Optical activity, transmission spectra, and structure of blue phases of liquid crystals

V. A. Belyakov, E. I. Demikhov, V. E. Dmitrienko, and V. K. Dolganov

All-Union Research Center for Surface Properties and Vacuum; Institute of Solid State Physics, USSR Academy of Sciences

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The transmission spectra and optical activity of single crystals and polycrystals of the BPI, BPII, and BPIII phases were measured. The experimental data were compared with theoretical expressions derived in the framework of kinematic and dynamic diffraction theory and relating the observed blue-phase properties with Fourier harmonics of the dielectric tensor. The absolute values and temperature dependences of the Fourier-harmonics were determined. Expressions that take into account up to eight Fourier harmonics are obtained by the Landau theory for the free energies of cubic-symmetry phases, and the minimum-energy structures are determined by numerical methods. It is shown that an approximate analytic description of the blue-phase structures is possible. In this approximation the structure of the order parameter is similar in all the phases and only the amplitude of its spatial modulation can change. In particular, the temperature dependence of the order parameter coincides with the corresponding dependence for the Landau theory with a scalar order parameter; this agrees well with the experimental data.

I. INTRODUCTION

Considerable progress has been achieved during the last few years in understanding the liquid-crystal blue phases observed in a narrow temperature interval between the cholesteric phase and the isotropic liquid (see the reviews[1–3] and the references therein). The molecules in the blue phases have a three-dimensional spatial ordering that leads, in particular, to finite elastic shear moduli; at the same time, since the centroids of the molecules have no long-range order, viscous flow of matter across the structure of the blue phases is possible. The molecule orientations can acquire a spatially inhomogeneous structure as a result of their right-left asymmetry (chirality); this asymmetry causes the molecule orientation to vary from point to point and to form a spiral structure (one-dimensional for cholesterics and three-dimensional for blue phases). It has by now been established that there exist at least three types of blue phase, BPI, BPII, and BPIII, with different spatial structures (the phases are listed in order of rising temperature; BPIII is called also the "fog" phase).

An important role in the experimental investigations of blue phases is played by optical modes. The most informative are measurements that reveal distinctive properties due to light diffraction, since the unit-cell size of these phases is of the order of the wavelength of light. It was concluded from the observable optical diffraction reflections that the blue phases have cubic phases,[4–6] and the most probable space groups of these phases were indicated. The spiral ordering of the molecules in the blue phases reveals strong circular dichroism[4,6] and optical activity, from which one can obtain information on the blue-phase structure. Optical activity was measured in Refs. 7 and 8, but the inability to control the sample quality and the unit-cell orientation made difficult a quantitative description of these experiments as well as a comparison of the data with one another. The BPI blue-phase order-parameter modulus was determined in Ref. 9 from the transmission spectra, but without data on their temperature dependence.

The theory of the structure and symmetry properties of blue phases was developed mainly within the framework of the Landau phase-transition theory.[10–13] Its predictions agree qualitatively with the experimental data, but no detailed comparison of the theory with experiment has been made so far (with the exception of Ref. 6, in which it is shown that the intensity ratio of individual reflections is close to the theoretically predicted one).

We present here a consistent comparison of the theory with the results of optical experiments, with the blue phases of cholesteryl nonanoate as the example. The temperature dependence of the transmission coefficient, and the optical activity, were measured both in the region of existence of blue phases and for supercooling into the cholesteric phase. The order parameter and its temperature dependence are determined from various experimental data for the BPI and BPII phases.

The organization of the theoretical analysis is the following. We derive first, within the framework of kinematic and dynamic diffraction theory, equations that relate the blue-phase optical properties observed in single crystals and polycrystals with their structural characteristics (the Fourier harmonics of the dielectric constant $\hat{\varepsilon}_\tau$). These equations are used to calculate from the experimental data the Fourier harmonics (apart from the phase) under the assumption that only one planar mode contributes to each Fourier harmonic (*vide infra*), and obtain their temperature dependence that follows from the experiment. The temperature dependence of $\hat{\varepsilon}_\tau$ is next calculated, under the same assumption, from the Landau theory and the theoretical and experimental data are compared.

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II. SAMPLE PREPARATION AND MEASUREMENT PROCEDURE

The measurements were made on cholesteryl nonanoate, which has three blue phases: BPI, BPII, and BPIII.[4,6] BPI and BPII single crystals were grown in quartz cells whose surfaces were coated with polyvinyl-alcohol film and rubbed with filter paper for alignment. Experiment has shown that better crystals are obtained by cooling from an isotropic liquid. The normal to the cell surface is then parallel to [110] in the BPI phase and to [100] in BPII. We used single crystals from 8 to 220 μm thick. The sample thickness was monitored by interference. An oriented cholesteric is obtained by relative shift of the cell cover glasses when the sample is in the cholesteric phase. Polycrystalline blue-phase samples were obtained in untreated quartz cells 2 mm thick by heating from the cholesteric phase. The measured BPIII samples were not oriented, since the standard cell-preparation methods used to obtain single crystals of BPI and BPII do not lead to formation of an oriented structure in the BPIII phase.

The transmission spectra and the light-polarization-plane rotation were measured from one and the same 0.1×1 mm section of a sample. The temperature was maintained and regulated to within 0.01 °C. The orientations of the BPI and BPII single crystals relative to the cell surface and the quality of the obtained single crystals were monitored against the transmission spectra; the textures obtained were also monitored by observation through a polarization microscope. We used DMR-4 and MDR-23 monochromators in the measurements. The light-polarization-plane rotation was measured by a modulation method, accurate to ~ 0.5 degree of angle at the wavelength of an He–Ne laser. The intrinsic (molecular) optical activity was 0.27 deg/mm at $\lambda = 6.33$ nm.

III. EXPERIMENTAL RESULTS

Figures 1–4 show the measured spectral-transmission line shapes, the line spectral positions, and the optical activity at various temperature. The reflection half-width varies little within the phase-existence temperature range, it changes insignificantly on going from BPII to BPI, and increases when a transition is made to the supercooled region of BPI; the latter is apparently due to the appearance of cholesteric-phase nuclei and to degradation of the sample quality. The intensity at the reflection maximum (Fig. 1) depends nonlinearly on the sample thickness (0.19 and 0.047 as the thickness is decreased from 20 to 10 μm), and the half-width increases with decreasing thickness of the single crystal (from 4.3 to 8.1 nm, respectively). The spectral positions of the reflections in the BPI and BPII phases (Fig. 2) agree with the results of earlier measurements.[4,6] It is known that no individual transmission spectrum bands are observed in fog phase. Figure 2 shows for BPIII the spectral location of the maximum of the selective reflection band in "backward" scattering.[15] Note that the maximum of the fog-phase reflection is shifted towards longer wavelengths relative to the reflection of the cholesteric and towards shorter wavelengths relative to BPII.

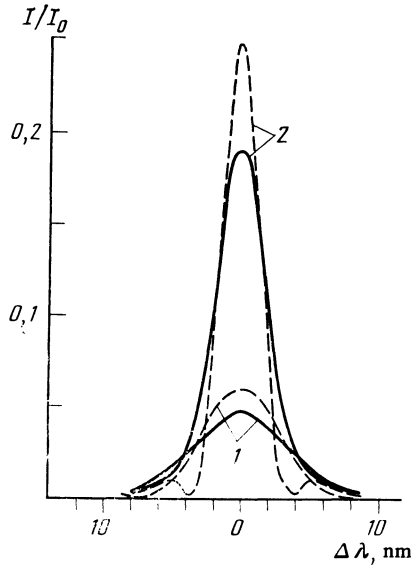

FIG. 1. Line shape in BPI transmission spectrum: 1) $T = 90.88$ °C, sample thickness $L = 10\,\mu$m; 1) $T = 90.80$ °C, $L = 20\,\mu$m. The dashed curves follow from the kinematic theory.

