Optics of the blue phase of cholesteric liquid crystals

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A theory is developed for the optical properties of the blue phases of cholesteric liquid crystals, with account taken of the symmetry restrictions on their experimentally determined structures. The diffraction features of the optics of blue phases (possible reflections and their polarization properties) are found for all the admissible structures, and their optical properties are analytically described within the framework of the dynamic theory. The experimental data are analyzed. The limitations on the blue phase and on the details of these structures, which follow from the experimental data, are indicated. The importance of optical and particularly polarization measurements for the unambiguous determination of the blue-phase structures are noted, as are the possibilities of using the effects of multiple scattering to extract quantitatively more exact structural information.

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Historically, the blue phase of cholesterics was the first of the liquid-crystal phases observed by the very discoverer of liquid crystal, Reinitzer.[1] Although almost a century has elapsed already, the blue phase remains an intriguing object of research, since the nature of this surprisingly complex and delicately organized liquid-crystal state is still unclear. However, the substantial progress reached in the experimental and theoretical investigations of the blue phase during the last several years (see the reviews[1,2]) gives grounds for assuming that the presently evolving notions concerning the blue phase are in accord with its nature, and the solution of the blue-phase problem is expected in the nearest future. This solution, however, calls for research in accordance with a program that has already been formulated, and the result of this research will be the choice from among the quite numerous models proposed so far for the blue phase.[3–11] It must be noted here that although the main hope is placed here on optical research methods, the theory of the optical properties of the blue phase is still in the initial stage of its development.

In this article we develop for the optics of the blue phase a systematic description that connects the features of its optical properties with its structure. The starting points are reliably established experimental facts, namely the optical scattering and the presence of selective scattering and gyrotropy of the blue phase. The symmetry limitations on the structural characteristics of the blue phase, which are introduced in accordance with the foregoing properties, while allowing us to exclude from consideration a large number of structures, still do not permit an unequivocal choice from among the remaining possibilities. For this choice, as shown below, it is necessary to compare the observed characteristics (frequencies and frequency intervals of the selective scattering, as well as its polarization characteristics) with the corresponding quantities obtained theoretically for each of the possible type of blue-phase structure. The results of this paper make just such a comparison possible. In particular, they establish the symmetry restrictions on the dielectric tensor $\hat{\varepsilon}(\mathbf{r})$ of the blue phase and the connection between these restrictions and the characteristics of the selective scattering. Particular emphasis is placed on the exceeding importance of polarization measurements for a complete determination of the blue-phase structure.

OBSERVABLE PROPERTIES AND MODELS OF THE BLUE PHASE

The blue phase is observed for certain cholesterics in a narrow temperature interval, on the order of fractions of a degree or one degree, between the isotropic liquid and the usual cholesteric phase. Investigations by various physical methods show that the blue phase is in a thermodynamically stable state. Moreover, in this narrow temperature interval one can observe in different compounds not one but several (up to three) modifications of the blue phase. The transitions between these phases, as well as the transition between the blue and the cholesteric phases, are of first order, as is evidenced by the possibility of supercooling these phases. A possible exception may sometimes be the transition from an anisotropic liquid to the blue phase.

Without dwelling in detail on the description of all the investigated properties of the blue phase (see Ref. 1), we confine ourselves hereafter to consideration of only its unusual optical properties. 1) The blue phase scatters visible light selectively, so that this phase has therefore a bluish color, which accounts for its name. In contrast to cholesterics, where only the first order of the selective scattering is strong, several reflections of comparable strength are observed. Only light of definite circular polarization, the same as in the cholesteric, undergoes selective backward reflection. 2) The blue phase exhibits strong optical gyrotropy, and the rotation of the plane of polarization reverses sign at the frequency of the selective reflection. 3) There is no birefringence, i.e., the blue phase is optically isotropic.

On the basis of the optical isotropy, Saupe has proposed as long ago as in 1969 that a cubic lattice of point defects is produced in the blue phase in the field of the director (i.e., a three dimensional lattice of points with indeterminate direction of the director).[3] Also proposed was a conical-helix model, with the director inclined 54.74° to the optical axis,[8] which ensures optical isotropy of the structure. Brazovskiĭ and Dmitriev, on the basis of the Landau theory of phase transitions, predicted a hexagonal structure of the field of the order parameter in the blue phase.[6,7] In recent optical measurements of various selective-scattering reflections, a cubic symmetry with primitive or body-centered unit cell was ascribed to the structure of the blue phase.[12,13]

Developing further the approach of Ref. 7, Hornreich and Strikman also arrived, within the framework of the Landau theory, at the conclusion that the blue phase has cubic symmetry.[2,10] A cubic lattice of linear disclinations in the director field was proposed for the blue phase within the framework of a continual analysis with allowance for the customarily omitted surface terms of the free energy.

It can be seen thus that quite a number of structures that agree with the known experimental facts, or at least with the principal ones, have been proposed for the blue phase. For an unambiguous description of the structure (more accurately, structures of the blue phases) it is therefore necessary to analyze and indicate the factors on the basis of which, using the already available experimental material, it is possible to give preference to one of the considered possibilities. If, however, it is impossible to arrive at an unambiguous conclusion on the basis of the available data, it is desirable to point out measurements capable of eliminating the remaining ambiguity. In the sections that follow we propose a method for realizing this program on the basis of optical measurements.

DIELECTRIC TENSOR OF THE BLUE PHASE

To describe the optical properties of the blue phase it is necessary to solve Maxwell's equations, which reduce to the following equation for the electric-field vector $\mathbf{E}(\mathbf{r},t)$

$$\hat{\varepsilon}(\mathbf{r})\,\partial^2\mathbf{E}/\partial t^2=-c^2\,\mathrm{rot\,rot}\,\mathbf{E}, \tag{1}$$

where $\hat{\varepsilon}(\mathbf{r})$ is the dielectric tensor.

Since the entire optical information on the blue phase is contained in the dielectric tensor $\hat{\varepsilon}(\mathbf{r})$, the question of describing its optical properties or of extracting information concerning this constant from optical data involves in final analysis an explicit expression for $\hat{\varepsilon}(\mathbf{r})$. Since the structure of the blue phase, and by the same token also the tensor $\hat{\varepsilon}(\mathbf{r})$, has not yet been established, we shall not make any concrete assumptions concerning the form of $\hat{\varepsilon}(\mathbf{r})$, but consider the restrictions imposed on the dielectric tensor by the established experimental facts. This is done most conveniently by representing $\hat{\varepsilon}(\mathbf{r})$ as a Fourier series

$$\hat{\varepsilon}(\mathbf{r})=\sum_{\boldsymbol{\tau}}\hat{\varepsilon}_{\boldsymbol{\tau}}e^{i\boldsymbol{\tau}\mathbf{r}}, \tag{2}$$

where $\boldsymbol{\tau}$ is the reciprocal-lattice vector of the blue phase.

