of the reflections (Fig. 1). A qualitatively different pattern is observed for *BP III*. The scattering is wavelength-selective ( $\lambda_{\max} \cong 366$  nm), but the spectrum is a wide-band spectrum, in contrast with the scattering in the *BP I* and *BP II* phases. The half-width of the peak is  $\Delta\lambda \approx 76$  nm. The shape of the spectrum does not depend on whether the phase is obtained from *BP II* or from the isotropic liquid. Holding the sample in the *BP III* phase does not lead to a narrow-band diffraction. The scattering spectrum lies near the bend in the transmission spectrum of *BP III* (Ref. 1). The transition from the narrow-band scattering in *BP II* to a wide-band scattering in *BP III* occurs abruptly; no scattering with an intermediate half-width is observed. Within the *BP III* phase,  $\lambda_{\max}$  and  $\Delta\lambda$  remain basically constant. The scattering intensity decreases with increasing temperature. The spectral shift of the scattering at the transition *BP II*  $\rightarrow$  *BP III* indicates that *BP III* is not a textured version of *BP II*.

The fog phase of the mixture of cholesteryl nonanoate and cholesteryl chloride also exhibits a selective wide-band scattering, which, like the diffraction, is shifted from *BP I* and *BP II* in the long-wave direction. In the cubic *BP I* and *BP II* phases, diffraction peaks are observed at wavelengths  $\lambda/\sqrt{2}$  ( $\lambda$  is the position of the long-wave reflection). In the fog phase we do not observe a diffraction peak at the corresponding wavelengths.

The large half-width of the scattering peak in the *BP III* phase should be attributed to the finite dimensions of the region of ordering of the director. The correlation length  $L$  (the effective distance over which order persists), which is estimated from the paracrystal model<sup>11</sup> ( $L \cong \pi^2/6.25\Delta S$ , where  $\Delta S$  is the half-width of the diffraction peak in units of  $S = 2n \sin \theta/\lambda$ ), is  $L \sim 1.1 \mu\text{m}$ , which corresponds to  $Ln/\lambda \sim 4-5$ . Such short correlation lengths cannot be assigned to an ordinary polydomain sample. Interestingly, the value found for the ratio  $Ln/\lambda$  from x-ray measurements of amorphous substances is of the same order of magnitude<sup>12</sup> ( $L$  characterizes the molecular order in this case), although the size of the coherent-scattering region itself in *BP III* is two or three orders of magnitude greater. The distinction between the fog phase and an ordinary isotropic liquid consists of either a change in the short-range order (corresponding to the peak in the reflection) or a possible, but as yet undetected, orientational order. In the former case, the transition from the isotropic liquid to *BP III* would be the first case of a first-order phase transition between liquids differing in short-range order. An analogy can be seen in the stratification of solutions, but in that case the change in short-range order is of a trivial nature and is due to a change in concentration.

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<sup>1)</sup>V. E. Dmitrienko called our attention to the possibility of this interpretation of the structure.

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