

The blue phase of liquid crystals

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This review describes the present status of research on the blue phase of cholesteric liquid crystals—a phase state of liquid crystals with unusual properties, whose order parameter exhibits three-dimensional spatial periodicity and which appears in a narrow temperature interval (of the order of 1°). Experimental results and current theoretical models of the blue phase are presented. The phase transitions between the isotropic liquid, the blue phase, and the cholesteric phase are studied using Landau's theory. The discussion of methods for studying the blue phase emphasizes both the most informative optical methods and the theory of the optical properties of the blue phase. It is pointed out that the study of the blue phase is of substantial interest for the physics of the condensed state as a whole, and unsolved problems in this area are briefly discussed.

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"Liquid crystals are beautiful and mysterious; I am fond of them for both reasons."

P. de Gennes, The Physics of Liquid Crystals

1. INTRODUCTION

One of the most interesting and intensively studied questions in the physics of liquid crystals at the present time is the so-called blue phase of cholesteric liquid crystals. Its puzzling physical properties have stumped researchers for almost 100 years since Reinitzer discovered liquid crystals in 1888.¹⁾ Moreover, it was even doubted that the blue phase exists as an equilibrium thermodynamic state. Within the last several years there has been a qualitative jump in the level of understanding of the physical essence of and the methods for studying the blue phase. The general features of the nature of the blue phase may be regarded as understood, the 100-year puzzle has been solved, and researchers must now clarify many specific questions regarding the structure, thermodynamics, and optics of the blue phase and other problems. As often happens, reality turned out to be richer than the first notions about the blue phase, and studies of the

blue phase have a much deeper significance than the problem of liquid crystals itself. Thus, in particular, it turned out that there exist not one but at least three modifications of the blue phase, and phase transitions between them are interesting from the viewpoint of the physics of phase transitions in general and the problem of melting in particular.

Liquid crystals generally characteristically exhibit an enormous variety of phases and corresponding phase transitions between them.¹⁻³ For this reason liquid crystals are both a convenient object for experimental study of phase transitions and a unique proving ground for testing different approaches used in the theory of phase transitions (in solids, two-dimensional systems, etc.). The blue phase, which is the subject of this review, is an excellent illustration of this general assertion.

We shall briefly describe the physical properties of the blue phase.⁴ This phase is observed in several cholesteric

liquid crystals in a narrow temperature interval of the order of $1-0.1^\circ$ between the isotropic liquid and the cholesteric phase. As is well known,¹⁻⁶ in the cholesteric phase the direction of predominant orientation of the molecules varies along some axis so that a one-dimensional spiral structure is formed. In contrast to this, in the blue phase the tensor order parameter, characterizing the correlation in the orientation of the molecules, exhibits a spatial three-dimensional periodicity; in addition, as in cholesterics, the period is of the order of the wavelength of the light. This leads to the unusual and, at first glance, contradictory optical properties of the blue phase: optical isotropy and gigantic optical activity, selective scattering, and complicated polarization characteristics of scattering. The phase transitions out of the blue phase (blue phases) into neighboring phase states are weak first-order transitions and in some cases, possibly, second-order transitions.

This review summarizes and generalizes the results of studies of the blue phase in the light of the latest theoretical and experimental achievements, which have led to a qualitative jump in the understanding of this "delicately" organized phase state of matter.

2. EARLY STUDIES OF THE BLUE PHASE²⁾

At the beginning of this century Lehmann discovered that in a narrow temperature interval (of the order of 1°C) near the point of the isotropic-liquid-cholesteric transition some substances exhibit an intermediate phase, which differs from both the isotropic liquid and the cholesteric phase.⁷ Lehmann's observations were later confirmed by many investigators,⁸⁻²⁰ in particular by Gray,⁸ who called this intermediate state the blue phase. It turned out that this phase is more easily observed when the temperature is lowered, i.e., by moving away from the isotropic liquid. It has been established experimentally that the blue phase has the following properties: 1) light is selectively scattered in the visible part of the spectrum (Fig. 1), as a result of which this phase appears to be colored blue, whence comes its name (in many cases colored "platelets" can be seen in it); 2) a

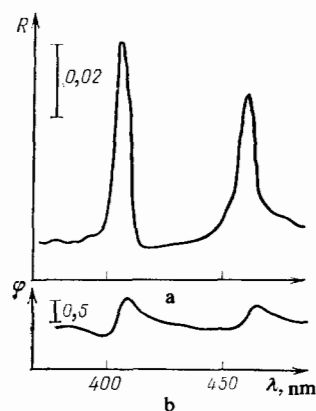


FIG. 1. The wavelength dependence of the selective reflection (a) and the rotation of the polarization plane of light (b) by cholesteryl pelargonate at the temperature of the transition 91.35°C from the blue phase I into the blue phase II.²¹ The samples were 25 and $12\ \mu\text{m}$ thick, respectively.

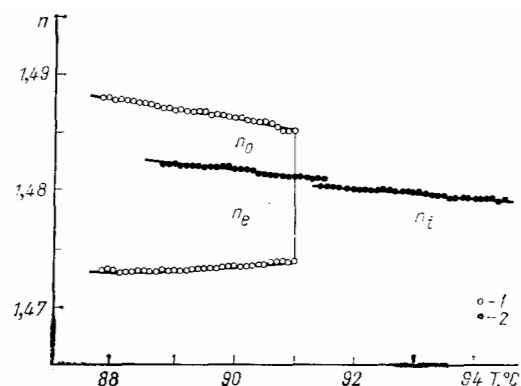


FIG. 2. The temperature dependence of the refractive indices of cholesteryl myristate at a wavelength of $589\ \text{nm}$.³¹ n_i is for the isotropic and blue phases, n_o and n_e are for the cholesteric phase. 1) Heating, 2) cooling.

strong wavelength-dependent rotation of the polarization plane of light appears²¹; 3) linear birefringence does not occur—the phase is optically isotropic¹⁴ (Fig. 2); 4) according to experimentally observed manifestations, the phase transition out of the isotropic liquid into the blue phase is thermodynamically analogous to the isotropic-liquid-cholesteric transition,^{20,22} a fact which is indicated by the anomalies in the heat capacity, which are of the same order of magnitude in both cases; 5) the cholesteric-blue-phase transition (observed when the temperature is raised) is characterized by a weak thermal anomaly^{20,22}; 6) the NMR spectra show that long-range orientational order exists in the blue phase and they differ both from the spectra for the isotropic liquid and from the spectra for the cholesteric phase²³; and, 7) the dynamics of the pretransitional fluctuations of the isotropic phase for liquid crystals in which the transition occurs into the blue phase differ from those cases when the transition occurs directly into the cholesteric phase, bypassing the blue phase.^{24,25}

These facts permit regarding as firmly established the assertion, first stated by Lehmann,⁷ that the blue phase is a new type of liquid crystal and is not simply a specific texture of cholesterics.⁸ The long time required to recognize the blue phase as an independent phase state of liquid crystals is a consequence of the unusual physical properties of this state, in particular, the fact that it is thermodynamically stable in a very narrow temperature interval but can be supercooled by several degrees below the temperature of the phase transition. Moreover, calorimetric^{20,22} and optical^{26,27} measurements have shown that within this narrow interval of thermodynamic stability a phase transition between two or even three different and thermodynamically stable phases (they are called BP I, BP II, and BP III) occurs.