Using now the known optical properties, we can impose certain restrictions on the coefficients of the Fourier expansion (2). 1) The presence of selective scattering (with several reflections) indicates that the expansion (2), unlike for a cholesteric, has more than three nonzero terms. We recall that in a cholesteric $\hat{\varepsilon}_{\boldsymbol{\tau}}\neq 0$ only at $\boldsymbol{\tau}=0$ and $\boldsymbol{\tau}=\pm 4\pi/p$, where p is the pitch of the cholesteric helix. The selective-scattering polarization properties known for the investigated reflections impose definite restrictions on the form of the corresponding tensor Fourier coefficients $\hat{\varepsilon}_{\boldsymbol{\tau}}$. They will be analyzed later. 2) The presence of optical activity and the reversal of its sign at the selective-scattering frequency give ground for assuming that the optical activity of the blue phase, just as that of cholesterics,[14] is due to its structural properties. Therefore, at least in first-order approximations, we can disregard in $\hat{\varepsilon}$ the molecular gyrotropy proper. 3) The absence of birefringence means that the zeroth harmonic $\hat{\varepsilon}_0$ is proportional to the unit tensor.

In accordance with the discussion above and with the experimental results, we shall assume that the blue phase has a cubic structure and that its tensor $\hat{\varepsilon}(\mathbf{r})$ is given by

$$\hat{\varepsilon}(\mathbf{r})=\hat{\varepsilon}_0+\hat{\varepsilon}^a(x,y,z), \tag{3}$$

where $\hat{\varepsilon}_0$ is the average dielectric constant and $\varepsilon^a_{ik}(x,y,z)$ is the three-dimensionally periodic part of the tensor $\hat{\varepsilon}(\mathbf{r})$. We shall disregard the possible periodic variation of the crystal density, the absorption of light, and the natural gyrotropy (since these effects are small), and assume therefore that the tensor $\hat{\varepsilon}^a(\mathbf{r})$ has a zero trace, is real, and is symmetrical. In crystal optics a crystal is usually regarded as homogeneous, since the wavelength of the light is much larger than the crystal-lattice period. In this case an important role is played only by the homogeneous part of the dielectric tensor $\hat{\varepsilon}_0$, whose symmetry is well known from optics and is determined by the point group of the crystal.

In the case of cubic structures, to which we confine ourselves hereafter, $\hat{\varepsilon}_0$, which coincides with the zeroth harmonic in (2), is proportional in accordance with the assumption made to the unit tensor. The axes x, y, and z in (3) will be assumed parallel to the faces of the cubic unit cell, and the origin will be chosen to lie on the threefold axis. For more details on the choice of the coordinate frame in cubic lattices see Refs. 15 and 16. We note that the tensor $\hat{\varepsilon}^a(\mathbf{r})$ plays in this case also the role of the order parameter.[2] In the blue phase, the lattice period is comparable with the wavelength of the light, and we must take into account the inhomogeneous part of $\hat{\varepsilon}^a(\mathbf{r})$, whose local symmetry need not necessarily be cubic, is different at different points of the unit cell, and is restricted by the space group of the crystal. We shall use these symmetry restrictions below to establish the most general form of $\hat{\varepsilon}^a(\mathbf{r})$ allowed by the concrete cubic space groups that can be used to describe the structure of the blue phase. In view of the chirality of the blue phase, the analysis is restricted to space groups in which there is no inversion center (i.e., to enantiomorphic groups).

It is clear that the tensor $\hat{\varepsilon}^a(\mathbf{r})$ must remain unchanged under all symmetry transformations g (rotations and (or) translations) that enter in the space group Φ of the crystal (reflections are excluded, since the crystal consists of chiral molecules). In the case of a symmetry transformation g, the arbitrary tensor $\hat{\alpha}(\mathbf{r})$ is transformed into a tensor $\hat{\alpha}_g(\mathbf{r})$ in accordance with the rule

$$\hat{\alpha}_g=\hat{R}_g\hat{\alpha}(\mathbf{r}')\hat{R}_g^{-1}, \tag{4}$$

where $\mathbf{r}'=\hat{R}_g(\mathbf{r}-\mathbf{a}_g)$, $\mathbf{a}_g$ is the translation vector, and $\hat{R}_g$ is the rotation matrix that enters in the transformation g (the matrices $\hat{R}_g$ for cubic space groups are given in Ref. 17). The invariance of $\hat{\varepsilon}^a(\mathbf{r})$ under the transformations $g\in\Phi$ denotes that the following relations should hold for $\hat{\varepsilon}^a(\mathbf{r})$

$$\hat{\varepsilon}^a(\mathbf{r})=\hat{R}_g\hat{\varepsilon}^a(\mathbf{r}')\hat{R}_g^{-1}. \tag{5}$$

The most general form of the tensor $\hat{\varepsilon}^a(\mathbf{r})$ that might satisfy the relation (5) can be directly obtained with the aid of the following averaging of the arbitrary tensor $\alpha(\mathbf{r})$ over the group Φ (Refs. 18 and 19):

$$\hat{\varepsilon}^a(\mathbf{r})=\langle\hat{\alpha}(\mathbf{r})\rangle_\Phi\equiv\frac{1}{N}\sum_{g\in\Phi}\alpha_g(\mathbf{r}), \tag{6}$$

where $\hat{\alpha}_g(\mathbf{r})$ is given by relation (4), N is the number of elements in the group Φ, and the tensor $\alpha(\mathbf{r})$ is assumed to be symmetrical. Obviously, the performance of any operation $g_i\in\Phi$ on the tensor $\hat{\varepsilon}^a(\mathbf{r})$ in the form (6) leads only to a permutation of the terms in the sum in the right-hand side of (5) and does not change this sum. Consequently, the tensor $\hat{\varepsilon}^a(\mathbf{r})$ obtained from (6) is invariant to any transformation that enters in the space group of the crystal. It is more convenient to regard the tensor $\hat{\alpha}(\mathbf{r})$ from the outset as periodic in all the variables, and then we need retain in the sum (6) only those g which either do not contain translations (point symmetry operations) or contain translations smaller than the lattice period. The number of these operations is finite and the averaging over them is easy.