The temperature variation of the light polarization plane rotation at a fixed wavelength are shown in Fig. 3. In the region where blue phases exist, the optical activity changes by approximately 40 times, while for the fog phase it does not depend on whether the BPIII was obtained from polycrystalline or single-crystal BPII samples. In the cholesteric phase, the measured samples were oriented with the spiral axis perpendicular to the cell plane. Strong birefringence is observed in the cholesteric polycrystalline samples and makes measurements of the optical activity impossible. In the case of phase transitions (see Fig. 3) jumps are observed in the rotation of the light polarization plane; it should be noted that unlike in Ref. 7 we have observed a jump also in a transition from the isotropic liquid to BPIII. The optical activity in BPI and BPII single crystals is higher

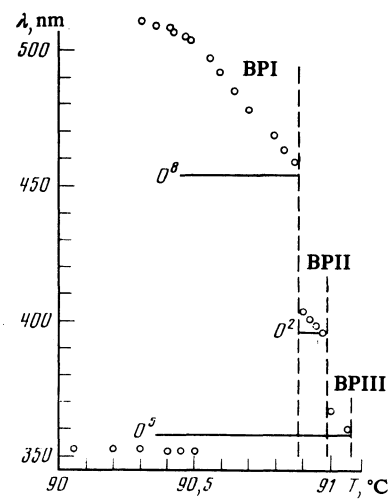

FIG. 2. Temperature dependence of the position of the long-wave reflection in BPI, BPII, and BPIII. Solid line—reflection location that follows from the Landau theory for the space groups O^2, O^5, O^8.

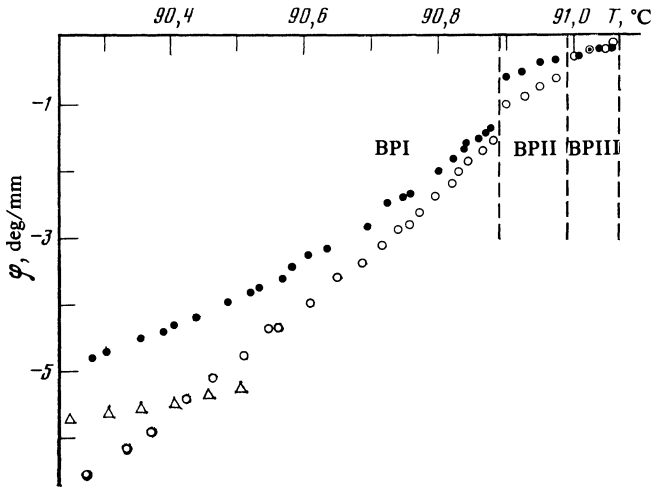

FIG. 3. Rotation of the light-polarization plane in the cholesteric, blue, and fog phases at $\lambda = 633$ nm: △—Cholesteric single crystal, $L = 50\,\mu$m; ●—BPI, BPII, and BPIII polycrystals, $L = 50\,\mu$m; ○—BPI, BPII, and BPIII single crystals, $L = 220\,\mu$m.

than in polycrystalline samples, and has a stronger temperature dependence.

Typical examples of the dispersion of the optical activity of blue-phase mono- and polycrystals, together with the corresponding transmission spectra, are shown in Fig. 4. For single crystals, the dependence on the wavelength is stronger, and reversal of the rotation in the diffractive-reflection region is typical also of the cholesteric phase. The curves for polycrystals are smoother, and no divergences are observed near the "steps" of the transmission spectrum bands. An even smoother dependence on λ is observed in the fog phase.

The integral intensity of the reflections in the transmission spectra of BPI and BPII single crystals increases with decreasing temperature. The measured integral intensities are reported below.

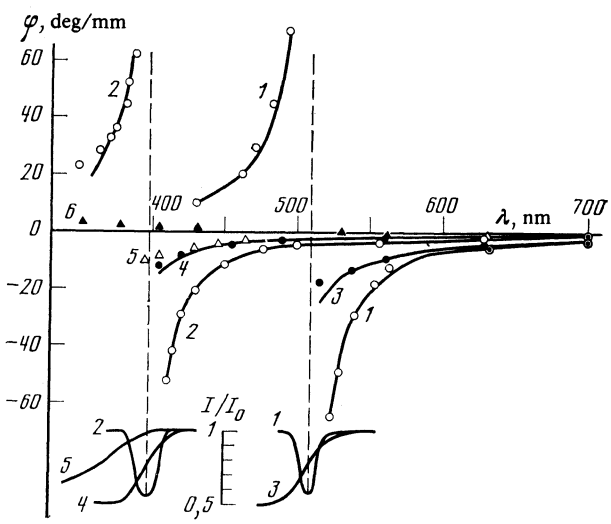

FIG. 4. Dispersion of optical activity in blue-phase mono- and polycrystals and in an isotropic liquid: 1—BPI single crystal, $T = 90.42$ °C; 2—BPII single crystal, $T = 90.95$ °C; 3—BPI polycrystal, 90.42 °C; 4—BPII polycrystal, $T = 90.95$ °C; 5—BPIII, $T = 91.02$ °C (△) 6—isotropic liquid, $T = 92.0$ °C (▲). The lower inset shows the corresponding transmission spectra for unpolarized light.

IV. THEORY OF OPTICAL PROPERTIES

The main purpose of optical measurements in the blue phase is to determine its structure, i.e., the spatial structure of the order parameter. Following Refs. 10–13, we choose the order parameter in the blue phase to be the zero-trace part of its dielectric tensor $\hat{\varepsilon}(\mathbf{r})$. Taking the spatial periodicity of the blue phase into account, it is convenient to represent $\varepsilon(\mathbf{r})$ as a Fourier expansion in the reciprocal-lattice vectors $\boldsymbol{\tau}$:

$$\hat{\varepsilon}(\mathbf{r}) = \sum_{\tau} \hat{\varepsilon}_{\tau} \exp(i\boldsymbol{\tau}\mathbf{r}), \tag{1}$$

where $\boldsymbol{\tau} = 2\pi d^{-1}(h\mathbf{x} + k\mathbf{y} + l\mathbf{z})$, d, is the dimension of the unit cell, h, k, and l are the Miller indices, and $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ are the unit vectors of the crystallographic axes.