The first experiment clearly demonstrating the validity of the notion of a blue phase as a thermodynamically stable independent phase was performed in 1975 by Armitage and Price.²⁰ Using the method of differential scanning calorimetry (DSC) (Fig. 3) they obtained a finite jump in the enthalpy at the point of the cholesteric-BP transition. Calorimetric measurements indicating the possibility of a phase transition prior to the transition of the isotropic liquid into

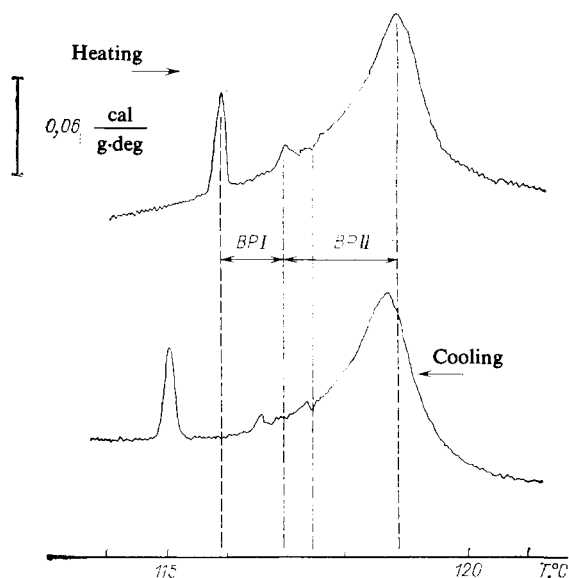


FIG. 3. Thermograms of cholesteric-blue-phase-isotropic-liquid transitions (DSC: 0.62 °C/min).⁵³

the cholesteric phase were also performed earlier.^{13,28} But the authors of these studies did not interpret the results obtained as being an indication of a transition into the blue phase.

In addition to everything else, Armitage and Price discovered a very small change in density (only about 0.004%) at the point of the cholesteric-texture-blue-phase transition.

These results, on the one hand, confirmed the existence of a blue phase which is thermodynamically stable in a very narrow (~1 K) temperature interval, while on the other hand, they indicated that the cholesteric-blue-phase transition is a first-order transition, since a discontinuity of the properties was observed. From the smallness of the jumps, however, it followed that the structures of the neighboring phases must not be very different from one another. The question regarding the nature of the molecular ordering in the blue phase, however, remained unresolved.

The approach to the solution of structural questions regarding the blue phase was complicated by the observation that the blue phase is optically isotropic (see Fig. 2). This fact was indirectly demonstrated by Saupe's work.¹⁴ Earlier quantitative measurements of the index of refraction were performed by Pelzl and Sackmann²⁹ and Demus *et al.*³⁰

Stegemeyer, Bergmann, *et al.*^{21,31} studied the selective reflection of light in the blue phase and showed that it is very similar to the selective reflection in the cholesteric (see Fig. 1). To wit, just as in cholesterics, frequency-selective reflection with normal incidence occurs only for light with a particular circular polarization. Light with the opposite circular polarization is not selectively reflected. The wavelength of the selective reflection is lower for oblique incidence. As the temperature is lowered, the wavelength of the selectively reflected light increases in the entire interval of existence of the blue phase, and at some temperature, corresponding to the transition between the different forms of the blue phase, it undergoes a jump.

Selective scattering in the blue phase was also observed to differ from the selective scattering in the cholesteric (see Fig. 1). Strong reflection occurred not in one frequency region, as in the cholesteric, but rather in two frequency regions. Characteristically, the wavelength of selective reflection in the lowest observed order was always longer than the wavelength of selective reflection in the cholesteric.

The frequency dependence of the rotation of the polarization plane of light also was analogous to that in the cholesteric. Just as in the cholesteric, high optical activity was observed and the direction of rotation of the polarization plane depended on the frequency of the light (see Fig. 1). The direction of rotation was opposite on different sides of the region of selective reflection, and at some frequency in the region of selective reflection, the rotation vanished, i.e., the point where the sign of the rotation changed was observed. In the blue phase, in contrast to the cholesteric phase, several points where the sign changed could be observed.

Because of the difficulties arising in the experimental study of the blue phase, owing, in particular, to the narrow temperature range in which the blue phase exists, the results of the early studies were often of a qualitative character. Nevertheless, indications of the polymorphism of the blue phase, i.e., the fact that in the indicated narrow temperature interval the investigator could be dealing with not one but several modifications of the blue phase, already appeared in the 1970s. This was indicated both by optical and calorimetric studies⁴ and by NMR studies³² (Fig. 4).

a) The nature of the blue phase

The nature of the molecular ordering in the blue phase cannot be regarded as being finally established. Several possibilities are under discussion, but intensive experimental and theoretical studies currently being performed suggest that the puzzle of the blue phase will be finally solved in the near future. Here it is worthwhile to underscore the fact that independently of which of the possibilities under discussion for the structure of the blue phase is (are) realized in nature,

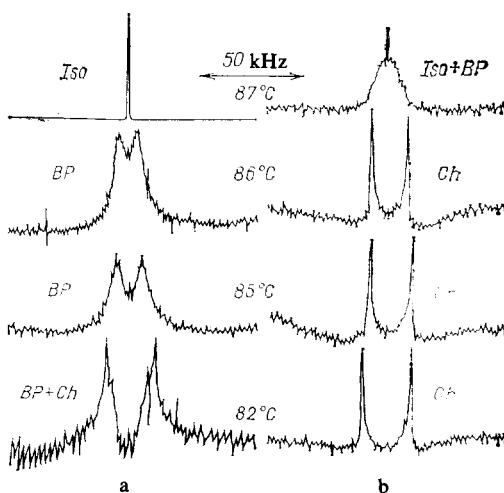


FIG. 4. NMR spectra of deuterated cholesteryl nonanoate.³² a) Cooling, b) heating.

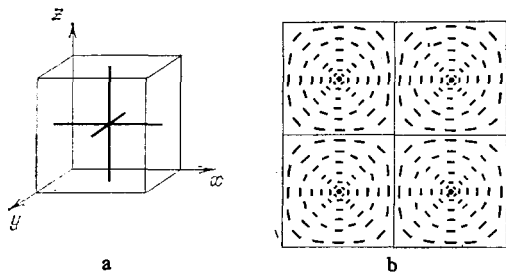


FIG. 5. The structure of the blue phase first proposed by Saupe.¹⁴ a) Cubic body-centered lattice, b) arrangement of molecules projected onto the face of the cubic lattice.

the blue phase is an example of an extremely interesting and very complicated structural state, the physics of which is of interest on general grounds, and the results obtained here have a deeper significance than the problem of liquid crystals as such.

The possible structure of the blue phase was proposed in 1969 by Saupe¹⁴ (Fig. 5). Based on the observed optical isotropy, he proposed that a body-centered cubic lattice of point defects in the orientation of the director appears in the blue phase and, excluding the immediate neighborhood of these defects, the local configuration of the director is similar to the configuration in the usual cholesteric phase. As Saupe himself pointed out, however, he did not present sufficient theoretical justification for the possibility of the realization of this structure.

The theoretical justification for the fact that the structure exhibiting three-dimensional periodicity is theoretically stable was presented by Brazovskii, Dmitriev, and Filev,^{33,34} who studied the isotropic-liquid-cholesteric transition within the framework of Landau's theory of phase transitions. These studies led to the conclusion that depending on the values of the parameters in Landau's expansion of the free energy, aside from the direct isotropic-liquid-cholesteric transition, intermediate phases, in particular a hexagonal phase, can exist between the isotropic liquid and the cholesteric.