It is easily seen that for cubic structures the presence of a three-fold axis aligned with a body diagonal of the cube greatly restricts the form of $\varepsilon^a(\mathbf{r})$. Let

$$\varepsilon_{xx}{}^a=f(x,y,z),\quad \varepsilon_{xy}{}^a=\varphi(x,y,z),$$

where $f(x,y,z)$ and $\varphi(x,y,z)$ are arbitrary periodic functions. Then, as can be easily seen from (5) and (6), the presence of a threefold axis makes it possible to obtain all the remaining components of the tensor $\hat{\varepsilon}^a(\mathbf{r})$ by cyclic permutation of the coordinates x,y,z in f and φ, i.e., the tensor $\hat{\rho}^a(\mathbf{r})$ in cubic crystals is defined by at most two arbitrary periodic functions and takes the form

$$\hat{\varepsilon}^a(x,y,z)=\begin{pmatrix} f(x,y,z) & \varphi(x,y,z) & \varphi(z,x,y)\\ \varphi(x,y,z) & f(y,z,x) & \varphi(y,z,x)\\ \varphi(z,x,y) & \varphi(y,z,x) & f(z,x,y)\end{pmatrix}. \tag{7}$$

The condition that the tensor $\hat{\varepsilon}^a(\mathbf{r})$ have a zero trace imposes on the function $f(\mathbf{r})$ one more restriction $f(x,y,z)+f(y,z,x)+f(z,x,y)=0$. The presence of other symmetry elements (two-fold or four-fold axes, screw axes) leads to additional restrictions on the functions $f(\mathbf{r})$ and $\varphi(\mathbf{r})$, but to no relations whatever between these functions. In particular, for the simplest cubic group T^1–$P23$ the presence of the 2 axis leads, as can be easily seen from (5) and (6), to the following restrictions on the functions $f(x,y,z)$ and $\varphi(x,y,z)$:

$$f(-x,-y,z)=f(-x,y,-z)=f(x,-y,-z)=f(x,y,z),$$

$$\varphi(-x,-y,z)=-\varphi(-x,y,-z)=-\varphi(x,-y,-z)=\varphi(x,y,z).$$

No other restrictions follow from symmetry considerations. In addition, in body-centered groups we have

$$f(x+{}^1/_2,\ y+{}^1/_2,\ z+{}^1/_2)=f(x,y,z),$$

$$\varphi(x+{}^1/_2,\ y+{}^1/_2,\ z+{}^1/_2)=\varphi(x,y,z),$$

and in face-centered groups

$$f(x+{}^1/_2,\ y+{}^1/_2,\ z)=f(x+{}^1/_2,\ y,\ z+{}^1/_2)$$

$$=f(x,\ y+{}^1/_2,\ z+{}^1/_2)=f(x,y,z),$$

$$\varphi(x+{}^1/_2,\ y+{}^1/_2,\ z)=\varphi(x+{}^1/_2,\ y,\ z+{}^1/_2)$$

$$=\varphi(x,\ y+{}^1/_2,\ z+{}^1/_2)=\varphi(x,y,z).$$

If we impose on $\hat{\varepsilon}(\mathbf{r})$ restrictions that do not follow from rigorous symmetry considerations then, of course, additional constraints and restrictions on the functions f and φ can arise. Thus, if it is assumed that $\hat{\varepsilon}(\mathbf{r})$ is uniaxial at each point of the unit cell, then f and φ turn out to be connected by the relation

$$f(x,y,z)-f(y,z,x)=\frac{\varphi(x,y,z)\left[\varphi^2(z.x,y)-\varphi^2(y,z,x)\right]}{\varphi(z,x,y)\varphi(y,z,x)}. \tag{8}$$

We note that on a three-fold axis the tensor $\hat{\varepsilon}^a(\mathbf{r})$ is always uniaxial and takes the form

$$\hat{\varepsilon}^a(x,x,x)=\varphi(x,x,x)\begin{pmatrix}0&1&1\\1&0&1\\1&1&0\end{pmatrix}, \tag{9}$$

while the tensor axis is directed along a three-fold axis.

It is interesting to note that from (7) and from the cited restrictions on f and φ it follows for T^1 that $\hat{\varepsilon}^a(0,0,0)=\hat{\varepsilon}^a(1/2,1/2,1/2)=0$, i.e., the crystal is locally isotropic at the points 0,0,0 and 1/2,1/2,1/2, so that the order parameter is likewise zero (we shall arbitrarily call such points defects, since the orientation of the principal axes of $\hat{\varepsilon}$ is not defined in them). A local vanishing of the order parameter must take place in the cubic groups $T^1,T^2,T^3,O^1,O^2,O^3,O^4,O^5$, which contain from two to 16 points with symmetry 23 or 432 in each cell, and for which $\hat{\varepsilon}$ is locally isotropic and the order parameter vanishes. For the groups T^4,T^5,O^6,O^7,O^8 the unit cell does not have points at which $\hat{\varepsilon}^a(\mathbf{r})$ must unconditionally be locally isotropic, and therefore the order parameter does not vanish locally in the general case.

FOURIER COMPONENTS OF THE TENSOR $\hat{\varepsilon}$

The Fourier components $\hat{\varepsilon}_\tau$ of the tensor $\hat{\varepsilon}^a(\mathbf{r})$ are defined by the expression

$$\hat{\varepsilon}_\tau=\frac{1}{V}\int\varepsilon^a(\mathbf{r})e^{i\tau\mathbf{r}}d\mathbf{r}, \tag{10}$$

in which the integration is over the volume V of the unit cell. Knowing the most general form of $\hat{\varepsilon}^a(\mathbf{r})$, which was determined in the preceding section, we easily determine the most general form of $\hat{\varepsilon}_\tau$ for the considered space groups (see Table I). In the table, R_i, I_i, and C_i are arbitrary real, imaginary, and complex numbers which are different for different $\hat{\varepsilon}_\tau$. When calculating the Fourier components, the origin was

Table I. Reflections in cubic groups and restrictions on the components of $\hat{\varepsilon}$.

Reflection indices			ε^τ_{xx}	ε^τ_{yy}	ε^τ_{xy}	ε^τ_{xz}	ε^τ_{yz}
			T^1, T^2, T^3				
$h00$		c	R	R_1	0	0	I
$hk0$		c	R	R_1	R_2	I	I_1
hhh			0	0	C	C	C
hkl		c	C	C_1	C_2	C_3	C_4
			T^4, T^5				
$h00$	$h=2n+1$	*	0	0	I	R	0
	$h=2n$	c	R	R_1	0	0	I
$hk0$	$h=2n+1$	c	I	I_1	I_2	R	R_1
	$h=2n$	c	R	R_1	R_2	I	I_1
hhh			0	0	C	C	C
hkl		c	C	C_1	C_2	C_3	C_4
			O^6, O^8				
$h00$	$h=4n\pm1$	*	0	0	iR	$\pm R$	0
	$h=4n+2$	*, c	0	R	0	0	I
	$h=4n$		$-2R$	R	0	0	0
$hh0$	$h=2n+1$	c	I	I	I_1	R	$-R$
	$h=2n$	c	R	R	R_1	I	$-I$
hhh	$h=4n\pm1$		0	0	$(1\mp i)R$	$(1\mp i)R$	$(1\mp i)R$
	$h=4n+2$		0	0	I	I	I
	$h=4n$		0	0	R	R	R
hkl		c	C	C_1	C_2	C_3	C_4
			O^1, O^3, O^5				
$h00$			$-2R$	R	0	0	0
$hh0$		c	R	R	R_1	I	$-I$
hhh			0	0	C	C	C
hkl		c	C	C_1	C_2	C_3	C_4
			O^2				
$h00$	$h=2n+1$	*, c	0	R	0	0	I
	$h=2n$		$-2R$	R	0	0	0
$hh0$		c	R	R	R_1	I	I
$hk0$		c	R	R_1	R_2	I	I_1
hhh	$h=2n+1$		0	0	I	I	I
	$h=2n$		0	0	R	R	R
hkl		c	C	C_1	C_2	C_3	C_4
			O^4, O^7				
$h00$	$h=4n\pm1$	*	0	0	$-iR$	$\pm R$	0
	$h=4n+2$	*, c	0	R	0	0	I
	$h=4n$		$-2R$	R	0	0	0
$hh0$	$h=2n+1$	c	I	I	I_1	R	$-R$
	$h=2n$	c	R	R	R_1	I	$-I$
hhh	$h=4n\pm1$		0	0	$(1\pm i)R$	$(1\pm i)R$	$(1\pm i)R$
	$h=4n+2$		0	0	I	I	I
	$h=4n$		0	0	R	R	R
hkl		c	C	C_1	C_2	C_3	C_4