The theory of optical properties of blue phases is the subject of many studies.[16–18] We consider here in detail cases in which terms quadratic in the Fourier harmonics of $\hat{\varepsilon}_{\tau}$ suffice for the description of the light-polarization plane rotation and of the reflection and transmission coefficients. This is valid for thin single crystals, polycrystals with small individual blocks, as well as for light propagation outside the regions of strong diffractive reflection (specific criteria for these approximations will be given below; they all reduce in fact to the requirement that the diffracted-wave intensity by much lower than that of the incident). From the practical point of view, the situations considered here are the most favorable for the determination of the Fourier harmonics of $\hat{\varepsilon}_{\tau}$ from experimental data, since the optical properties are practically independent of the degree of perfection of the single crystals or of the shapes of the individual blocks of polycrystals, and are determined only by the form of $\hat{\varepsilon}_{\tau}$.

a) Kinematic approximation

We consider first diffractive scattering of light from a thin single crystal in the form of a plane-parallel slab of thickness L. Using the results for crystals of arbitrary thickness,[3,17] we obtain for the coefficient R of light reflection from a thin single crystal

$$R(\mathbf{e}_0, \mathbf{e}_d) = I_d/I_0 = |\mathbf{e}_d^* \hat{\varepsilon}_{\tau} \mathbf{e}_0|^2 R_{\tau}, \tag{2}$$

where I_0 is the intensity of an incident wave with polarization $\mathbf{e}_0$, I_d is the intensity of the diffracted-wave component with polarization $\mathbf{e}_d$, and $|\mathbf{e}_d^* \hat{\varepsilon}_{\tau} \mathbf{e}_0|^2$ is a polarizational-structural factor. The geometric factor R_{τ} is of the form

$$R_{\tau} = \frac{1}{|b|\alpha^2 \varepsilon_0^2} \sin^2[\alpha \varkappa_0^2 L/2(\boldsymbol{\varkappa}_{\tau}\mathbf{s})], \tag{3}$$

where ε_0 is the average dielectric constant,

$$\alpha = [\tau^2 + 2(\boldsymbol{\varkappa}_0 \boldsymbol{\tau})]/2\varkappa_0^2, \quad b = (\boldsymbol{\varkappa}_0 \mathbf{s})/(\boldsymbol{\varkappa}_{\tau}\mathbf{s}),$$

$\mathbf{s}$ the normal to the crystal surface, $\boldsymbol{\tau}$ the reciprocal lattice vector, and $\boldsymbol{\varkappa}_0$ and $\boldsymbol{\varkappa}_{\tau} = \boldsymbol{\varkappa}_0 + \boldsymbol{\tau}$ the wave vectors of the incident and diffracted waves, respectively. The parameter α describes the deviation of the wave incident on the crystal from the Bragg condition, and vanishes when this condition is met. Equation (2) was obtained under the assumption that the parameter α is much less than unity for only one of the reciprocal-lattice vectors, and is of order unity for all

others. One more assumption used to obtain (2), viz., that the crystal is thin, means that

$$L^2 \ll \varkappa_0^{-4}\varepsilon_0^2 |(\varkappa_0 s)(\varkappa_\tau s)| |\mathbf{e}_d \hat{\varepsilon}_\tau \mathbf{e}_0|^{-2}$$

for any of the polarizations $\mathbf{e}_0$ and $\mathbf{e}_d$. Expression (2) reveals clearly a characteristic feature of diffraction from small crystals: the structure of the blue phase enters (via $\hat{\varepsilon}_\tau$) only in the polarizational-structural factor, while the dependence on the shape and size of the crystal and on the diffraction geometry is contained in the factor R_τ. For a plane-parallel slab this factor takes the form (3) whereas, say, for a spherical crystal or diameter D we have

$$R_\tau = \alpha^{-4}\varepsilon_0^{-2}(1+x^2/2-\cos x - x\sin x), \tag{4}$$

where $x = \alpha D \varkappa_0$. We note that when the Bragg condition is met ($\alpha = 0$) the quantity R_τ reaches a maximum value $R_\tau \sim L^2$; the angular and frequency width of the reflection is proportional to $L^{-1} \sim D^{-1}$.

For maximal exclusion of the effect of the experimental geometry, it is convenient to transform to the scattered-wave intensity I_{tot} integrated over the wavelength

$$I_{tot} = \frac{|\mathbf{e}_d^* \hat{\varepsilon}_\tau \mathbf{e}_0|^2 8\pi V I_0}{\varepsilon_0^{1/2}\lambda_B^2 \tau^2}, \tag{5}$$

where V is the volume of the blue-phase crystal. It must be emphasized that (5) contains only the total volume and this expression is valid at any crystal shape, and also if the crystal is not perfect and consists of individual slightly disoriented blocks.

After measuring I_{tot} at various polarizations $\mathbf{e}_0$ and $\mathbf{e}_d$ and at various incidence angles, all the components of the tensor $\hat{\varepsilon}_\tau$ can be determined accurate to within a common phase shift. The theory predicts that the tensor form of $\hat{\varepsilon}_\tau$ for the observed reflections is determined mainly by the so-called planar mode,[10–13] as is confirmed by experimental data.[19,20] If only a planar mode is considered, we have

$$(\hat{\varepsilon}_\tau)_{ij} = \varepsilon(\boldsymbol{\tau}, 2) m_{\tau i} m_{\tau j}, \tag{6}$$

where $\varepsilon(\boldsymbol{\tau}, 2)$ is the amplitude of the planar mode in the expansion (1), $\mathbf{m}_\tau = 2^{-1/2}(\mathbf{m}_1 - i\mathbf{m}_2)$, and the unit vectors $\mathbf{m}_1$, $\mathbf{m}_2$, and $\boldsymbol{\tau}/|\boldsymbol{\tau}|$ form a right-hand triad. In this case diffractive scattering is experienced only by light with a definite elliptic polarization $\mathbf{e}_\tau$ (with polarization-ellipse axis ratio $\sin\theta_B = \tau/2\varkappa_0$). The polarizational-structural factor for this polarization is $|\varepsilon(\boldsymbol{\tau}, 2)|^2(1+\sin^2\theta_B)^2/4$, whereas for polarized light this factor takes the form $|\varepsilon(\boldsymbol{\tau}, 2)|^2(1+\sin^2\theta_B)^2/8$. Using (2) and (5) we can calculate from the experimental data the modulus of the plane-wave amplitude.

b. Rotation of the polarization plane (dynamic effects)

The rotation of the polarization plane has been thoroughly investigated in cholesteric crystals for light propagating along the helix, i.e., at $\varkappa_0 \| \boldsymbol{\tau}$ (and exact solution of the Maxwell equations is known for this case). The problem is more complicated in blue phases, for which a set of reciprocal-lattice vectors $\boldsymbol{\tau}$ exists, and vectors $\boldsymbol{\tau}$ that are not parallel to $\varkappa_0$ can be found for any light-propagation direction. The physical cause of the strong rotation of the polarization plane in blue phases and in cholesterics is the macroscopic twisting of these structures. From a more general viewpoint[3,21] one should speak not simply of rotation of the polarization plane, but of spatial-dispersion effects in cubic blue-phase structures. In ordinary crystals these effects are small because d/λ is small, where d is the crystal-lattice period. In blue phases, d is of the order of the optical wavelengths, and spatial dispersion effects are generally speaking not small. The blue phases are therefore strictly speaking optically isotropic only in the limit as $\lambda \to \infty$.

We begin the quantitative treatment of diffractive birefringence and of the polarization-plane rotation with the case of perfect crystals. The electric-field vector $\mathbf{E}(\mathbf{r}, t)$ takes then inside the crystal the form of a Bloch wave

$$\mathbf{E}(\mathbf{r}, t) = \sum_\tau \mathbf{E}_\tau \exp[i\mathbf{k}_\tau \mathbf{r} - i\omega t], \tag{7}$$

where the summation is over all the reciprocal-lattice vectors $\boldsymbol{\tau}$.

