

Structure of blue phase of cholesteric liquid crystals

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(Submitted 6 July 1983; resubmitted 2 August 1983)

Pis'ma Zh. Eksp. Teor. Fiz. **38**, No. 6, 283–287 (25 September 1983)

The circular dichroism of blue phases was measured under normal and oblique incidence of light. It is demonstrated that the low-temperature blue phase has a body-centered cubic structure, while the high-temperature phase has a simple cubic structure. The orientation of structures in the specimen is determined. The magnitudes of the Fourier coefficients of the dielectric-constant tensor of both structures are estimated.

PACS numbers: 61.30.Eb, 77.20. + y, 78.20.Ek

The existence of two thermodynamically stable blue phases (BP) in chiral liquid crystals has now been established.^{1,2} In this work, we measured the circular dichroism (CD) of a mixture of cholesterol nonanoate and cholesterol chloride in a ratio of 73 : 27 molar percent. Chromatographically pure substances were used. Qualitatively similar results were obtained for two other mixtures. The measurements were performed on a Mark-III Jobin Yvon dichrograph. Quartz cells, polished to 1/2 of a strip with a thickness of 6 μm , were used. The orientation of the structures was fixed by the boundary surface, for which the walls of the cell were coated with a thin layer of polyvinyl alcohol and rubbed in a particular direction. The uniformity of the structure within the boundaries of the entire specimen was monitored by observation under a polarizing microscope. The temperature of the specimen was held constant to within 0.005°C. The angle of incidence (θ) and the azimuth of the direction of rubbing (φ) relative to the incidence plane could be varied over the ranges 0–25° and 0–360°, respectively, by rotating the thermostat as a whole. All phases give several chiral reflections and, correspondingly, peaks in the CD (Figs. 1–3). The CD spectra of the low-temperature phase BP-I depend on the thermal history. Figure 1 shows curves of CD for BP-I, obtained by cooling from the high-temperature phase BP-II. Figure 2 shows the curves with heating from the usual cholesteric phase (CP). The position of the reflections of CD in BP-II did not depend on the thermal history. Figure 3 shows data for BP-II, obtained by heating from BP-I.

The interpretation of the results is based on the "cubic model."^{3,4} We shall choose a system of coordinates ξ , η , ζ , in the following way: the ξ axis is oriented along the normal to the boundary surface; the η axis is oriented along the direction of rubbing; and, the ζ axis forms a right-handed triplet with them. The direction of the wave vector of the incident beam is determined by the polar and azimuthal angles θ and φ . The angle θ is measured from the ξ axis and the angle φ is measured from the η axis in the plane $\eta\zeta$ in the counter clockwise direction. We performed calculations of the spectral position of the reflections, starting from the different physically equivalent variants of the orientation of the structures in the specimen. It turned out that agreement with experiment for BP-I is achieved only under the assumption that its structure is a body-centered structure with the following orientation relative to the normals

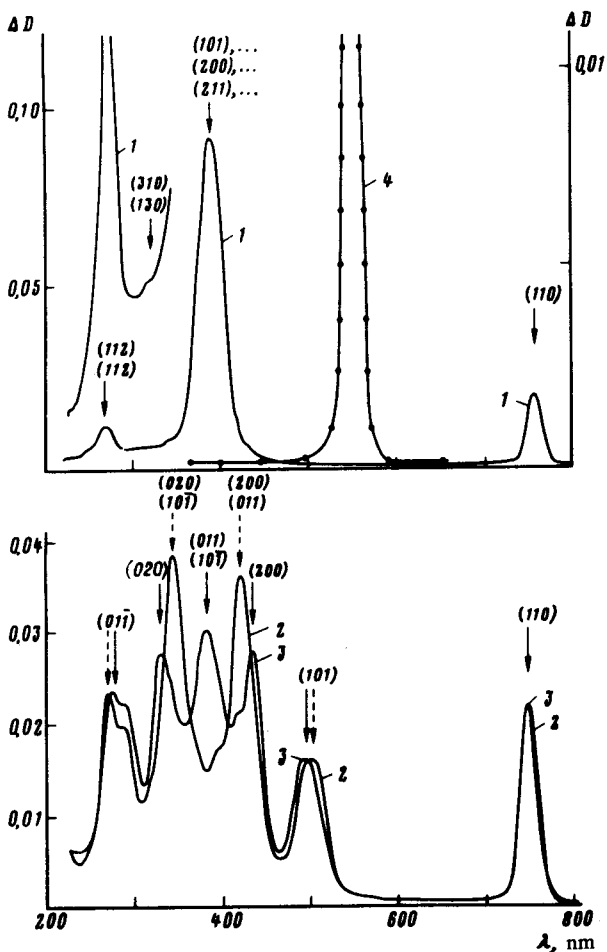


FIG. 1. CD spectrum of BP-I, obtained by cooling from BP-II at 78 and 60°C: 1 - $\theta = 0$, $\varphi = 0$; 2 - $\theta = 15^\circ$, $\varphi = 35^\circ$; 3 - $\theta = 15^\circ$, $\varphi = 55^\circ$; 4 - $X\Phi$.

to the boundary surface: in BP-I, obtained by cooling from BP-II, the direction [110] coincides with the normal, while with heating out of the cholesteric phase (CP), the [100] direction coincides with the normal. The calculations for other possible assumptions of the orientation and referral of reflections do not give even qualitative agreement with experiment (the identification of the reflections is additionally verified from the nature of the splitting with oblique incidence, see below).