Notes. R, I, and C denote real, imaginary, and complex quantities, respectively; the letter c marks chiral reflexes, while asterisks mark reflections made allowed by the local anisotropy of $\hat{\varepsilon}$. The condition for the existence of reflections for body-centered lattices (T^3,T^5,T^5,O^8) is $h+k+l=2n$, and for face-centered lattices (T^2,O^3,O^4) identical parity of h, k, and l.

chosen in standard fashion. It follows from Table I that the vanishing of the Fourier components (the extinction of the reflections) in the presence of local anisotropy of $\hat{\varepsilon}$ can be due only to the centering of the lattices. It must be noted that an analysis of the symmetry properties of $\hat{\varepsilon}^a(\mathbf{r})$ in the blue phase was carried out also in Ref. 20, but our table contains more information than the tables in Ref. 20. First, our table, in contrast to Ref. 20, gives all the $\hat{\varepsilon}_\tau$ in one and the same coordinate frame connected with the crystallographic axes; second, it contains the relative phase shifts of the various Fourier components, which are important for the determination of the structure of the blue phase and which can in principle be measured in experiment. Knowledge of the Fourier components of $\hat{\varepsilon}$ yields, as will be shown below, all the characteristic optical properties of the blue phase.

FUNDAMENTAL EQUATIONS

The formulated restrictions on $\hat{\varepsilon}$ makes possible substantial progress in the general description of the optical properties of the blue phase. Indeed, by solving Maxwell's equations (2) in the two-wave approximation[1)] of the dynamic theory of diffraction[14] and representing the electric field of the light wave of frequency ω in the form

$$\mathbf{E}(\mathbf{r},\ t)=(\mathbf{E}_0e^{i\mathbf{k}_0\mathbf{r}}+\mathbf{E}_1e^{i\mathbf{k}_1\mathbf{r}})\,e^{i\omega t},$$

we obtain for the amplitudes $\mathbf{E}_0$ and $\mathbf{E}_1$ the system of equations

$$(1-\mathbf{k}_0^2/\varkappa^2)\mathbf{E}_0+\mathbf{E}_1\hat{\varepsilon}_\tau/\varepsilon_0=0, \quad \mathbf{E}_0\hat{\varepsilon}_{-\tau}/\varepsilon_0+(1-\mathbf{k}_1^2/\hat{\varkappa}^2)\mathbf{E}_1=0 \tag{11}$$

where $\varkappa^2=\varepsilon_0\omega^2/c^2$.

The absence of birefringence in the blue phase leads to simpler polarization properties of the solutions of the system (11) compared with the corresponding relations for cholesterics.[14] Namely, in the blue phase the intrinsic polarizations are always separated and the system of four equations for the vector amplitudes $\mathbf{E}_0$ and $\mathbf{E}_1$ breaks up into two unconnected systems of two equations each for the wave amplitudes with intrinsic polarizations:

$$(1-\mathbf{k}_0^2/\varkappa^2)E_0^\sigma+F_\sigma E_1^\sigma=0, \quad F_\sigma E_0^\sigma+(1-\mathbf{k}_1^2/\varkappa^2)E_1^\sigma=0, \tag{12}$$

where $F_\sigma=(\mathbf{n}_\sigma^{0*}\hat{\varepsilon}_\tau\mathbf{n}_\sigma^1)/\varepsilon_0, \sigma$ is here and elsewhere the polarization index, and the intrinsic polarizations $\mathbf{n}_\sigma^0$ and $\mathbf{n}_\sigma^1$ of the waves $\mathbf{E}_0$ and $\mathbf{E}_1$ are determined by $\hat{\varepsilon}_\tau$, i.e., only by scattering through the Bragg angle, and are given by the solution of the following eigenvalue equations (see Ref. 21, Russ. p. 583):

$$\mathbf{n}^0=\frac{\hat{S}^0\mathbf{n}^0}{|\hat{S}^0\mathbf{n}^0|} \quad \mathbf{n}^1=\frac{\hat{S}^1\mathbf{n}^1}{|\hat{S}^1\mathbf{n}^1|}, \quad \hat{S}^0=\hat{F}_{01}\hat{F}_{10}, \quad \hat{S}^1=\hat{F}_{10}\hat{F}_{01}; \tag{13}$$

$$(\hat{F}_{10})_{ik}=\mathbf{e}_i^{1*}\hat{\varepsilon}_\tau\mathbf{e}_k^0, \quad (\hat{F}_{01})_{ik}=\mathbf{e}_i^{0*}\hat{\varepsilon}_{-\tau}\mathbf{e}_k^1,$$

where $\mathbf{e}_i^0$ and $\mathbf{e}_i^1$ are the polarization unit vectors for the directions 0 and 1, i.e., unit vectors perpendicular to $\mathbf{k}_0$ and $\mathbf{k}_1$, respectively, and the $\hat{\varepsilon}_\tau$ are defined in accordance with (10) and are listed in Table I.

The presence in the expansion (2) of $\hat{\varepsilon}(\mathbf{r})$ of nonzero Fourier components $\hat{\varepsilon}_\tau$ at $\tau\neq 0$, just as in a cholesteric, leads to diffraction or selective scattering of light, which influences decisively the optical properties of the blue phase.

It is important that in contrast to a cholesteric, in which the eigenpolarizations of the waves (propagating at an angle to the cholesteric axis) vary within the limits of the region of selective reflection, in the blue phase the eigenpolarizations remain unchanged, with high accuracy, within the limits of the region of selective reflection. The description of diffraction of light in the blue phase is therefore analogous to the case of x-ray scattering in crystals, except that the vectors $\mathbf{n}^0$ and $\mathbf{n}^1$ of the eigenpolarizations in the blue phase correspond in the general case to elliptic polarization, i.e., they need not coincide with the linear $\boldsymbol{\pi}$ and $\boldsymbol{\sigma}$ polarizations in the scattering plane and in a plane perpendicular to it, respectively.