Other models of the blue phase, purporting to explain the optical isotropy, have also been proposed. These include a model of an ensemble of globules with a cholesteric structure in which the distinguished axes of separate globules are oriented completely randomly^{35,36} and a model of a conical helix with the director tilted at an angle of 54.74° to the axis of the helix.³⁷ Both models give optical isotropy on a macroscopic scale, but they do not explain the other properties of the blue phase. As will be evident from what follows, reality turned out to be more complicated and more interesting than the first models of the blue phase mentioned above.

b) Experimental studies of the blue phase

The theoretical work performed by Brazovskii *et al.*^{33,34} stimulated further experimental and theoretical studies of the blue phase. A very favorable opportunity for studying the properties of the blue phase arose. The theory, developed primarily within the framework of Landau's theory of phase transitions, made very general predictions regarding the

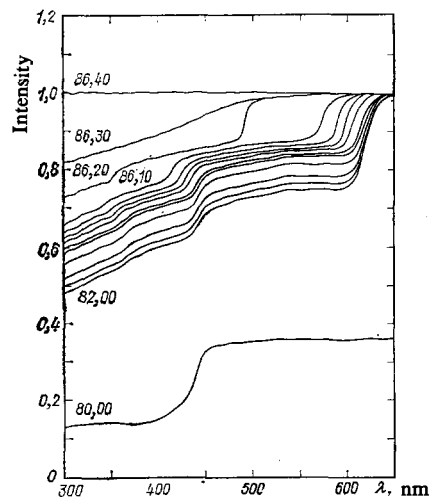


FIG. 6. Transmission spectra with cooling of a mixture of 85% cholesteryl nonanoate and 15% cholesteryl chloride (polycrystalline sample).²⁶ 86.40 °C— isotropic liquid; 86.30 °C—fog phase; 86.20 °C—BP II; from 86.10 to 82.00 °C—BP I phase; 80.00 °C—cholesteric. The steps on the curves correspond to the interplanar distances.

physical properties of the blue phase, in particular, its structure, since the complexity of the object under study precluded an unequivocal theoretical prediction of all properties of the blue phase. Under these conditions, experimental studies of the blue phase permitted narrowing the range of models of the blue phase under consideration and checking the validity of the theoretical predictions regarding the nature of this phase.

Very substantial progress in elucidating the structure of the blue phase and the symmetry properties of the order parameter (its space group) was made by the experimental studies performed by Meiboom and Sammon²⁶ as well as by Johnson, Flack, Crooker, and Svoboda.^{27,38} These two experimental groups used optical methods. The first group studied transmission spectra (Fig. 6), while the second group studied spectra of selective reflection by the blue phase (Fig. 7). In this sense the results of these groups,

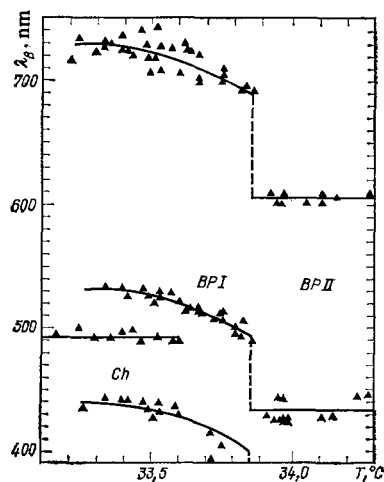


FIG. 7. The temperature dependence of the wavelength of selective scattering for the cholesteric and the blue phases BP I and BP II for 50:50 mixtures of chiral and nonchiral biphenyls.²⁷ BP I is supercooled below 33.6 °C.

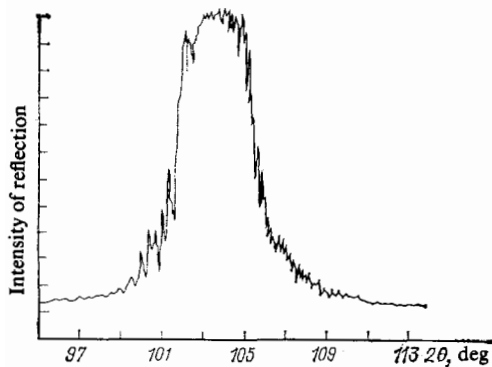


FIG. 8. Angular dependence of the coefficient of reflection for a single crystal of BP II at 76.74 °C.⁴¹ $\lambda = 4880 \text{ \AA}$, mixture of cholesteryl nonanoate and the nematic 60CB.

which are essentially close, successfully supplement one another. Using a different technique, based on the observations of the faceting of the crystallites (perfect regions) of the blue phase, Marcus also established limits on the possible space groups of the blue phase.^{39,40} He was the first to observe clearly multiple-scattering effects in selective reflection from the blue phase (Fig. 8).⁴¹ The latter results indicate that Marcus was able to obtain quite large perfect sections of the blue phase (see also Refs. 119 and 120), while the quantitative characteristics of selective reflection indicate that the characteristic values of the spatial Fourier harmonics of the dielectric-permittivity tensor for the blue phase are several times smaller than those in the cholesteric phase of the same substance.

Nicastro and Keyes⁴² carried out systematic optical studies of the blue phase of a homologous series of cholesteryl *n*-alkanoates (for $n \leq 18$). In most compounds they observed two forms of the blue phase, low-temperature BP I and high-temperature BP II. It is interesting that they observed the existence of optical anisotropy in the blue phase, though it is small ($\Delta n \approx 0.004$). We should also mention earlier studies by Chistyakov and Gusakova,¹⁰⁻¹² who studied the textures of the blue phase by optical methods.

Kizel' and Prokhorov⁴³ made a quantitative determination of the structural parameters of the blue phases from circular-dichroism spectra (Fig. 9). Demikhov and Dolganov observed jumps in the temperature dependence of the rotation of the polarization plane of light at the points of the phase transitions of the blue phase.⁴⁴

Because the blue phase exists in short-pitch cholesterics, in the experimental studies considerable attention was devoted to studying the blue phase of different compounds and mixtures, for which the pitch in the cholesteric phase depends on the concentration of the components (Fig. 10).^{42,45-48} These studies provided quantitative information on the correlation between the cholesteric pitch and the existence of the blue phase. Moreover, they revealed that the width of the temperature interval and the number of observed blue phases depend on the cholesteric pitch. The pattern established here is on the whole as follows. The blue phase is first observed with a pitch less than some definite value (a unique value for each type of compound or compo-

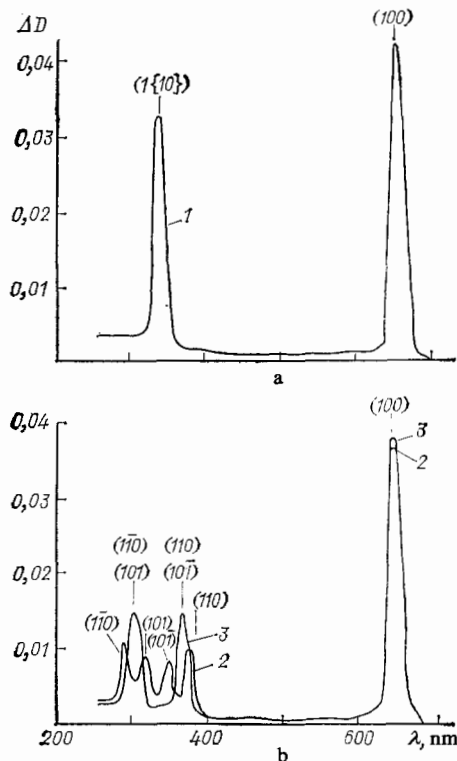


FIG. 9. Spectra of circular dichroism in BP II, obtained and identified in Ref. 43. Mixture of cholesteryl nonanoate and cholesteryl chloride. a) Normal (1) and b) oblique incidence of light on the sample (2, 3 for different directions of incidence of light on the crystal).