Substituting (7) in Maxwell's equation, we obtain a set of equations that describe the interaction of the electromagnetic wave with the crystal

$$(\varkappa_0^2 - \mathbf{k}_0^2)\mathbf{E}_0 + \mathbf{k}_0(\mathbf{k}_0\mathbf{E}_0) + \frac{\omega^2}{c^2}\sum_{\tau\neq 0} \hat{\varepsilon}_{-\tau}\mathbf{E}_\tau = 0, \tag{8a}$$

$$(\varkappa_0^2 - \mathbf{k}_\tau^2)\mathbf{E}_\tau + \mathbf{k}_\tau(\mathbf{k}_\tau\mathbf{E}_\tau) + \frac{\omega^2}{c^2}\sum_{\tau'\neq\tau} \hat{\varepsilon}_{\tau-\tau'}\mathbf{E}_{\tau'} = 0. \tag{8b}$$

We confine ourselves to wave propagation outside the region of strong diffractive reflection. The amplitude $\mathbf{E}_0$ of the direct wave is then large, and the remaining amplitudes $\mathbf{E}_\tau$ are small and can be obtained from (8b) by perturbation theory:

$$\mathbf{E}_\tau = \frac{\varkappa_0^2 \hat{\varepsilon}_\tau \mathbf{E}_0 - \mathbf{k}_\tau(\mathbf{k}_\tau \hat{\varepsilon}_\tau \mathbf{E}_0)}{\varepsilon_0(\mathbf{k}_\tau^2 - \varkappa_0^2)} \tag{9}$$

($\tau \neq 0$). Substituting (9) in (8a) we find that the propagation of the wave $\mathbf{E}_0$ is described by the effective dielectric constant $\hat{\varepsilon}_{\text{eff}}$, which contains diffraction corrections, while $\hat{\varepsilon}_{\text{eff}}$ is given by

$$\hat{\varepsilon}_{eff}\mathbf{E}_0 = \varepsilon_0\mathbf{E}_0 + \sum_{\tau\neq 0} \frac{\hat{\varepsilon}_{-\tau}[\varkappa_0^2 \hat{\varepsilon}_\tau \mathbf{E}_0 - \mathbf{k}_\tau(\mathbf{k}_\tau \hat{\varepsilon}_\tau \mathbf{E}_0)]}{\varepsilon_0[\tau^2 + 2(\varkappa_0\tau)]}. \tag{10}$$

The condition for (10) to be valid is that the diffraction corrections of ε_0 be small, i.e., the second term in the right-hand side of (10) must be small compared with the first. Obviously, this condition is not met if the Bragg condition

$$\tau^2 + 2(\varkappa_0\tau) = 0$$

holds. We note that a similar method was used to calculate the diffractive increments to $\hat{\varepsilon}$ for cholesterics[22] and in the case of x rays [23,24] for ordinary crystals.

At arbitrary direction of $\varkappa_0$ the tensor $\hat{\varepsilon}_{\text{eff}}$ is not Hermitian and is asymmetric (but the condition

$$[\hat{\varepsilon}_{eff}(\varkappa_0)]_{ij} = [\hat{\varepsilon}_{eff}(-\varkappa_0)]_{ji},$$

is satisfied, as it should in the absence of a magnetic field). The polarizations of the eigenwaves are then elliptic and both gyrotropy and linear birefringence obtain. In the case of light propagation along threefold or fourfold symmetry axes

the eigenwaves are circular and there is no circular birefringence.

We derive specific expressions for the polarization-plane rotation in BPI and BPII under additional assumptions. The first is that only one planar mode contributes to each Fourier harmonic $\hat{\varepsilon}_\tau$, i.e., $\hat{\varepsilon}_\tau$ takes the form (6). Under this assumption we obtain from (10)

$$\hat{\varepsilon}_{eff}\mathbf{E}_0 = \varepsilon_0\mathbf{E}_0 + \sum_{\tau\neq 0} \frac{\varepsilon(\tau,2)\,\varepsilon(-\tau,2)\,\mathbf{m}_\tau^*(\varkappa_0^2 - |\varkappa_0\mathbf{m}_\tau|^2)(\mathbf{m}_\tau\mathbf{E}_0)}{\varepsilon_0[\tau^2 + 2(\varkappa_0\tau)]}. \tag{11}$$

Second, when comparing theory with experiment we neglect linear birefringence, since estimates in accordance with (11) show that in the region where experimental data are available the intrinsic polarizations are close to circular. Under this assumption we obtain from (11) the following expression for the specific rotation of the polarization plane:

$$\frac{\varphi}{L} = \varkappa_0\frac{\varepsilon_+ - \varepsilon_-}{4\varepsilon_0} = \sum_{\tau\neq 0}\frac{|\varepsilon(\tau,2)|^2[\varkappa_0^2\tau^2 + (\varkappa_0\tau)^2](\varkappa_0\tau)^2}{4\varepsilon_0\tau^3[\tau^4 - 4(\varkappa_0\tau)^2]}. \tag{12}$$

Equation (12) generalizes, to include the blue phase, the familiar de Vries formula for cholesterics, and becomes identical with the latter if it is assumed that $\varkappa_0 \| \tau$ and $|\tau| = 4\pi/p$, where p is the pitch of the cholesteric spiral [it is assumed in (12) and thereafter that the crystal is non-absorbing, so that $\varepsilon(-\tau,2) = \varepsilon^*(\tau,2)$].

A shortcoming of Eq. (12) as well as of the de Vries formula is that they diverge, unlike in the exact equations, when the Bragg condition is met. Actually, Eqs. (10)–(12) become invalid only in the immediate vicinity of the region of strong diffractive reflection when one of the inequalities, $|\tau^2 + 2(\varkappa_0\tau)| \lesssim \varkappa_0^2|\varepsilon(\tau,2)|$ or $|\tau^2 + 2(\varkappa_0\tau)| \lesssim \varkappa_0 L^{-1}$, holds. It is interesting to note that in the long-wave limit φ/L is of the order d^3/λ^4 and depends on the light-propagation direction, whereas the specific rotation in ordinary crystals[25] is of the order of d/λ^2 and is independent in cubic crystals of the light-propagation direction.

Let us consider actual experimental situations. Only two types of intense reflections ({100} and {110}) are observed in BPII, whereas rotation of the polarization plane was observed by us for light propagation along a fourfold axis [100] perpendicular to the sample axis. From (12) we obtain for this case

$$\frac{\varphi}{L} = \frac{\varkappa_0}{8\varepsilon_0^2\lambda'}\left[\frac{|\varepsilon(100,2)|^2}{(\lambda'^2-1)} + \frac{3|\varepsilon(110,2)|^2}{\sqrt{2}(4\lambda'^2-1)}\right], \tag{13}$$

where $\lambda' = \lambda/(2d\varepsilon_0^{1/2})$. In BPI are observed only intense reflections of the type {110}, {200}, {211} and for the experimentally investigated case of light propagation along the [110] axis we get

$$\frac{\varphi}{L} = \frac{\varkappa_0}{8\varepsilon_0^2\lambda'}\left[\frac{|\varepsilon(110,2)|^2}{(\lambda'^2-1)} + \frac{5|\varepsilon(110,2)|^2}{2(4\lambda'^2-1)} + \frac{3|\varepsilon(200,2)|^2}{2\sqrt{2}(4\lambda'^2-1)} + \frac{7|\varepsilon(211,2)|^2}{2\sqrt{3}(4\lambda'^2-1)} + \frac{4|\varepsilon(211,2)|^2}{3\sqrt{3}(9\lambda'^2-1)} + \frac{13|\varepsilon(211,2)|^2}{6\sqrt{3}(36\lambda'^2-1)}\right], \tag{14}$$

where $\lambda' = \lambda/(d(2\varepsilon_0)^{1/2})$.