BOUNDARY-VALUE PROBLEM

Using the noted analogy between the optics of the blue phase and x-ray diffraction (see Refs. 21-23), we present directly the end results for the optical characteristics of a plane-parallel layer of the blue phase in the case when a monochromatic plane wave is incident on it (see Fig. 1). For the Bragg geometry (see Fig. 1a), the reflection coefficient R and the transmission coefficient T of arbitrarily polarized light is given for the reflection $\boldsymbol{\tau}$ by the expressions

$$R(P,\mathbf{e})={}^1/_2(1-P)(R_\sigma+R_{\sigma'})+P(|\mathbf{e}^*\mathbf{n}_\sigma{}^0|^2R_\sigma+|\mathbf{e}^*\mathbf{n}_{\sigma'}{}^0|^2R_{\sigma'}), \tag{14}$$

$$R_\sigma=\sin^2(\varkappa\tilde{\Delta}L)[|b|\Delta_\sigma^2+\sin^2(\varkappa\tilde{\Delta}_\sigma L)]^{-1}, \quad T=1-R(P,\mathbf{e}),$$

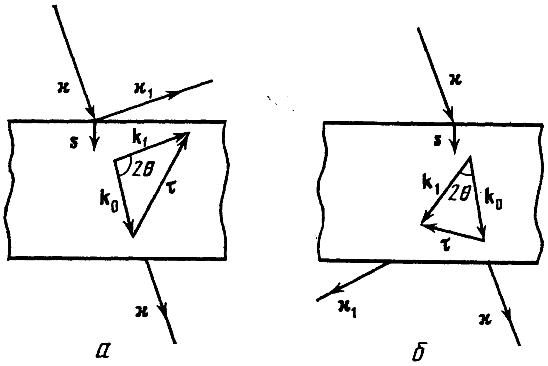

FIG. 1. Diffraction scattering in the blue phase: a) Bragg geometry, b) Laue geometry.

where

$$\Delta_\sigma=[\alpha^2+(b/|b|)(F_\sigma F_\sigma^*)]^{1/2}, \quad \tilde{\Delta}_\sigma=\Delta_\sigma/2\cos\sphericalangle(\mathbf{k}_0\mathbf{s}),$$

$$b=\frac{\cos\sphericalangle(\mathbf{k}_0\mathbf{s})}{\cos\mathbf{k}_1\mathbf{s}}, \quad \alpha=\frac{\boldsymbol{\tau}(\boldsymbol{\tau}+2\boldsymbol{\varkappa})}{2\varkappa^2},$$

$\mathbf{e}$ and P are respectively the vector and the degree of polarization of the incident beam, $\mathbf{s}$ is the inward normal to the surface of the sample. For a fixed incidence angle, the parameter α is given by

$$\alpha=4(\omega-\omega_B)\sin\theta/\omega, \quad \omega_B=\tau c(2\sin\theta\sqrt{\varepsilon_0})^{-1}, \tag{15}$$

where 2θ is the scattering angle and $\pi/2-\theta$ is the angle between $\mathbf{k}_1$ and $\boldsymbol{\tau}$; for a fixed frequency we have

$$\alpha=2(\theta-\theta_B)\sin 2\theta_B, \quad \sin\theta_B=\tau/2\varkappa. \tag{16}$$

The polarization vectors $\mathbf{e}_r$ and $\mathbf{e}_t$ of the reflected transmitted light beams are determined, in the case of a completely polarized incident beam ($P=1$) by the equations

$$\mathbf{e}_q=[\mathbf{n}_1\cos\alpha_q+\mathbf{n}_2\sin\alpha_q e^{i\beta_q}]e^{i\eta_q}, \tag{17}$$

where $\mathbf{n}_1$ and $\mathbf{n}_2$ are the eigenpolarizations defined by Eq. (13). For the reflected ($q=r$) and transmitted ($q=t$) beams we have

$$(\mathrm{tg}\,\alpha e^{i\beta})_r=\left[\frac{2i\xi_+\xi_-E_1{}^e\sin(\varkappa\tilde{\Delta}L)}{\xi_+e^{i\varkappa\tilde{\Delta}L}-\xi_-e^{-i\varkappa\hat{\Delta}L}}\right]_{\sigma=1} \times\left[\frac{2i\xi_+\xi_-E_2{}^e\sin(\varkappa\tilde{\Delta}L)}{\xi_+e^{i\varkappa\Delta L}-\xi_-e^{-i\varkappa\tilde{\Delta}L}}\right]_{\sigma=2}^{-1} \tag{18}$$

$$(\mathrm{tg}\,\alpha e^{i\beta})_t=\left[\frac{(\xi_+-\xi_-)E_1{}^e}{\xi_+e^{i\varkappa\tilde{\Delta}L}-\xi_-e^{-i\varkappa\hat{\Delta}L}}\right]_{\sigma=1}\cdot\left[\frac{(\xi_+-\xi_-)E_2{}^e}{\xi_+e^{i\varkappa\tilde{\Delta}L}-\xi_-e^{-i\varkappa\tilde{\Delta}L}}\right]_{\sigma=2}^{-1},$$

where $\xi_\pm$ define the ratio of the amplitudes E_1^σ/E_0^σ in the corresponding solutions of the system (12) and are equal to

$$\xi_\pm=[-{}^1/_2 b\alpha\pm\Delta_\sigma]F_\sigma^{-1}, \tag{19}$$

$\eta_{r,t}$ are equal to the phases of the first multipliers in (18), and $E_{1,2}^e$ are the projections of the field of the incident wave (on the sample surface) on the eigenpolarizations. In the case of an unpolarized incident beam ($P=0$) the expressions for the polarization characteristics of the reflected and transmitted light take the form

$$P^r=|R_\sigma-R_{\sigma'}|\,(R_\sigma+R_{\sigma'})^{-1}, \tag{20}$$

$$P^t=|R_\sigma-R_{\sigma'}|\,(2-R_\sigma-R_{\sigma'})^{-1}, \tag{21}$$

and the polarization vector of the reflected beam coincides with $\mathbf{n}^1_\sigma$, if $R_\sigma>R_{\sigma'}$ and with $\mathbf{n}^1_{\sigma'}$, if $R_{\sigma'}>R_\sigma$. The transmitted beam, however, contains an additional polarization, i.e., $\mathbf{n}^0_\sigma$ at $R_\sigma<R_{\sigma'}$ and $\mathbf{n}^0_{\sigma'}$ at $R_{\sigma'}<R_\sigma$. Using Eqs. (14)–(21) we can easily find the polarization density matrix, i.e., all the polarization characteristics of the reflected (ρ^r) and transmitted (ρ^t) beams for a partially polarized incident beam:

$$\rho^r(P,\mathbf{e})=\frac{P\rho^r(\mathbf{e})R_\mathbf{e}+\rho^r(1-P)R}{PR_\mathbf{e}+(1-P)R}, \tag{22}$$

$$\rho^t(P,\mathbf{e})=\frac{P\rho^t(\mathbf{e})T_\mathbf{e}+\rho^t(1-P)T}{PT_\mathbf{e}+(1-P)T}$$

where $\rho(\mathbf{e}),\rho,R_e,R,T_e$, and T are the polarization density matrices and the reflection and transmission coefficients in the case of polarized and unpolarized incident beams, and are determined by relations (14)–(21) with $P=1$ and $P=0$.