nent of the mixture). As the pitch decreases, the temperature interval in which the blue phase exists becomes wider. Moreover, near the threshold value of the pitch the blue phase exists in a narrow temperature range and only one form of the blue phase is observed, whereas in compounds or mixtures with a shorter pitch the temperature range of the blue phase becomes wider and a larger number (up to three) of its modifications can be observed. The transition out of the blue phase directly into the smectic phase, bypassing the cholesteric, was also studied.¹²¹

In Refs. 49 it was observed that the blue phase is very sensitive to the pressure. As the pressure is raised, the optical

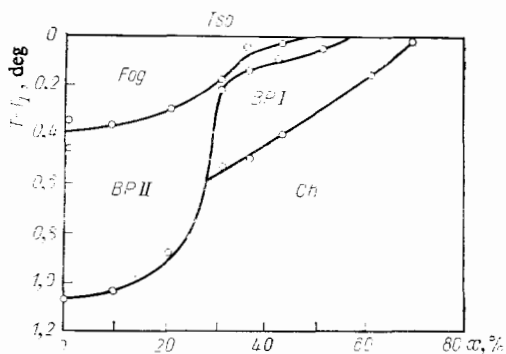


FIG. 10. Phase diagram for a mixture of chiral and racemic forms of the same substance.⁴⁶ The temperature is measured from the point of transition into the isotropic phase; the concentration of the racemic component is plotted along the abscissa axis.

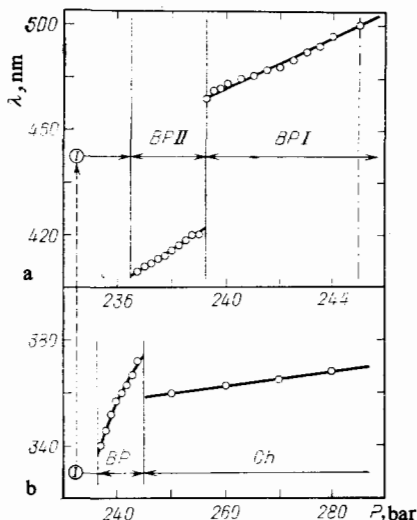


FIG. 11. Pressure dependence of the wavelength of selective reflection at constant temperature (102 °C) for cholesteryl nonanoate with increasing (a) and decreasing (b) pressure.⁴⁹

characteristics of the blue phase change in a manner entirely analogous to the way they change when the temperature is lowered. For cholesteryl nonanoate,⁴⁹ appreciable changes appear in the selective scattering (appearance and vanishing of reflections) when the pressure is changed by only several bars (at a pressure of the order of 100 bar), and the blue phase exists in a pressure range of the order of 10 bar (Fig. 11). In addition, the blue phase is observed in a wider range when the pressure is raised than when it is lowered, i.e., a phenomenon analogous to the well-established possibility of supercooling of the blue phase when the temperature is lowered apparently appears.

An anomalous increase was also observed in the viscosity of the mesophase in the temperature range of the blue phase⁵⁰; it was observed in binary mixtures of cholesterics and appeared only for concentration compositions exhibiting a blue phase (Fig. 12). The existence of elastic shear moduli of the blue phase, which owe their existence to the three-dimensional spatial periodicity in the structure of the phase, was discovered experimentally by Clark *et al.*⁵¹ and Cladis *et al.*⁵²

The effect of an external electric field on the blue phase was studied in Refs. 48, 53, 54, and 122. It was found that the application of a comparatively low voltage causes the appearance of birefringence and increases the wavelength of selective reflection. Then as the voltage is raised the blue phase transforms into a cholesteric or nematic, and in some voltage range transitions are induced between different modifications of the blue phase.

Summarizing the results of the experimental studies, it should be stated that up to three modifications of the blue phases, which are customarily denoted as BP I, BP II and BP III in order of increasing temperature of existence, have now been observed in a narrow temperature interval between the cholesteric and isotropic phases. The low-temperature phases BP I and BP II exhibit a three-dimensional spatially periodic order-parameter field (dielectric permittivity ten-

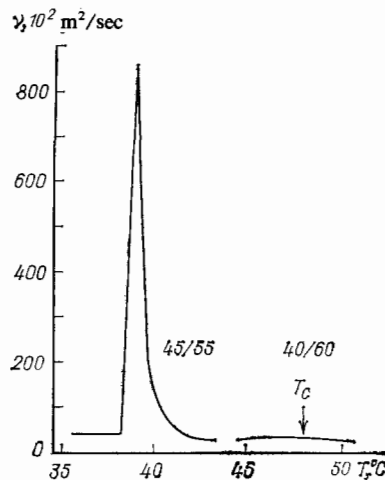


FIG. 12. The temperature dependence of the kinematic viscosity of mixtures in the region of the isotropic-liquid-cholesteric transition.⁵⁰ The blue phase occurs in the 45:55 mixture and is absent in the 40:60 mixture.

sor), which forms a primitive or body-centered cubic lattice, belonging to space groups of classes *O* or *T*. With regard to the highest-temperature phase BP III, which is also referred to as the fog phase because it exhibits strong and wavelength-nonspecific scattering of light, the nature and the structure of the order-parameter field of this phase remain unclear. At the temperatures at which the blue phases exist and the phase transitions between them occur, many physical properties of the substance, which in this region are easily affected by very weak external perturbations, undergo a change. Phase transformations in blue phases are, however, probably manifested most sharply in the optical properties, as a result of which optical studies have proved to be the most sensitive method for studying blue phases and have provided most of the information on these surprising and still puzzling liquid-crystalline phases.

c) Theoretical results

Brazovskii *et al.*,^{33,34} having pointed out the general direction of study, left adequate scope for the construction of specific theoretical models of the blue phase and for the development of methods for studying this phase. Hornreich, Shtrikman *et al.*⁵⁵⁻⁶¹ have worked most actively with Landau's theory. This group makes definite assertions about the structure of the phases BP I and BP II and has begun study⁶⁰ of the fog phase (BP III) as well as the effect of an external field on the blue phase.¹²³ A detailed analysis of the possible structures of the blue phase was carried out by Kleinert and Maki within the framework of Landau's theory.⁶² Kleinert also studied the relation between the cholesteric pitch and the period of the blue phase as a function of the number and magnitude of the harmonics in the Fourier expansion of the dielectric permittivity tensor of the blue phase.⁶³ It follows from the theory that the period of the blue phase is not shorter than the pitch of the helix, and the longer the pitch, the higher is the harmonic represented in the Fourier expansion. This is in agreement with the observational data, in particular, with the observed increase in the period of the

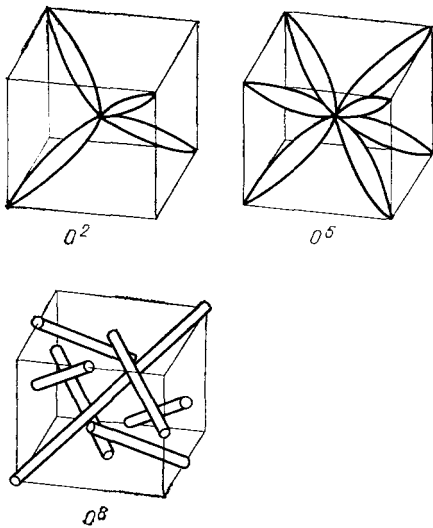


FIG. 13. The structure of disclinations in cubic cells of different space groups.⁷⁸

blue phase as the temperature is lowered.

An alternative approach to the description of the blue phase, based on a modification of Frank's theory, was proposed by Meiboom *et al.*⁶⁴⁻⁶⁶ This theory, starting from the description of the structure with the help of the director, predicts the existence of a three-dimensional lattice of linear defects (disclinations) in the director field in the blue phase (Fig. 13). The appearance of disclinations is linked to the fact that a double twisting of the director is locally energetically advantageous, but for topological reasons the double twisting of the director leads to the formation of disclinations. We note that, as will be shown below, a structure similar to the disclination structure can also be obtained within the framework of Landau's theory.