c) Polycrystals

Consider the polarization-plane rotation and the wave damping on passage of the blue phase through a polycrystal. We assume for the sake of argument that these polycrystals consist of individual perfect blocks whose crystallographic axes are randomly oriented. The per-unit rotation of the polarization plane in such a polycrystalline sample can be obtained by averaging (12) over all orientations of the vector τ. This averaging yields

$$\frac{\varphi}{L} = \sum_{|\tau|\neq 0}\frac{|\varepsilon(\tau,2)|^2\varkappa_0^2 N_\tau}{16\varepsilon_0^2\tau}\left\{\frac{\tau}{4\varkappa_0}\left(1 + \frac{\tau^2}{4\varkappa_0^2}\right) \times \ln\left[\frac{\tau + 2\varkappa_0}{|\tau - 2\varkappa_0|}\right] - \frac{\tau^2}{4\varkappa_0^2} - \frac{4}{3}\right\}, \tag{15}$$

where the summation is only over τ having unequal moduli, and N_τ is the recurrence vector, i.e., the number of vectors τ with given $|\tau|$: $N_{100} = N_{200} = 6$, $N_{110} = 12$, and $N_{211} = 24$. A shortcoming of (16) is its divergence (albeit logarithmically weak) at $\varkappa_0 = \tau/2$, which results from the divergence in the initial expression (12).

To exclude this divergence, we treat the region $\varkappa_0 \approx \tau/2$ differently. We assume that the individual blocks have finite dimensions, and that the kinematic approximation considered above applied to each block. It is known[26] that the scattering-induced correction to the effective dielectric constant of the medium is proportional to the amplitude $\psi(0)$ of forward scattering by an individual scatterer (in our case, by an individual block of the polycrystal)

$$\varepsilon_{eff} = \varepsilon_0 + \frac{4\pi c^2}{v_0\omega^2}\overline{\psi(0)}, \tag{16}$$

where v_0 is the volume of one block and the bar above $\psi(0)$ denotes averaging over the orientations of the blocks, i.e., over all possible orientations of τ. Using the kinematic theory of diffraction, we can show that for spherical blocks of diameter D and for intrinsic polarization $\mathbf{e}_\tau$, the amplitude $\psi(0)$ averaged over the orientation is of the form

$$\psi(0) = \frac{|\varepsilon(\tau,2)|^2[\varkappa_0^2\tau^2 + (\varkappa_0\tau)^2]}{64\alpha^4\varkappa_0^5\tau^4\varepsilon_0^2} \times\left[1 + \frac{x^2}{2} + \frac{ix^3}{3} - (1+ix)e^{-ix}\right], \tag{17}$$

where $x = \alpha\varkappa_0 D$; for polarization perpendicular to $\mathbf{e}_\tau$ we have $\psi(0) = 0$. Obviously, after averaging over all block orientations the intrinsic polarizations can be only circular, since there are no preferred directions. Projecting the polarization $\mathbf{e}_\tau$ on the circular polarization and averaging $\psi(0)$ over all orientations of the vectors τ, we obtain the following expressions for the per-unit rotation of the polarization plane [from the real parts of (16) and (17)] and for the transmission coefficients $I_\pm$ of the waves with circular polarizations [from the imaginary parts of (16) and (17)]:

$$\frac{\varphi}{L} = \frac{3\varkappa_0^2 D}{32\varepsilon_0^2}\sum_{|\tau|\neq 0} N_\tau|\varepsilon(\tau,2)|^2\int_{-1}^{1}\left(\sin x - x\cos x - \frac{x^3}{3}\right) \times(1+y^2)\frac{y}{x^4}\,dy, \tag{18}$$

$$I_\pm = \exp\left[-\frac{3\varkappa_0^2 DL}{16\varepsilon_0^2}\sum_{|\tau|\neq 0} N_\tau|\varepsilon(\tau,2)|^2\right.$$

$$\times\int_{-1}^{1}\left(1-\cos x-x\sin x+\frac{x^2}{2}\right)$$
$$\times(1+y^2)\frac{(1\pm y)^2}{x^4}\,dy\Big],\qquad(19)$$

where $x=\tau D(y+\tau/2\varkappa_0)$. Expression (18), in contrast to (15), does not result in divergence at $\varkappa_0=\tau/2$ and is close to (15) at $|\varkappa_0-\tau/2|\gg D^{-1}$.

V. BLUE-PHASE STRUCTURE IN THE LANDAU THEORY

Phase transitions between an isotropic liquid, blue phases, and cholesterics were treated by the Landau theory in a number of papers[10–13] (see also the review[3]). We omit therefore all the calculation details, describe only the general scheme, and present the results in a form convenient for comparison with experiment.

The order parameter usually chosen for the considered phase transitions is the zero-trace part $\varepsilon(\boldsymbol{\tau})$ of the dielectric tensor. The expansion of the free energy in powers of the order parameter and of its derivatives is of the form[10–13]

$$F=F_2\{\hat{\varepsilon}\}+F_3\{\hat{\varepsilon}\}+F_4\{\hat{\varepsilon}\},\qquad(20)$$

where

$$F_2=\frac{1}{2V}\int dr\left\{a\,\mathrm{Sp}(\hat{\varepsilon}^2)+c_1\left(\frac{\partial\varepsilon_{ij}}{\partial x_k}\right)^2+c_2\left(\frac{\partial\varepsilon_{ij}}{\partial x_i}\right)^2+2c_1q_ce_{ijk}\varepsilon_{il}\frac{\partial\varepsilon_{jl}}{\partial x_k}\right\},\qquad(21)$$

$$F_3=\frac{\beta}{V}\int dr\,\mathrm{Sp}(\hat{\varepsilon}^3),\qquad(22)$$

$$F_4=\frac{\gamma}{V}\int dr[\mathrm{Sp}(\varepsilon^2)]^2.\qquad(23)$$

As is customary in the Landau theory, it is assumed that only the coefficient $a=a_1(T-T_c)$ depends on the temperature, but not the coefficients c_1, c_2, q_c, β, and γ. At each temperature there is realized a structure that ensures a minimum of F. Since the absolute minimum of (20) cannot be found in the general case, we shall compare the free energies of the isotropic phase ($F_I=0$), of the cholesteric phase (F_{ch}), and of several cubic phases. We use for these phases the Fourier expansion (1) of the tensor order parameter and assume, in accordance with the experimental data, that only a planar mode contributes to each $\hat{\varepsilon}_\tau$ in (1) (this mode ensures a minimum of the quadratic part of $F_2\{\hat{\varepsilon}\}$,[10–13]) i.e., the tensor $\hat{\varepsilon}$ is given by (6). The scalar quantities $\varepsilon(\boldsymbol{\tau},2)$ in (6) can be regarded as components of the order parameter, and our problem is to find those $\varepsilon(\boldsymbol{\tau},2)$ that ensure a minimum of the free energy (20). These quantities, however, are not independent, since the cubic symmetry imposes constraints on the form of $\hat{\varepsilon}(\mathbf{r})$ and by the same token interrelates all the $\varepsilon(\boldsymbol{\tau},2)$ for the equivalent $\boldsymbol{\tau}$ (Ref. 17), (i.e., those $\boldsymbol{\tau}$ that go over into one another under the symmetry operations in the space group Φ of the crystal).