It must be noted that the expressions given here were obtained neglecting the reflection of the beam from the dielectric boundaries, i.e., assuming equality of the average dielectric constant of the blue phase to that of the bordering medium. When the average dielectric properties of the blue phase and of the external medium differ noticeably, the reflection from the dielectric boundaries can exert a noticeable influence on the considered properties. It is necessary then to use the known methods[24,25] to take into account the dielectric boundaries. In our problem this raises no fundamental difficulty.

Equation (18) determines also a traditionally measured quantity, namely the rotation of the plane of polarization of linearly polarized incident light in the sample. From this equation, in the case of circular eigenpolarizations $\mathbf{n}_\sigma$, we obtain the following expression for the rotation angle φ of the polarization plane of light passing through a layer of the blue phase:

$$\varphi=\frac{1}{2}\left\{\arg\left[\frac{\xi_+-\xi_-}{\xi_+e^{i\varkappa\tilde{\Delta}L}-\xi_-e^{i\varkappa\breve{\Delta}L}}\right]_{\sigma=1}\right.$$

$$\left.-\arg\left[\frac{\xi_+-\xi_-}{\xi_+e^{i\varkappa\tilde{\Delta}L}-\xi_-e^{i\varkappa\Delta L}}\right]_{\sigma=2}\right\}. \tag{23}$$

The optical properties of a planar blue-phase layer, for a Laue geometry (Fig. 1b), are also described by equations (14)–(23), provided the quantities $R_\sigma,\alpha,\beta,\eta$ employed are given by the relations

$$R_\sigma=\frac{\sin^2(\varkappa\tilde{\Delta}_\sigma L)}{\Delta_\sigma^2},\qquad \eta^r=\arg\left[\frac{e^{i\varkappa sL}(\xi_-e^{i\varkappa\tilde{\Delta}L}-\xi_+e^{i\varkappa\tilde{\Delta}L})}{\xi_--\xi_+}\,\frac{E_1^0}{}\right]$$

$$(\operatorname{tg}\alpha e^{i\beta})^r=\left[\frac{\xi_-e^{i\varkappa\tilde{\Delta}L}-\xi_+e^{-i\varkappa\tilde{\Delta}L}}{\xi_--\xi_+}\right]_{\sigma=1}\left[\frac{\xi_-e^{i\varkappa\tilde{\Delta}L}-\xi_+e^{i\varkappa\tilde{\Delta}L}}{\xi_--\xi_+}\right]^{-1}_{\sigma=2}$$

$$(\operatorname{tg}\alpha e^{i\beta})^t=\left[\frac{\xi_+\xi_-\sin(\varkappa\tilde{\Delta}L)}{\xi_--\xi_+}\right]_{\sigma=1}\left[\frac{\xi_+\xi_-\sin(\varkappa\tilde{\Delta}L)}{\xi_--\xi_+}\right]^{-1}_{\sigma=2},$$

$$\eta^t=\arg\left[\frac{2ie^{i\varkappa sL}\xi_+\xi_-\sin(\varkappa\tilde{\Delta}L)}{\xi_--\xi_+}\right]_{\sigma=1}. \tag{24}$$

THICK AND THIN SAMPLES

The equations of the preceding section, which are valid for an arbitrary thickness L of a blue-phase layer, take a simpler form for small ($L\varkappa|F_\sigma|\ll1$) and large ($L\varkappa|F_\sigma|\gg1$) sample thicknesses.

For thick layers, just as in a cholesteric, total reflection of the light with one of the eigenpolarizations $\mathbf{n}^0_\sigma$ takes place in a certain range of frequencies (or angles). The polarization of the reflected light coincides in this case with the corresponding polarization $\mathbf{n}^1_\sigma$. Inside this region there exists in the general case an interval of total reflection of light of any polarization (see Fig. 2). The total-reflection interval $(\Delta\omega/\omega)^T$ and the selective reflection interval $(\Delta\omega/\omega)^s$ coincide with the smaller and larger of the quantities, $|F_\sigma|,|F_{\sigma'}|$, respectively, and their midpoint coincides with ω_B.

For unpolarized incident light, the polarization characteristics of the reflected light, averaged over the frequency (or the angle) within the region of the selective reflection, correspond to a partially polarized beam with a degree of polarization

$$P^r=|\,|F_\sigma|-|F_{\sigma'}|\,|/[\,|F_\sigma|+|F_{\sigma'}|\,] \tag{25}$$

and with a polarization vector $\mathbf{n}^1_i$ that describes the polarization-selective reflection of the light.

For thin layers, the equations of the preceding section go over into the customarily analyzed[1,2] simpler expressions of the kinematic theory of scattering. We then obtain for the diffraction reflection coefficient

$$R(\mathbf{e},\,\mathbf{e}')\sim|\mathbf{e}'^{*}\hat{\varepsilon}_{\tau}\mathbf{e}|^2, \tag{26}$$

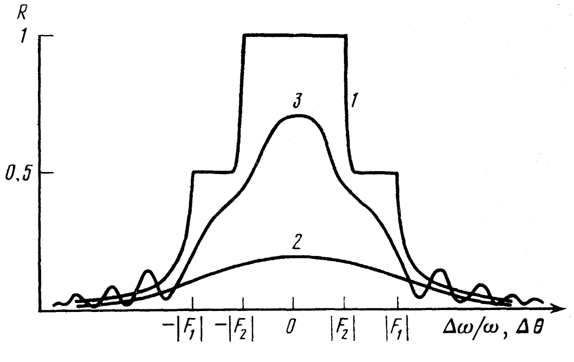

FIG. 2. Qualitative form of the frequency (angular) dependence of the reflection coefficient of unpolarized light for samples with various thicknesses: 1) thick, 2) thin, 3) intermediate.

where $\mathbf{e}$ and $\mathbf{e}'$ are the polarization vectors for the incident and reflected beams. The maximum and minimum reflection is obtained, just as in the dynamic analysis, for light with eigenpolarizations $\mathbf{n}_\sigma^0$ defined in (13). The polarization of the reflected light, just as above, is then described by the vectors $\mathbf{n}_\sigma^1$. Thus, the polarization characteristics of the scattering turn out to be independent of the sample thickness for light with eigenpolarization $\mathbf{n}_\sigma^0$. For arbitrary polarization of the incident light, however, the characteristics become dependent on the thickness. In particular, for unpolarized incident light we obtain now for the degree of polarization of the reflected light, in place of (25),

$$P^r = \left| |F_\sigma|^2 - |F_{\sigma'}|^2 \right| / \left[|F_\sigma|^2 + |F_{\sigma'}|^2 \right]. \tag{27}$$

On the other hand, the polarization represented in the reflected light is described as before by the vector $\mathbf{n}_1'$ (we assume for the sake of argument that the first term in the numerator of (27) is larger than the second).