We shall mention an even earlier variant of the theory of the blue phase, proposed by Finn and Cladis.⁴⁸ Based on microscopic optical observations and thermodynamic considerations they proposed an emulsion model for the structure of the blue phases: BP I is the emulsion of spatially ordered intrusions of the isotropic phase into the cholesteric matrix; BP II is an emulsion of spatially ordered, cholesteric, spherical, microscopic formations in the isotropic phase; and BP III is a disordered emulsion of cholesteric intrusions in the isotropic phase (Fig. 14). For all its attractiveness, this model, which solves the problem of the structure of all three modifications of the blue phase at once, has still not been adequately substantiated.

Because of the informativeness of optical studies of the blue phase, considerable attention has been devoted to the theory of its optical properties. The relationship between the selective scattering of the blue phase and its symmetry properties was studied in Refs. 57, 67, and 68, and the pretransitional rotation of the polarization plane of light near the point of the transition into the blue phase was studied in Refs. 69 and 70.

The fog phase remains possibly the most puzzling and least studied phase from both the theoretical and experimental viewpoints (see Refs. 39, 60, 48). Most investigators feel,

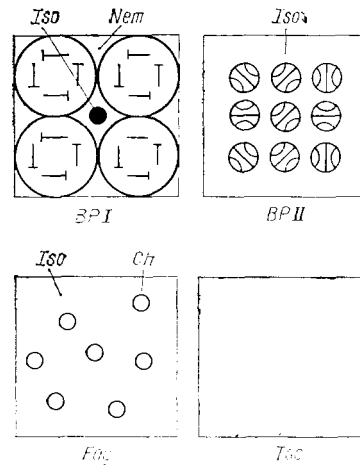


FIG. 14. The qualitative form of the structure of blue phases in the emulsion theory.^{48,115}

however, that the 100-year old puzzle of the blue phase is close to being completely solved, since physical models appropriate to the nature of the blue phase and methods for describing it and studying it experimentally have been found.

3. THEORETICAL MODELS OF THE BLUE PHASE

a) The dielectric permittivity tensor and the order parameter

As mentioned in the Introduction, blue phases exist in the temperature range between the isotropic liquid and the cholesteric. It is therefore natural to suppose that the blue phase is structurally similar to the cholesteric, i.e., the centers of gravity of the molecules are randomly distributed but the molecules have some predominant orientation, which can be different at different points \mathbf{r} . We shall accordingly select the parameter of orientational order in the blue phase, as in cholesterics and nematics, in the form of a traceless rank-two tensor $\hat{Q}(\mathbf{r})$, characterizing the degree of the predominant orientation of the molecules at each point.^{1,2} In nematics and cholesterics the order parameter is usually assumed to be a uniaxial tensor, which is expressed as follows in terms of the director \mathbf{n} (the unit vector fixing the predominant direction of orientation of the molecules):

$$Q_{ij} = S \left(n_i n_j - \frac{1}{3} \delta_{ij} \right), \quad (3.1)$$

where $S = (3 \langle \cos^2 \theta \rangle - 1) / 2$, and the brackets indicate averaging over the orientation of the molecules; θ is the angle between the director and the long axis of the molecule; and, the scalar S is also often called the order parameter, because it characterizes quantitatively the degree of orientation of the molecules. Generally speaking, however, the tensor \hat{Q} is biaxial both in cholesteric crystals and in the blue phase, and according to both theory and experiment the biaxial nature of \hat{Q} is maximum near the transition into the isotropic phase and is of the order of (ξ/p) (ξ is the correlation length at the transition point and p is the pitch of the helix).^{2,71} We shall therefore assume below that the tensor \hat{Q} is biaxial, i.e., we shall not require that it be represented in the form (3.1).

We shall now discuss the relationship between the physical characteristics of the liquid crystal and the order-parameter tensor. In principle any tensor or scalar equilibrium characteristic of the blue phase (more precisely, its difference from the corresponding characteristic in the isotropic phase) can be expressed, based on symmetry considerations, in the form of a series in powers of the tensor $\hat{Q}(\mathbf{r})$ and its derivatives. The expression for the free energy is presented below as an example [see (3.26)]. Phenomenological expressions can be obtained in an analogous manner for the viscosity, density, elastic moduli, and other physical quantities.

It may thus be regarded that the most characteristic physical properties of a liquid crystal are determined in terms of the order parameter $\hat{Q}(\mathbf{r})$, and the spatial structure of the crystal is given simply by the variation of the tensor $\hat{Q}(\mathbf{r})$ in space. However, because the transition from the isotropic liquid into the liquid crystal is a first-order transition and the jump in the order parameter is not very small (experimentally $S \sim 0.3$ for the transition into the cholesteric phase and somewhat smaller at the point of the transition into the blue phase), the expansions of physical quantities in powers of \hat{Q} in most cases are suitable only for semiquantitative estimates. In combination with symmetry considerations, such expansions are nevertheless very useful.

Thus, for example, the existence of a predominant orientation of molecules is manifested in the dielectric characteristics by the fact that the dielectric permittivity tensor of the blue phase $\hat{\epsilon}^d(\mathbf{r})$, just as of other types of liquid crystals, is locally anisotropic. If the anisotropic traceless part $\hat{\epsilon}(\mathbf{r})$ is separated from $\hat{\epsilon}^d(\mathbf{r})$

$$\epsilon_{ij} = \epsilon_{ij}^d - \frac{1}{3} S_p (\hat{\epsilon}^d)_{ij}, \quad (3.2)$$

then in the case of uniaxial crystals [the order parameter has the form (3.1)] it follows immediately from symmetry considerations that the tensor $\hat{\epsilon}$ is proportional to \hat{Q} :

$$\epsilon_{ij} = 4\pi A \gamma_a N_m Q_{ij} \equiv \epsilon_a \left(n_i n_j - \frac{1}{3} \delta_{ij} \right), \quad (3.3)$$

where $\gamma_a = \gamma_{\parallel} - \gamma_{\perp}$ is the anisotropy of the polarizability of one molecule, N_m is the number of molecules per unit volume, and A is a coefficient of proportionality of order unity, which appears because of the effects of the local field.⁷² The value of ϵ_a is numerically small in the blue phase and in cholesterics: $|\epsilon_a| \lesssim 0.1$ in the optical frequency range.

If, however, the crystal is biaxial, then the expression (3.3) is generally speaking not valid, since the principal axes of the tensors $\hat{\epsilon}$ and \hat{Q} may not coincide because of the anisotropy of the local field. In the case of small anisotropy of ϵ_a and small biaxiality η (η is defined below), however, the corrections to (3.3) are of the order of $\eta \epsilon_a^2$ and can be neglected.

It will therefore be assumed everywhere below that $\hat{\epsilon}$ is proportional to \hat{Q} and, as is usually done,^{33,34} $\hat{\epsilon}$ will be used below as the order parameter.

We note that a tensor of rank four can also be used to give a phenomenological description of the liquid-crystal phase transition.¹⁰⁵ This approach, however, precludes a complete description of the spatial symmetry of the ordered

phase (in the best case it determines only its crystal class). Using a spatially modulated rank-two tensor as the order parameter of the blue phase, however, makes possible the description of not only the crystal class but also the space group of the blue phase. The theory presented below can be regarded ideologically as an extension of Landau's theory⁷³ to a liquid-crystal transition in which the modulation of a scalar quantity (density) is used as the order parameter.

b) Symmetry restrictions on the order parameter

1) Local characteristics

As follows from the definition (3.2), the tensor $\hat{\epsilon}$, which, unless otherwise stated, will be assumed to be real, is a symmetrical traceless tensor of rank two. Such a tensor can be locally completely specified by five real numbers, which are functions of the coordinates (for example, three nondiagonal and two diagonal elements). The symmetry of the crystal imposes additional restrictions on the components of the order parameter. For example, in uniaxial nematic crystals with a symmetry axis of infinite order the tensor $\hat{\epsilon}$ has the form (3.1). The quantity S , which depends on the thermodynamic quantities (for example, on the temperature) and can be calculated in some theory or other (for example, Landau's theory; see Sec. 3c), is therefore the only remaining parameter.