From an elementary geometrical analysis, it is not difficult to obtain the following two relations for the wavelength of reflections with the Miller indices (hkl) for these two orientations:

$$\lambda_{hkl} = \sqrt{2}(h^2 + k^2 + l^2)^{-1} [(h + k)\cos\theta' - (h - k)\sin\theta'\sin\varphi' + \sqrt{2}l\sin\theta'\cos\varphi'] an, \quad (1a)$$

$$\lambda_{hkl} = 2(h^2 + k^2 + l^2)^{-1} [h \cos \theta' + k \sin \theta' \sin \varphi' + l \sin \theta' \cos \varphi'] an, \quad (1b)$$

$$\varphi' = \varphi + \psi,$$

where a is the size of the elementary BP cell; n is the index of refraction of BP; φ is the azimuth of the direction of rubbing relative to the plane of incidence; ψ is the angle between the direction of rubbing and the [001] direction in BP; and θ' is the angle of incidence in BP: $\sin \theta' = \sin \theta / n$.

The azimuthal orientation of the structures in the specimen is determined, for this reason, from data for oblique incidence: according to the splitting of the reflections. In the first case (Fig. 1), it follows from the CD curves that within the boundaries of the entire specimen, the [001] direction of the BP-I structure obtained by cooling from BP-II coincides with the direction of rubbing. To obtain such a single-domain specimen, BP-I was held at a constant temperature for several hours. On the other hand, the

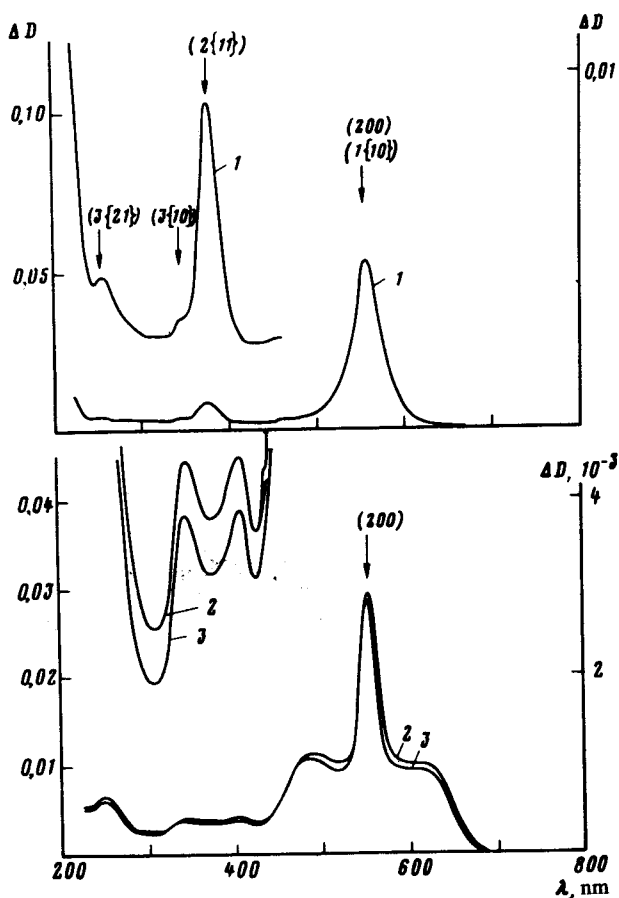


FIG. 2. Same for BP-I, heated from CP at 78 and 70°C: 1 - $\theta = 0$, $\varphi = 0$; 2 - $\theta = 12^\circ$, $\varphi = 15^\circ$; 3 - $\theta = 12^\circ$, $\varphi = 45^\circ$.