CONCLUSIONS AND COMPARISON WITH EXPERIMENT

Let us examine the specific optical properties of the blue phase that follow from the restrictions obtained above on the forms of $\hat{\varepsilon}^a(\mathbf{r})$ and $\hat{\varepsilon}_\tau$. We note first that almost all the reflections are chiral. A reflection is defined here as chiral if it has different diffraction reflection coefficients for right- and left-hand circular polarizations [the eigenpolarizations (see (13)) are elliptic for chiral reflections and linear for nonchiral ones]. This is not surprising since we have confined ourselves to left-right asymmetric (enantiomorphic space groups).

Reflections are nonchiral if the reciprocal-lattice vector is parallel to three-fold and four-fold axes (i.e., the reflections $\{hhh\}$ for all groups and the reflections $\{h00\}$ for the groups O^1, O^3, O^5), as well as the reflections $\{h00\}$ at $h = 2n + 1$ for the group T^4, at $h = 2n$ for the group O^2, at $h = 4n + 1$ for the groups O^7 and O^6, and at $h = 4n$ for the groups O^4, O^6, O^8, O^7.

Let us discuss briefly on the basis of the foregoing analysis the experimental data on the optical properties of the blue phase and those restrictions, which follow from the known results, on its structural properties. We must first note once more that the restrictions imposed here on the possible structures, which reduces to considering only cubic blue phases, is connected with the experimental data, but it still leaves a wide scope for an unambiguous choice (there exist thirteen noncentrosymmetric cubic space groups[16]). The results of recent investigations,[26,27] which have revealed in particular the chirality of the reflections observable in the blue phase, make it possible to decrease substantially the number of possible structures and to discard the primitive and phase-centered cubic lattices. The only remaining possible space groups of the blue phase are T^3, T^5, O^8, inasmuch as for the remaining groups (see Table I), there must be nonchiral ones among the first four reflections. It must be emphasized here that the fact that only one of the investigated circular-polarization reflections is selectively backward[26] imposes on $\hat{\varepsilon}_\tau$ restrictions that do not follow from pure symmetry considerations for any of the considered groups (see Table I), and can be used to decrease the number of the parameters of the theory that describes phase transitions into the blue phase. For example, for τ corresponding to the $h\,00$ reflections, this restriction takes the form of the relation

$$\varepsilon^\tau_{yy} - \varepsilon^\tau_{zz} \pm 2i\varepsilon^\tau_{yz} = 0,$$

in which either sign of $2i\varepsilon^\tau_{yz}$ is admissible.

The relations presented above, particularly Table I, show that the structures T^3 and T^5 can be experimentally distinguished from O^8 in the polarization properties of the reflections, without resorting to phase relations between the $\hat{\varepsilon}_\tau$. Indeed, it follows from Table I, e.g., that reflections 200 in the groups T^3 and T^5 correspond to nonzero ε^τ_{xx} components, which are indeed those which distinguish the polarization properties of these reflections for T^3 and T^5 from those for O^8. Thus, the intensity of the diffraction of π-polarized light into π-polarized in the kinematic approximation for T^3 and T^5 is given by the expression

$$\begin{aligned} I_{\pi\pi} \sim (\varepsilon^\tau_{xx})^2 - 2\varepsilon^\tau_{xx}(\varepsilon^\tau_{xx}\cos^2\varphi + \varepsilon^\tau_{yy}\cos 2\varphi)\sin^2\theta \\ + [(\varepsilon^\tau_{xx}\cos^2\varphi + \varepsilon^\tau_{yy}\cos 2\varphi)^2 + (\varepsilon^\tau_{yz})^2\sin^2 2\varphi]\sin^4\theta, \end{aligned} \tag{28}$$

and for O^8 by the expression

$$I_{\pi\pi} \sim [(\varepsilon^\tau_{yy})^2\cos^2 2\varphi + (\varepsilon^\tau_{yz})^2\sin^2 2\varphi]\sin^4\theta, \tag{29}$$

where φ is the azimuthal angle of the scattering plane measured relative to the x axis (from the y axis). From (28) and (29) it follows that when the Bragg angle θ is decreased the intensity $I_{\pi\pi}$ tends to zero for O^8 but remains finite for T^3 and T^5. Another possibility of distinguishing between these groups is that the reflection 400 is chiral in the groups T^3 and T^5 and nonchiral in O^8. This reflection has not yet been observed, and in connection with the foregoing its observation and investigation of its polarization properties might be decisive for an unambiguous determination of the structure of the blue phase. As for the space groups T^3 and T^5, an experimental determination of the intensities and polarization properties of the scattering for the observed reflection still does not permit a choice between them, and for an unambiguous determination of the space group it is necessary to establish experimentally the phase relations between the $\hat{\varepsilon}_\tau$, or else to invoke independent premises or data. Thus, it is useful to bear in mind that out of the three groups discussed, only one, T^3, is bound to correspond to the space group of the defects, i.e., to a lattice of points at which the dielectric anisotropy and the order parameter vanish. This circumstance can be used to distinguish between the groups T^3 and T^5, e.g., with the aid of the NMR spectra which depend on the order parameter.

It is of interest also to cast light on the degree to which the admissibility of local biaxiality of cholesterics and of the blue phase, which is discussed in the literature,[28] can manifest itself in optical measurements. As seen from Table I, the presence of local anisotropy in the dielectric characteristics of the blue phase leads to consequence that manifest themselves clearly, namely the lifting of the extinction for a number of reflections that are forbidden in the absence of anisotropy. One might assume that confinement to only uniaxial local anisotropy of $\hat{\varepsilon}(\mathbf{r})$ could lead to elimination of certain extinctions, while biaxial anisotropy of $\hat{\varepsilon}(\mathbf{r})$ lifts additional extinction of the reflections. This is not the case, however, in cubic groups, and the aggregate of the allowed reflections turns out to be the same for both uniaxial and biaxial anisotropy of $\hat{\varepsilon}(\mathbf{r})$. The presence of local biaxiality of $\hat{\varepsilon}(\mathbf{r})$ does not require satisfaction of the relation (8) between the functions f and φ, and leads for the Fourier harmonics $\hat{\varepsilon}_\tau$ only to an elimination, connected with (8), of the integral relation between the $\hat{\varepsilon}_\tau$, which imposes at any rate weak restrictions on the intensities and phases of the existing reflections. On the whole, it must be stated that the prospects of determining the structure of the blue phase are more favorable compared with diffraction x-ray and neutron determinations of the structures of ordinary crystals. This pertains primarily to the determination of the phase shifts of the structure amplitudes, i.e., $\hat{\varepsilon}_\tau$. It is known that for an unambiguous determination of the structure it is necessary to know, besides the modulus of the structure amplitude, also the phase. The phase of $\hat{\varepsilon}_\tau$, and by the same token uniquely also the structure of the blue phase, can be determined with the aid of polarization measurements, which have been quite well developed for optics. It is important here that the polarization vector of the form (17) must be determined in experiment completely, i.e., without neglecting the phase factors $e^{i\eta}$. To determine $e^{i\eta}$ in turn, it is necessary, e.g., to produce interference between a beam reflected from the blue phase and a beam having known phase and amplitude characteristics.