As another example we shall study a cholesteric^{1,6} which exhibits a one-dimensional helical structure. This means that the properties of the cholesteric are invariant under a rotation of the crystal by an angle φ around the axis of the helix (which we choose to be the z axis) and a simultaneous displacement along z by $\varphi p / 2\pi$ (p is the pitch of the helix). Locally the cholesteric has two mutually orthogonal second-order axes orthogonal to the z axis. In these axes the tensor $\hat{\epsilon}$ is diagonal (point symmetry 222)

$$\hat{\epsilon} = \begin{pmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_2 & 0 \\ 0 & 0 & \epsilon_3 \end{pmatrix}, \quad (3.4)$$

where $\epsilon_1 + \epsilon_2 + \epsilon_3 = 0$. Experiment shows that in all cholesterics the tensor $\hat{\epsilon}$ is almost uniaxial, i.e., in (3.4) two principal values almost coincide, for example $\epsilon_2 \approx \epsilon_3$. It is therefore convenient to introduce a parameter η characterizing the biaxial nature of $\hat{\epsilon}$:

$$\hat{\epsilon} = \frac{\epsilon_1}{2} \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 + \eta & 0 \\ 0 & 0 & -1 - \eta \end{pmatrix}, \quad (3.5)$$

where $\eta = (\epsilon_2 - \epsilon_3) / \epsilon_1 = (2\epsilon_2 + \epsilon_1) / \epsilon_1$. When $\eta = 0$ (3.5) becomes a uniaxial tensor. We underscore once again, however, that based on purely symmetry considerations in general $\epsilon_2 \neq \epsilon_3$, since the z axis corresponding to ϵ_3 is distinguished—this is the axis of the helix. At an arbitrary point z the tensor $\hat{\epsilon}(z)$ is obtained from (3.5) by a rotation by an angle φ :

$$\hat{\epsilon}(z) = \hat{T}_\varphi \hat{\epsilon} \hat{T}_\varphi^{-1}, \quad (3.6)$$

where T_φ is the matrix describing a rotation by an angle φ

around the z axis. From here we obtain the tensor $\hat{\varepsilon}(z)$ in the cholesteric

$$\hat{\varepsilon}(z) = \frac{\varepsilon_1}{4} \begin{pmatrix} 1 + \eta + (3 - \eta) \cos 2\varphi & (3 - \eta) \sin 2\varphi & 0 \\ (3 - \eta) \sin 2\varphi & 1 + \eta - (3 - \eta) \cos 2\varphi & 0 \\ 0 & 0 & -2 - 2\eta \end{pmatrix}. \quad (3.7)$$

Two parameters ε_1 and ε_2 (or ε_1 and η) are functions of the thermodynamic quantities and the pitch of the spiral (in Sec. 3c it is shown how they can be calculated).

The most general form of the tensor $\hat{\varepsilon}(\mathbf{r})$ in the blue phase,⁶⁷ i.e., the most general form of the tensor that is invariant under all transformations of the space group describing the symmetry properties of the blue phase, can be determined in an analogous manner from symmetry considerations. Experiments show^{26,27,38-40,43} that the observed symmetry of the blue phases is described by cubic space groups.

In studying the symmetry properties of $\hat{\varepsilon}(\mathbf{r})$ in the blue phases we shall make use of a general feature of all cubic groups: the existence of a third-order symmetry axis oriented along the diagonal of the cube. The existence of such an axis leads to the fact that all components of the tensor $\hat{\varepsilon}(\mathbf{r})$ depend on two arbitrary periodic functions of the coordinates $f_1(\mathbf{r})$ and $f_2(\mathbf{r})$:

$$\hat{\varepsilon}(\mathbf{r}) = \begin{pmatrix} f_1(x, y, z) & f_2(x, y) & f_2(y, z, x) \\ f_2(x, x, y) & f_1(y, z, x) & f_2(x, y, z) \\ f_2(y, z, x) & f_2(x, y, z) & f_1(z, x, y) \end{pmatrix}. \quad (3.8)$$

It may be directly verified that the tensor (3.8) is indeed invariant under rotations by 120 and 240° around the third-order axis, which is equivalent to simple cyclical permutation of the coordinates x, y, z and a corresponding cyclical permutation of the components of the tensor $\hat{\varepsilon}(\mathbf{r})$ (for example, $x \rightarrow y \rightarrow z \rightarrow x$, $\varepsilon_{xx} \rightarrow \varepsilon_{yy} \rightarrow \varepsilon_{zz} \rightarrow \varepsilon_{xx}$ etc.).

Aside from the third-order axes, the cubic groups necessarily contain other symmetry elements—second- and fourth-order rotational axes, screw axes, and translations (because of the chirality of the blue phases we do not study groups with centers of inversion⁷⁴ and reflection planes, i.e., our analysis is restricted to enantiomorphic groups). These symmetry elements further restrict the form of the functions $f_i(\mathbf{r})$.^{67,75} Thus for the groups $T^1 - P23$, $T^2 - F23$, $T^3 - I23$, because of the presence of second-order rotational axes, the functions $f_i(\mathbf{r})$ satisfy the following relations:

$$\begin{aligned} f_1(x, y, z) &= f_1(x, \bar{y}, \bar{z}) = f_1(\bar{x}, \bar{y}, z) = f_1(\bar{x}, y, \bar{z}), \\ f_2(x, y, z) &= f_2(x, \bar{y}, \bar{z}) = -f_2(\bar{x}, \bar{y}, z) \\ &= -f_2(\bar{x}, y, \bar{z}), \end{aligned} \quad (3.9)$$

where $\bar{x} = -x$, $\bar{y} = -y$, $\bar{z} = -z$. For the groups $T^4 - P2_13$ and $T^5 - I2_13$, because of the presence of the screw axes 2_1 we have

$$\begin{aligned} f_1(x, y, z) &= f_1\left(\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}\right) = f_1\left(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z\right) \\ &= f_1\left(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z\right), \end{aligned} \quad (3.10)$$

$$\begin{aligned} f_2(x, y, z) &= f_2\left(\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}\right) \\ &= -f_2\left(\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z\right) \\ &= -f_2\left(\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z\right). \end{aligned}$$

All remaining cubic groups contain the subgroups T^1 or T^4 , and for this reason the relations (3.9) or (3.10) and the following additional relations also hold for them: for $O^1 - P432$, $O^3 - F432$ and $O^5 - I432$ the relations (3.9) and

$$f_i(x, y, z) = f_i(\bar{x}, \bar{z}, \bar{y}), \quad (3.11)$$

for $O^2 - P4_232$ the relations (3.9) and

$$f_i(x, y, z) = f_i\left(\frac{1}{2} - x, \frac{1}{2} - z, \frac{1}{2} - y\right), \quad (3.12)$$

for $O^4 - F4_132$, $O^6 - P4_332$, $O^8 - I4_132$ the relations (3.10) and

$$f_i(x, y, z) = f_i\left(\frac{1}{4} - x, \frac{1}{4} - z, \frac{1}{4} - y\right), \quad (3.13)$$

and, for $O^7 - P4_132$ the relations (3.10) and

$$f_i(x, y, z) = f_i\left(\frac{3}{4} - x, \frac{3}{4} - z, \frac{3}{4} - y\right). \quad (3.14)$$