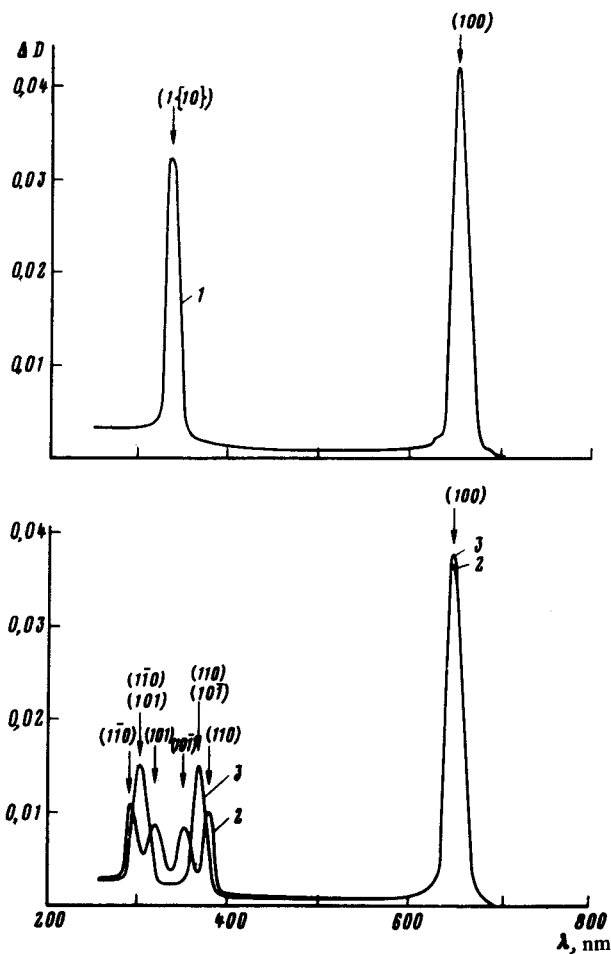


FIG. 3. Spectrum of CD for BP-II, obtained by heating BP-I at 78 and 76 °C: 1— $\theta = 0$, $\varphi = 0$; 2— $\theta = 12^\circ$, $\varphi = 20^\circ$; 3— $\theta = 12^\circ$, $\varphi = 45^\circ$.

curves of CD in BP-I obtained from the cholesteric phase indicate that the specimen is a multidomain specimen. This is also confirmed by polarimetric observations; the size of the domains is $\sim 100 \mu\text{m}$, while the azimuthal orientation of these domains is arbitrary, since the CD curves do not depend on the azimuth φ . It was impossible to obtain a single-domain specimen in this case. Five reflections are observed in BP-I: (110), (200), (211), (310), and (321); the first three reflections were observed previously.^{1,2} The arrows in Figs. 1 and 2 indicate their positions calculated from (1). We did not observe the reflection (220) reported in Ref. 2 (the peak in CD at $\lambda = 290 \text{ nm}$ is missing in Fig. 2). It is evident from Figs. 1 and 2 that the proposed model permits identifying all observed reflections. The symbol $(h\{kl\})$ above a reflection indicates that all reflections (hkl) , $(hk\bar{l})$, $(h\bar{k}l)$, $(h\bar{k}\bar{l})$, $(h\bar{l}k)$, $(h\bar{l}\bar{k})$, $(h\bar{l}\bar{k})$, $(h\bar{l}\bar{k})$ are degenerate with respect to frequency.

The pattern observed in Fig. 3 for the BP-II phase is also uniquely explained assuming a simple cubic structure with reflections (100) and (110) and with the following orientation: the [100] direction is normal to the boundary surface, while [010] coincides with the direction in which it was rubbed. Other reflections were not observed in BP-II.

On the basis of our results, the results of Ref. 5, and the analysis of Ref. 3, it is possible to determine the space group of both BP. Only O^8 for BP-I and O^2 for BP-II are possible.

The theory of the optical properties of BG was developed in Ref. 4. We used the results of the analysis presented there to estimate the relative values of the Fourier components ϵ_{hkl} of the order-parameter tensor (dielectric constant) from the observed integral intensities I_{hkl} of the corresponding reflections of CD. The small thickness of the specimen makes it possible to use the kinematic approximation. Based on the results in Ref. 4, it is easy to obtain the following equation for I_{hkl} :

$$I_{hkl} = \int \Delta D_{hkl}(\lambda) d\lambda \sim L \epsilon_{hkl}^2 (1 + \sin^2 \theta_B^{hkl}) / \sin \theta_B^{hkl},$$

where L is the thickness of the specimen, ΔD is CD, and θ_B^{hkl} is the Bragg angle.

The measured values of the integral intensities of CD reflections with normal incidence are as follows (in relative units):

Fig. 1: $I(760) = 440, \quad I(390) = 3500, \quad I(270) = 120;$

Fig. 2: $I(560) = 1900, \quad I(380) = 170;$

Fig. 3: $I(660) = 820, \quad I(340) = 570.$

The estimates obtained from these data are as follows:

$$\epsilon_{200}^I : \epsilon_{110}^I : \epsilon_{211}^I = 1.1 : 1.0 : 0.3;$$

$$\epsilon_{100}^{II} : \epsilon_{110}^{II} = 2.5; \quad \epsilon_{100}^{II} : \epsilon_{200}^I = 1.4.$$

The average error in the estimates of ϵ , including the errors in the measurements (the difficulties of taking into account the background and the wings) and the uncontrollable difference between the specimens, amounts to 10–15%.

We thank V. E. Dmitrienko for many useful discussions and N. V. Usol'tseva for providing us with the specimens.

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