In optics, especially when laser sources are used, this interference can be realized by various methods. In particular, it takes place between the diffraction reflection in the blue phase, as considered here, and the "dielectric" reflection of light from its boundary, the latter reflection having well known polarization, phase, and amplitude properties. Without going into details of the corresponding methods of experimentally determining the phase shift from observations of the influence of interference of the intensity and polarization properties of the reflections, we emphasize that the use of these interference relations is a practically fully realizable method of measuring not only the modulus but also the phase of $\hat{\varepsilon}_\tau$.

MULTIPLE SCATTERING EFFECTS

We have so far invoked, as usual, simplified kinematic formulas that follow from relations (14)–(24) in the limit of small sample thickness, to interpret the experimental results of the investigation of the structure of the blue phase. In this approach, the Fourier harmonics $\hat{\varepsilon}_\tau$ are determined from the intensities of the reflections, and in view of the known difficulties of absolute measurements of the intensity, their accuracy is limited by the relatively low accuracies of absolute intensity measurements. The latter in turn can raise difficulties in the experimental determination of the blue-phase structure, and in particular in the choice of a concrete model from among the number of competing possibilities.

It should be noted that in principle $\hat{\varepsilon}_\tau$ can be determined with much higher accuracy if dynamic effects are used rather than measurements of the reflection intensities. As follows from (14)–(24), the reflection and transmission coefficients, as well as the polarization characteristics, are subject at a fixed sample thickness to beats with changing frequency of the light (of the angle of deviation from the Bragg condition), or when the thickness is changed with the remaining parameters fixed. The period of these dynamic beats and, in particular, the size of the region of selective reflection, are directly connected with the scattering tensor $\hat{F}$, i.e., with $\hat{\varepsilon}_\tau$, and it is this which makes it possible to determine these quantities without measuring the absolute intensities. The situation here is perfectly analogous to the realized precision method of determining the structural amplitudes from Pendellosung (dynamic) beats in the diffraction of x rays[29] and neutrons.[3] The difference is that the corresponding measurements in the optical band are much simpler to perform and have already been performed, e.g., for cholesterics.[31] To be sure, it must be kept in mind that to observe dynamic effects the blue-phase samples must be perfect, and the feasibility of obtaining sufficiently perfect samples has not yet been investigated. Another conclusion of the performed dynamic analysis is the possible appearance in the blue phase of linear birefringence, the existence of which is connected with multiple-scattering effects and does not contradict the cubic space group structure of this phase. We have in mind here the diffraction birefringence, which turns out to be circular only for particular directions of light propagation in the blue phase, just as for light propagation along the cholesteric axis (see (23)), but leads in the general case to the appearance of linear birefringence. A characteristic feature of this birefringence is its strong frequency (angular) dependence and the reversal of the sign in the selective-reflection region.

The formulated statement follows from an analysis based on the formulas obtained. Thus, near an individual nonchiral reflection, but outside the selective-reflection region, we find from (17) and (23) that the birefringence Δn is given by

$$\Delta n=\frac{\alpha}{|\alpha|}\left[\left(\alpha^2+\frac{b}{|b|}|F_1|^2\right)^{1/2}-\left(\alpha^2+\frac{b}{|b|}|F_2|^2\right)^{1/2}\right], \tag{30}$$

where F_1 and F_2 are the amplitudes of the Bragg-angle scattering of the natural waves (see (12)). For chiral reflections, at intrinsic polarizations that differ considerably from circular, the order of magnitude of the linear birefringence is also determined by (30). In the general case, the diffraction birefringence receives contributions not from one but from many reflections, and a special analysis is needed in this case (this problem was solved for x rays in Ref. 32). It can thus be concluded that the experimentally observed small linear birefringence[33] can be of diffraction origin, and it cannot be unconditionally regarded as an argument against the assumption that the blue phase is cubic. One more qualitative conclusion, connected with allowance for multiple scattering, is the depolarization of the light beam, which follows from (14)–(24), even in perfect blue-phase samples, if the beams have a finite angular (or frequency) width. As a result, in a perfect sample even for fully polarized incident beam, in view of its inevitable frequency and angular divergences, the diffracted beams are only partially polarized and are characterized by polarization density matrices averaged over the frequency ω and over the divergence angle Ω:

$$\rho^r = \int R\rho^r d\Omega d\omega \Big/ \int R d\Omega d\omega, \quad \rho^t = \int T\rho^t d\Omega d\omega \Big/ \int T d\Omega d\omega \tag{31}$$

and by a non-unity degree of polarization

$$P = [(\rho_{11} - \rho_{22})^2 + 4|\rho_{12}|^2]^2.$$

The quantities contained in (31) are defined in (22). The criterion for the need to take into account the discussed depolarization source is the degree of perfection of the sample, since in imperfect crystals the depolarization appears even for an ideally collimated monochromatic beam and can be substantially larger than the value given by (31) (Ref. 34).

CONCLUSION

In conclusion, it must be emphasized that the treatment of the blue-phase optics in the present paper is based on pure symmetry considerations and does not depend in any way on various details of the concrete models of the phase transitions into the blue phase.[3–11] It is therefore subject to less restrictions than the aforementioned theories, and the restrictions revealed by a comparison with experiment can be used to construct various concrete models of the phase transitions; this, in particular, was noted above in connection with the observed selectivity of the diffractive backward reflection with respect to the circular polarizations. The experimental observation of only four nonequivalent reflections in the blue phase gives grounds for retaining only four nonequivalent vectors $\boldsymbol{\tau}$ in the Fourier expansion of the free energy[10] in terms of the order parameter. At any rate, one can definitely regard the discarded terms as small.

We note in this connection that the results of the symmetry analysis presented here for the possible space groups of the blue phase agree with the results of Hornreich and Strikman, who used in their analysis a concrete model of the transition and, in particular, who connected the dimensions of the unit blue-phase cell at the transition point with the pitch of the helix in the cholesteric phase.

As for the correspondence, proposed in Ref. 10, of the modifications of the blue phases to the following space groups:

$$T^5 - BPI, \quad O^8 - BPIIa, \quad T^3 - BPIIb,$$

where the notation of Ref. 26 is used for the plasmas, it would be useful here, in order to establish reliable unambiguity, to verify in experiment whether the corresponding phases have optical-property singularities that follow from the analysis carried out here for the concrete groups. It would also be useful, for the identification of the blue-phase structures, to measure the circular dichroism on the lines of the dichroic dye introduced into the liquid crystal. This pertains primarily to the least investigated phase *BP* III (in the notation of Ref. 27), which precedes directly the isotropic liquid.

[1)] The applicability of the two-wave approximation is due to the smallness of the dielectric anisotropy, which turns out to be even less than in the cholesteric phase.[1]

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