In addition, for body-centered groups ($I23$, $I2_13$, $I432$, $I4_132$) the additional relation

$$f_i(x, y, z) = f_i\left(\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z\right), \quad (3.15)$$

holds, while for face-centered groups ($F23$, $F432$, $F4_132$) the additional relation

$$\begin{aligned} f_i(x, y, z) &= f_i\left(\frac{1}{2} + x, \frac{1}{2} + y, z\right) \\ &= f_i\left(\frac{1}{2} + x, y, \frac{1}{2} + z\right) \\ &= f_i\left(x, \frac{1}{2} + y, \frac{1}{2} + z\right). \end{aligned} \quad (3.16)$$

holds. It should be noted that the relations (3.9)–(3.14) are presented for coordinate systems whose axes are oriented along the edges of the cubic unit cell, and the origin is located at the point with maximum point symmetry.⁷⁴ No other relations follow from the requirements that $\hat{\varepsilon}(\mathbf{r})$ be invariant under transformations of enantiomorphic cubic space groups. Of course, the expressions (3.9)–(3.16) are not sufficient for determining the form of the functions $f_i(\mathbf{r})$, but they do impose strong restrictions on the tensor $\hat{\varepsilon}(\mathbf{r})$ and the spatial Fourier harmonics represented in it, as well as on the phase relations between different Fourier harmonics.

2) Fourier representation of the order parameter

We shall expand the tensor $\hat{\varepsilon}(\mathbf{r})$ in a Fourier series in terms of reciprocal-lattice vectors of the crystal τ :

$$\hat{\varepsilon}(\mathbf{r}) = \sum_{\tau} \hat{\varepsilon}^{\tau} \exp(i\tau\mathbf{r}), \quad (3.17)$$

where $\tau = (2\pi/d)(h\mathbf{x} + k\mathbf{y} + l\mathbf{z})$; $\mathbf{x}, \mathbf{y}, \mathbf{z}$ are the unit coordinate axes; h, k , and l are arbitrary integers called Miller indices; d is the size of the unit cell of the crystal; and the

Fourier harmonics $\hat{\varepsilon}^\tau$ are determined by the relation

$$\hat{\varepsilon}^\tau = \frac{1}{d^3} \int \hat{\varepsilon}(\mathbf{r}) \exp(-i\tau\mathbf{r}) d\mathbf{r} \quad (3.18)$$

[the integration in (3.18) extends over the volume of the unit cell]. First of all, from the form of the tensor $\hat{\varepsilon}(\mathbf{r})$ (3.8) or from (3.18) it follows that $\hat{\varepsilon}^\tau$ in cubic crystals has the form

$$\hat{\varepsilon}^{hkl} = \begin{pmatrix} f_1^{hkl} & f_2^{hkh} & f_2^{hkh} \\ f_2^{hkh} & f_1^{hkl} & f_2^{hkl} \\ f_2^{hkh} & f_2^{hkh} & f_1^{hkl} \end{pmatrix}, \quad (3.19)$$

where

$$f_i^{hkl} = \frac{1}{d^3} \int f_i(x, y, z) \exp[2\pi i(hx + ky + lz)] d^3r. \quad (3.20)$$

It follows from (3.19) and the traceless nature of the tensor $\hat{\varepsilon}$ that the Fourier harmonics $\hat{\varepsilon}^{hkl}$, $\hat{\varepsilon}^{lkh}$ and $\hat{\varepsilon}^{khk}$ are expressed in terms of the same set of five (in general complex) numbers. Further, from (3.20), using the properties of the functions $f_i(x, y, z)$ (3.9)–(3.16), we can obtain restrictions on the quantities f_i^{hkl} for particular reflections (they are presented in Table I). These relations, as will be evident from what follows, substantially simplify the analysis of the optical properties of the blue phase and of phase transitions in it.

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

Indices of reflections	Types	ε_{xx}^τ	ε_{yy}^τ	ε_{xy}^τ	ε_{xz}^τ	ε_{yz}^τ	m	
T^1, T^2, T^3								
$h00$	c	R	R_1	0	0	I	$0, \pm 2$	
$hk0$	c	R	R_1	R_2	I	I_1	$0, \pm 1, \pm 2$	
hhh	c	0	0	C	C	C	0	
hkl	c	C	C_1	C_2	C_3	C_4	$0, \pm 1, \pm 2$	
T^4, T^5								
$h00$	$\begin{cases} h=2n+1 \\ h=2n \end{cases}$	$\begin{cases} * \\ c \end{cases}$	$\begin{cases} 0 \\ R \end{cases}$	$\begin{cases} 0 \\ R_1 \end{cases}$	$\begin{cases} I \\ 0 \end{cases}$	$\begin{cases} R \\ 0 \end{cases}$	$\begin{cases} 0 \\ I \end{cases}$	$\begin{cases} \pm 1 \\ 0, \pm 2 \end{cases}$
$hk0$	$\begin{cases} h=2n+1 \\ h=2n \end{cases}$	$\begin{cases} c \\ c \end{cases}$	$\begin{cases} I \\ R \end{cases}$	$\begin{cases} I_1 \\ R_1 \end{cases}$	$\begin{cases} I_2 \\ R_2 \end{cases}$	$\begin{cases} R \\ I \end{cases}$	$\begin{cases} R_1 \\ I_1 \end{cases}$	$\begin{cases} 0, \pm 1, \pm 2 \\ 0, \pm 1, \pm 2 \end{cases}$
hhh	c	0	0	C	C	C	0	
hkl	c	C	C_1	C_2	C_3	C_4	$0, \pm 1, \pm 2$	
O^6, O^8								
$h00$	$\begin{cases} h=4n \pm 1 \\ h=4n \pm 2 \\ h=4n \end{cases}$	$\begin{cases} * \\ *, c \end{cases}$	$\begin{cases} 0 \\ 0 \\ -2R \end{cases}$	$\begin{cases} 0 \\ R \\ R \end{cases}$	$\begin{cases} \mp iR \\ 0 \\ 0 \end{cases}$	$\begin{cases} R \\ 0 \\ 0 \end{cases}$	$\begin{cases} 0 \\ I \\ 0 \end{cases}$	$\begin{cases} 1 \\ \pm 2 \\ 0 \end{cases}$
$hh0$	$\begin{cases} h=2n+1 \\ h=2n \end{cases}$	$\begin{cases} c \\ c \end{cases}$	$\begin{cases} I \\ R \end{cases}$	$\begin{cases} I \\ R \end{cases}$	$\begin{cases} I_1 \\ R_1 \end{cases}$	$\begin{cases} R \\ I \end{cases}$	$\begin{cases} -R \\ -I \end{cases}$	$\begin{cases} 0, \pm 2 \\ 0, \pm 2 \end{cases}$
hhh	$\begin{cases} h=4n \pm 1 \\ h=4n \pm 2 \\ h=4n \end{cases}$	$\begin{cases} c \\ c \\ c \end{cases}$	$\begin{cases} 0 \\ 0 \\ 0 \end{cases}$	$\begin{cases} 0 \\ 0 \\ 0 \end{cases}$	$\begin{cases} (1 \mp i)R \\ I \\ R \end{cases}$	$\begin{cases} (1 \mp i)R \\ I \\ R \end{cases}$	$\begin{cases} (1 \mp i)R \\ I \\ R \end{cases}$	$\begin{cases} 0 \\ 0 \\ 0 \end{cases}$
hkl	c	C	C_1	C_2	C_3	C_4	$0, \pm 1, \pm 2$	
O^1, O^3, O^5								
$h00$	c	$-2R$	R	0	0	0	0	
$hh0$	c	R	R	R_1	I	$-I$	$0, \pm 2$	
hhh	c	0	0	R	R	R	0	
hkl	c	C	C_1	C_2	C_3	C_4	$0, \pm 1, \pm 2$	
O^2								
$h00$	$\begin{cases} h=2n+1 \\ h=2n \end{cases}$	$\begin{cases} *, c \\ *, c \end{cases}$	$\begin{cases} 0 \\ -2R \end{cases}$	$\begin{cases} R \\ R \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} 0 \\ 0 \end{cases}$	$\begin{cases} I \\ 0 \end{cases}$	$\begin{cases} \pm 2 \\ 0 \end{cases}$
$hh0$	c	R	R	R_1	I	$-I$	$0, \pm 2$	
hhh	c	R	R_1	R_2	I	I_1	$0, \pm 1, \pm 2$	
hkl	c	C	C_1	C_2	C_3	C_4	$0, \pm 1, \pm 2$	
O^4, O^7								
$h00$	$\begin{cases} h=4n \pm 1 \\ h=4n \pm 2 \\ h=4n \end{cases}$	$\begin{cases} * \\ *, c \end{cases}$	$\begin{cases} 0 \\ 0 \\ -2R \end{cases}$	$\begin{cases} 0 \\ R \\ R \end{cases}$	$\begin{cases} \pm iR \\ 0 \\ 0 \end{cases}$	$\begin{cases} R \\ 0 \\ 0 \end{cases}$	$\begin{cases} 0 \\ I \\ 0 \end{cases}$	$\begin{cases} -1 \\ \pm 2 \\ 0 \end{cases}$
$hh0$	$\begin{cases} h=2n+1 \\ h=2n \end{cases}$	$\begin{cases} c \\ c \end{cases}$	$\begin{cases} I \\ R \end{cases}$	$\begin{cases} I \\ R \end{cases}$	$\begin{cases} I_1 \\ R_1 \end{cases}$	$\begin{cases} R \\ I \end{cases}$	$\begin{cases} -R \\ -I \end{cases}$	$\begin{cases} 0, \pm 2 \\ 0, \pm 2 \end{cases}$
hhh	$\begin{cases} h=4n \pm 1 \\ h=4n \pm 2 \\ h=4n \end{cases}$	$\begin{cases} c \\ c \\ c \end{cases}$	$\begin{cases} 0 \\ 0 \\ 0 \end{cases}$	$\begin{cases} 0 \\ 0 \\ 0 \end{cases}$	$\begin{cases} (1 \pm i)R \\ I \\ R \end{cases}$	$\begin{cases} (1 \pm i)R \\ I \\ R \end{cases}$	$\begin{cases} (1 \pm i)R \\ I \\ R \end{cases}$	$\begin{cases} 0 \\ 0 \\ 0 \end{cases}$
hkl	c	C	C_1	C_2	C_3	C_4	$0, \pm 1, \pm 2$	