a) Possible symmetry groups

We consider the least symmetric cubic groups T^1–$P23$ and T^4–$P2_13$, and take into account in (1) the harmonics $\hat{\varepsilon}_\tau$ right up to $\boldsymbol{\tau}=(220)$. In this case one can choose as the independent components the quantities $\varepsilon(100,2)$, $\varepsilon(110,2)$, $\varepsilon(200,2)$, $\varepsilon(210,2)$, $\varepsilon(120,2)$, $\mathrm{Re}[\varepsilon(211,2)]$, $\mathrm{Im}[\varepsilon(211,2]$, and $\varepsilon(220,2)$. All these $\varepsilon(\boldsymbol{\tau},2)$ are real, with the exception of $\varepsilon(211,2)$ and ($\varepsilon(100,2)=0$ in the T^4 group from symmetry considerations). Expressing all the remaining $\varepsilon(\boldsymbol{\tau},2)$ in terms of the ones listed above, we obtain an expression for $\hat{\varepsilon}(\mathbf{r})$, and by substituting $\hat{\varepsilon}(\mathbf{r})$ in (20) and integrating we obtain F for T^1 and T^4 in the form of fourth-degree polynomials of the independent $\varepsilon(\boldsymbol{\tau},2)$. Of course, most coefficients in these polynomials (on the order of one hundred in our case) can be obtained only by numerically summing the contributions from the different powers of $\varepsilon(\boldsymbol{\tau},2)$ (these coefficients can be calculated also analytically in the case of one or two harmonics[12,13]).

To determine the structure of a blue phase and its temperature dependence, the polynomials obtained were numerically minimized with respect to $\varepsilon(\boldsymbol{\tau},2)$ and with respect to the lattice period. It was found as a result of this minimization that the free energy has [as a function of $\varepsilon(\boldsymbol{\tau},2)$] several local minima. We confine ourselves to three of these minima, which minimize the free energy. At one of these minima we obtain for the T^1 group $\varepsilon(10,2)=\varepsilon(200,2)=\varepsilon(210,2)=\varepsilon(120,2)=\mathrm{Im}[\varepsilon(211,2)]=0$, i.e., there is realized in fact a structure that is more symmetric than T^1, with symmetry O^5–1432. In this structure $|\varepsilon(110,2)|$ is much larger than $|\varepsilon(212,2)|$ and $|\varepsilon(220,2)|$. For the second minimum in group T^1 we obtain $\varepsilon(210,2)=\varepsilon(120,2)$; $\varepsilon(200,2)=\mathrm{Im}[\varepsilon(211,2)]=0$, i.e., a structure with symmetry O^2–$P4_232$ is realized. In this structure $|\varepsilon(100,2)]$ and $|\varepsilon(110,2)|$ are much larger than $|\varepsilon(210)|$, $|\varepsilon(211,2)|$ and $|\varepsilon(220,2)|$. The third of the minima considered is realized in group T^4, and in it $|\varepsilon(210,2)=\varepsilon(120,2)=\mathrm{Im}[\varepsilon(211,2)]=0$, i.e., a group with symmetry O^8–14_132 is obtained. In this structure $|\varepsilon(220,2)|$ is small compared with $|\varepsilon(110,2)|$, $|\varepsilon(200,2)|$ and $|\varepsilon(211,2)|$. We note that unlike in Refs. 12 and 13, we take into account a larger number of $\varepsilon(\boldsymbol{\tau},2)$ harmonics, and the structures O^2, O^5, and O^8 are obtained as a particular case from the less symmetric structures T^1 and T^4.

The temperature dependence of the free energy F at these three minima is such that the O^5 structure turns out to be expedient only in a narrow region near the transition into the isotropic phase. It appears that no blue phase with this structure has yet been observed in experiment, and the feasibility of its realization will be discussed later on. At lower temperature, the free-energy minimum corresponds to an O^2 structure or to a cholesteric structure (the calculated phase diagram is given in Ref. 3). In a wide range of the parameters contained in F, the difference between the free energies of the structure O^2 and the competing O^8 amounts to only several percent. Clearly, the expounded approximate theory cannot claim such an accuracy, and it is not excluded that in a more detailed theory a transition between the O^2 and O^8 will become possible. The experimentally observed blue phases BPII and BPI have apparently respective symmetries O^2 and O^8, and a phase transition between them is possible.

b) Temperature dependence of the order parameter

Let us consider in greater detail the temperature dependence of the order parameter for the structures O^2 and O^8. Numerical calculations reveal two remarkable properties of these structures: first, in both structures several order-parameter components ($\varepsilon(100,2)$ and $\varepsilon(110,2)$ in O^2 and $\varepsilon(110,2)$, $\varepsilon(200,2)$ and $\varepsilon(211,2)$ in O^8) are found to be much larger than the others; second, the ratio of these large components turns out to be almost independent of temperature and of other parameters contained in the free energy (20). These two circumstances, confirmed by experimental data,[6] permit the following simplifications of the description of the blue-phase structure: first, we can omit all the weak Fourier components, and second, we can fix in the theory the ratio of the large components, i.e., write them in the form

$$\varepsilon(\tau,\ 2)=\varepsilon A_\tau, \tag{24}$$

where the factor ε (we shall call it the scalar order parameter), which is the same for all τ, contains the dependence on the temperature and on the other parameters that enter in the free energy, while A_τ are simply numbers (they are given below) which we shall regard as independent of the parameters that enter in the free energy. The blue-phase dielectric tensor takes in this approximation the form

$$\hat{\varepsilon}^\Phi(\mathbf{r})=\varepsilon\hat{Q}^\Phi(\mathbf{r}), \tag{25}$$

where $\Phi = O^2, O^5, O^8$, and the tensor $\hat{Q}^\Phi(\mathbf{r})$ determines the spatial structure of the dielectric constant in a form that depends in this approximation neither on the temperature nor on other parameters, and is in this sense universal. All the components of the tensor $\hat{Q}^\Phi(\mathbf{r})$ are expressed in terms of A and of trigonometric functions of the coordinates x, y, and z (Refs. 3, 12, 13): the corresponding formulas are obtained from pure symmetry considerations. It is interesting to note that (25) is similar in form to the corresponding relation for nematics

$$\hat{\varepsilon}^N=\varepsilon_a\hat{Q}^N, \tag{26}$$

where $Q^N_{ij} = (n_i n_j - 1/3\delta_{ij})$, $\mathbf{n}$ is the director, and ε_a is the anisotropy of the dielectric constant and depends on the temperature and on other parameters of the nematic.

The temperature dependence of the tensor order parameter of the blue phases is thus expressed in terms of the temperature dependence of the scalar order parameter ε. To calculate $\varepsilon(T)$ we specify actual values of A_τ obtained by minimizing F for some characteristic values of the parameters. Generally speaking, if F takes the form (20), then A_τ is a function of two dimensionless parameters t and k, defined as $t = 12a\gamma/\beta^2$ and $k = q_c(12c_1\gamma/\beta^2)^{1/2}$. As emphasized above, however, the dependence of A_τ on t and k is exceedingly weak, and we use therefore the values of A_τ obtained at $t = k = 1$:

$$\begin{aligned}&\text{for } O^2:\ A_{100}=0{,}291,\ A_{110}=0{,}115,\\&\text{for } O^5:\ A_{110}=0.236,\\&\text{for } O^8:\ A_{110}=0.175,\ A_{200}=0{,}187,\ A_{211}=0{,}0615,\\&\text{for a cholesteric: } A_{ch}=0{,}51.\end{aligned} \tag{27}$$

The numbers A_τ were determined accurate to a constant normalization factor chosen in (27) such that $\overline{\mathrm{Sp}[(\hat{Q}^\Phi)^2]} = 2/3$, by analogy with nematics, where $\mathrm{Sp}[(\hat{Q}^N)^2] = 2/3$; the superior bar denotes averaging over the volume of the unit cell. Using the foregoing values of A_τ, we obtain for the free energy of the blue phases the expression

$$F_\Phi={}^1/_3(a-C_\Phi c_1 q_c^2)\varepsilon^2-{}^2/_9B_\Phi\beta\varepsilon^3+{}^4/_9\Gamma_\Phi\gamma\varepsilon^4, \tag{28}$$

where $\Phi = O^2$, O^5, O^8; for the phase O^2: $C_{o^2} = 0{,}975$, $B_{o^2} = 1{,}031$, $\Gamma_{o^2} = 1{,}164$; for the phase O^5: $C_{o^5} = 0{,}997$, $B_{o^5} = 1{,}124$, $\Gamma_{o^5} = 1{,}214$; for the phase O^8: $C_{o^8} = 0{,}953$, $B_{o^8} = 1{,}017$, $\Gamma_{o^8} = 1{,}132$.

Minimizing (28) with respect to ε we find that the transition from the isotropic liquid to the blue phase occurs at

$$T_{I\Phi}=T_c+B_\Phi^2\beta^2/12a_1\gamma\Gamma_\Phi+C_\Phi c_1 q_c^2/a_1. \tag{29}$$

At $T\leqslant Y_{I\Phi}$ the temperature dependence of ε is given by

$$\varepsilon=\frac{3\beta B_\Phi+[\beta^2B_\Phi^2+96\gamma\Gamma_\Phi a_1(T_{I\Phi}-T)]^{1/2}}{16\gamma\Gamma_\Phi} \tag{30}$$

and takes the form typical of the temperature dependence of the order parameter in the Landau theory, particularly for the order parameter S of a nematic (the expressions for a nematic are obtained from (20)–(30) at $q_c = 0$ and $B_\Phi = \Gamma_\Phi = 1$). It follows from (30) that at equal temperatures the value of ε is practically the same for all blue phases, owing to the close values of the coefficients C_Φ, B_Φ, and Γ_Φ.

VI. DISCUSSION

The foregoing theoretical formulas relate uniquely the experimentally observed values with the structure of the order-parameter field. We shall show here that these equations do indeed describe quantitatively the optical properties of the blue phases, so that the Fourier harmonics $\hat{\varepsilon}_\tau$ and their temperature dependences can be determined. The calculations of the space groups possible for blue phases, carried out in Refs. 12 and 13 and in the present paper, predict structures with groups O^2, O^5, and O^8 for the blue phases. According to experimental data,[4–6] the BPI of cholestryl ionanoate corresponds to group O^8, BPII to O^2, and there is no agreement concerning to BPIII structure. The fact that light of one circular polarization is predominantly scattered in BPIII, and that this scattering is frequency-dependent,[15] suggests that in BPIII there is manifested mainly one Fourier harmonic ε_τ with $|\tau|$ somewhat smaller than in a cholesteric, and the main contribution to it is made by the planar mode. We shall assume therefore that BPIII is a polycrystal whose individual crystallites have the structure O^5. Figure 2 shows the reflection positions calculated for the O^2, O^5, and O^8 groups and it can be seen that they are closest to BPII, BPIII, and BPI, respectively. Some disparity between the theoretical and experimental results, particularly the observed variation of the period with temperature, can be attributed to failure to take enough Fourier harmonics into account in the theory (especially in O^8).

Since the ratios of the $|\varepsilon(\tau, 2)|$ have been found by Kizel' and Prokhorov[6] to be approximately constant, each $|\varepsilon(\tau, 2)|$ can be determined from any other. Following Ref.

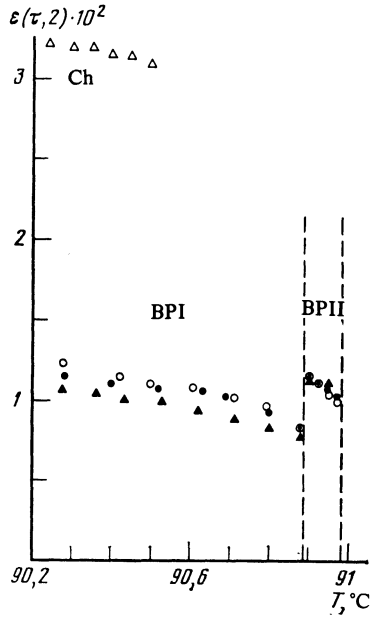

FIG. 5. Temperature dependence of the order-parameter Fourier harmonics $\varepsilon(\tau, 2)$, determined for the cholesteric, BPI, and BPII from the following data: △—rotation of the light-polarization plane in an oriented cholesteric sample; ▲—integrated intensity of the reflections of the BPI and BPII transmission spectra; ○—polarization-plane rotation at $\lambda = 633$ nm in BPI and BPIII single crystals; ●—the same for BPI and BPII polycrystals.

6, we used the ratios $\varepsilon^2(110,2)$: $\varepsilon^2(200,2)$: $\varepsilon^2(211,2) = 1:1:0{,}1$, for BPI and $\varepsilon^2(100,2)$: $\varepsilon^2(110,2) = 1:0{,}15$ for BPII.

Our experimental data and theoretical expressions permit the modulus of the Fourier harmonics to be determined by several methods. Using Eq. (5), we determined $|\varepsilon(\tau, 2)|$ for the longest-wavelength reflection from its integrated intensity (Fig. 5). The same figure shows the values of $|\varepsilon(\tau, 2)|$ obtained from data on the polarization-plane rotation at the He–Ne laser wavelength in blue-phase polycrystals and single crystals [see (12)–(15)]. The harmonics taken into account in the BPI calculations were (110) and (200), since the contribution of (211) at this wavelength is less than 2%. In BPII we took into account the harmonic (100), the contribution of (110) being likewise 2%. The values of $\varepsilon(\tau, 2)$ shown in Fig. 5, determined from various experiments, agree within $\pm 6\%$. The ratios of the moduli of the first harmonics at the transition points[6] agree within the indicated accuracy with our data. The values of $\varepsilon(\tau, 2)$ obtained in Ref. 9 for the BPI phase are somewhat higher than in our case, apparently because the mixture used in Ref. 9 has a higher dielectric anisotropy.

Knowing $\varepsilon(\tau, 2)$ we can determine from (2), (13)–(15), and (18) the transmission-spectrum line shape and the optical-activity dispersion spectrum for polycrystals and single crystals. The dashed lines in Fig. 1 show the transmission curves plotted in the kinematic approximation for thicknesses $L = 10$ and $20\,\mu$m. The dynamic effects are negligible for $L = 10\ \mu$m, and underestimate the theoretical curve by 5% for $L = 20\,\mu$m. The kinematic theory describes the experimental curves satisfactorily, as can be seen from Fig. 1. The experimental curve is somewhat broader than the

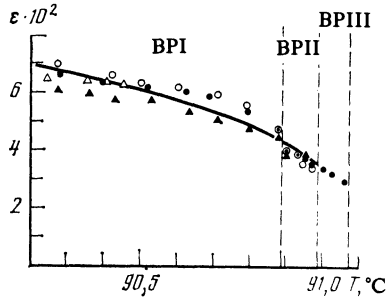

FIG. 6. Temperature dependence of the scalar order parameter $\varepsilon(T)$. The experimental points are designated in Fig. 5. Solid curve—theoretical dependence.

theoretical, probably owing to imperfection of the samples.

The solid lines of Fig. 4 show the theoretical optical activity dispersion spectra obtained at the values of $\varepsilon(\tau, 2)$ taken from Fig. 5 at the corresponding temperature. The theoretical curves describe well enough the experimental data for both single-crystal and polycrystalline samples; some discrepancy near the reflections can be due to the finite sizes of the blocks in the polycrystal. The temperature dependences of the Fourier-harmonic moduli can be described with the aid of the function $\varepsilon(T)$, which is determined from the experimental values of $\varepsilon(\tau, 2)$ and the theoretical coefficients A_τ in (27). The values of $\varepsilon(T)$ recalculated for BPI, BPII, and the cholesteric are shown in Fig. 6. The same figure shows, for the BPIII temperature region, the values of $\varepsilon(T)$ obtained from $\varepsilon(\tau, 2)$ for BPIII under the condition that the latter has the symmetry group O^5 (since the values of the coefficients B_Φ, C_Φ, and Γ_Φ for the groups O^2 and O^8 are close, so that the temperatures of their transitions to anisotropic liquid and the $\varepsilon(T)$ temperature dependence differ insignificantly in the theory). A single theoretical plot of Eq. (30), with variable parameters $\beta B_\Phi/\gamma\Gamma_\Phi$, $a_1/\gamma\Gamma\Phi$ and $T_c = 91.0$ °C, was drawn by least squares in Fig. 6 through the points $\varepsilon(T)$ obtained for BPI and BPII. The ratios for this curve are $\beta/\gamma = 0.167$ and $a_1/\gamma = 0.0063$. When extrapolated to the BPIII region this curve agrees well with the experimental points. The agreement between the theoretical curve and the experimental data illustrates the possibility of describing the temperature dependence of the order parameter for all blue phases by a single function (30), similar to the function that describes in the Landau theory the order parameter in nematics. Using the obtained values of β/γ and a_1/γ and the estimates of the parameters a_1 and c_1 in (29) from Ref. 27, we get estimates for the parameter $k \approx 1.3$ and for the Frank modulus $K = c_1\varepsilon^2 \approx 10^{-7}$. We note also that estimates of the enthalpies ΔH of the transitions ΔH BPI →BPII, BPII→BPIII, and BPIII→ isotropic liquid in accord with the formula $\Delta H = a_1 T\Delta(\varepsilon^2)$ show that ΔH is a maximum for the transition from an isotropic liquid to a blue phase, in agreement with directly measured[1] ΔH.

VII. CONCLUSION

Blue phases are perhaps the only objects for which measurements of optical activity yield specific information on the phase structure. For example, comparison of the data on the light-polarization plane near corresponding reflections

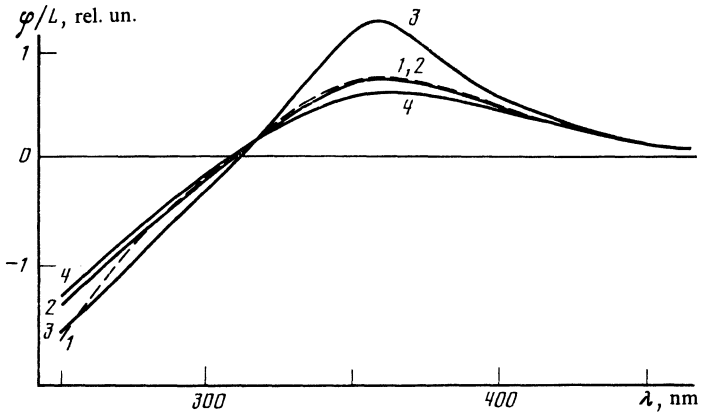

FIG. 7. Measured[14] and calculated [from (18)] optical activity of BPIII for cholesteryl nonionate: 1) experiment; 3, 3, 4) calculation for crystallites measuring 0.6, 1.2, and 0.5 μm, respectively.

from polycrystals and single crystals makes it possible to determine the recurrence index and hence distinguish between a bcc and a simple cubic lattice. In conjunction with other measurements, this simplifies considerably the identification of the symmetry group of a phase. Our data favor the groups O^8 for BPI and O^2 for BPII. Nothing can be said concerning BPIII by this method, since the transmission spectra show that the BPIII samples are not single crystals. It was shown above that the observed optical properties of BPIII phase and temperature dependence of its order parameter can be satisfactorily described by assuming this phase to consist of randomly oriented crystallites with the O^5 structure predicted by the Landau theory. Under this assumption it is also possible, using the described theory of optical properties [see Eq. (18)] and assuming that the crystallites measure about 1 μm, to describe quantitatively Collings's experimental data[14] on the optical activity of BPIII (Fig. 7). It must be emphasized, however, that other BPIII models are also possible, and that this phase calls for further study.

The agreement obtained between the $\varepsilon(\tau, 2)$ harmonic amplitudes obtained from various optical experiments, and the good agreement between the theory and the optical-activity dispersion curves based on the employed harmonics $\hat{\varepsilon}_\tau$, indicate that the theory of the optical properties agrees with experiment qualitatively and quantitatively, and that the correct values of $\varepsilon(\tau, 2)$ have thus been obtained. On the other hand, the employed variant of the Landau phase-transition theory, based on allowance for only planar modes, together with the correct prediction of the values of the various harmonics and of their temperature dependences, differs slightly from the experimental spectral positions of the reflections. In addition, this variant of the Landau theory does not describe satisfactorily the phase diagram and, in particular, does not predict the transition between the O^2 and O^8 structures. It is not clear whether these discrepancies can be eliminated within the framework of the Landau theory, or whether a qualitatively new approach must be used to achieve further progress.

An important conclusion of the treatment of blue phases in the Landau-theory approach and from the available experimental data is that the tensor form of the blue-phase structures BPI and BPII is almost independent of the temperature and of the pitch of the helix in a wide range of these parameters. The temperature dependence enters only in the scalar order parameter ε [see (24) and (30)] that determines the spatial modulation depth of the tensor order parameter, while the pitch of the helix influences only the temperatures of the transitions from the isotropic liquid to the blue phase and from the blue phase to the cholesteric. Clearly, the proposed approximate description of the blue-phase structure indicates that the problem contains some small parameter whose physical meaning has not yet been established. This small parameter is possibly the ratio of the volume in which the order parameter $\varepsilon(\mathbf{r})$ is essentially biaxial ("disclination" volume) to the total volume of the crystal (according to Ref. 3 this ratio is about 3%). It must be emphasized, however, that the experimentally observed changes in the relative value of the Fourier harmonics[6] and the temperature dependence of the lattice period (see Fig. 2) offer evidence that the tensor form of the order parameter is not quite universal, and it would be of interest to identify theoretically and experimentally just the Fourier-harmonics components with which these changes are connected. Nonetheless, the concept of an almost constant tensor form of the blue-phase modification can be a quite useful initial approximation (for example, for the understanding of such phenomena as the presence of shear moduli and fluctuations, or of the influence of the external field).

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