$R, I,$ and C are real, imaginary, and complex quantities, respectively; the letter c denotes chiral reflections, while the asterisk denotes reflections which become allowed as a result of the local anisotropy of $\hat{\varepsilon}$. The condition for the existence of reflections for body-centered lattices (T^3, T^5, O^5, O^8) is $h + k + l = 2n$, while for face-centered lattices (T^2, O^3, O^4) the condition is that $h, k,$ and l must have the same parity.

The expressions presented above for the order parameter $\hat{\varepsilon}(\mathbf{r})$ and its Fourier harmonics were obtained in the single coordinate system presented above. It is often convenient to study each Fourier harmonic $\hat{\varepsilon}^\tau$ in its own coordinate system, in which one of the axes (the z axis) is oriented along τ while the other two axes are perpendicular to τ . In this coordinate system the tensor $\hat{\varepsilon}^\tau$ can be expanded in terms of five basis tensors $\hat{\sigma}_m$ ($m = 0, \pm 1, \pm 2$), each of which has the property that its transformation under rotations of the coordinate system around τ by an angle φ reduces to multiplication by $\exp(im\varphi)$ (i.e., the tensor $\hat{\varepsilon}^\tau$ can be expanded in terms of the irreducible representations of the group of rotations around the vector τ):

$$\hat{\varepsilon}^\tau = \sum_{m=-2}^2 \varepsilon(\tau; m) \hat{\sigma}_m, \quad (3.21)$$

where $\varepsilon(\tau; m)$ are the coefficients in the expansion, and

$$\hat{\sigma}_0 = \frac{1}{\sqrt{6}} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad \hat{\sigma}_{\pm 1} = \frac{1}{2} \begin{pmatrix} 0 & 0 & \pm i \\ 0 & 0 & 1 \\ \pm i & 1 & 0 \end{pmatrix},$$

$$\hat{\sigma}_{\pm 2} = \frac{1}{2} \begin{pmatrix} 1 & \mp i & 0 \\ \mp i & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (3.22)$$

The basis tensors $\hat{\sigma}_m$ can also be expressed in terms of the vectors τ and $\mathbf{m} = (\mathbf{m}_1 - i\mathbf{m}_2)/\sqrt{2}$ (where the unit vectors $\mathbf{m}_1, \mathbf{m}_2$ and $\tau/|\tau|$ form a right-handed triplet):

$$\left. \begin{aligned} (\hat{\sigma}_0)_{ij} &= (3\tau_i\tau_j - \tau^2\delta_{ij}) \frac{1}{\sqrt{6}\tau^2}, \\ (\hat{\sigma}_1)_{ij} &= (m_i\tau_j + m_j\tau_i) \frac{1}{\sqrt{2}|\tau|}, \quad \hat{\sigma}_{-1} = \hat{\sigma}_1^*, \\ (\hat{\sigma}_2)_{ij} &= m_im_j, \quad \hat{\sigma}_{-2} = \hat{\sigma}_2^*. \end{aligned} \right\} \quad (3.23)$$

The expansion (3.21) is especially useful if the vector τ is parallel to one of the symmetry axes of the crystal. Selection rules with respect to m , characterizing the space group, appear for the corresponding Fourier harmonics in this case.⁵⁷ These rules determine for each group and for each τ those m for which $\varepsilon(\tau; m) \neq 0$ in (3.21).

We shall illustrate this assertion by a specific example. Let the vector τ be oriented parallel to the second-order axis. The tensor $\hat{\varepsilon}(\mathbf{r})$ does not change under rotations by an angle π around this axis and, therefore, the corresponding Fourier component $\hat{\varepsilon}^\tau$ also must not change. As noted above, however, the basis tensors $\hat{\sigma}_m$ acquire under such a rotation a factor $\exp(im\pi)$. When $m = \pm 1$ this factor is equal to -1 , and therefore terms with $m = \pm 1$ must be absent in (3.21). If the vector τ is parallel to the third- or fourth-order axes, then only the term with $m = 0$ remains in (3.21). The selection rules for the case when the vector τ is parallel to the screw axis n_j can be found in an analogous manner. In this case, terms with those values of m for which $(m - jh)/n$ is not equal to an integer (for definiteness the screw axis here is assumed to be parallel to the x axis and $\tau = 2\pi h\mathbf{x}/d$ vanish in (3.21). The selection rules found in this manner were used in constructing Table I (see the last column).

Symmetry restrictions are thus most important for the Fourier harmonics $\hat{\varepsilon}^\tau$ with vectors τ parallel to the symmetry axes [for cubic crystals these are vectors of the type $(h00)$, $(hh0)$, and (hhh)]. In addition, using the expres-

sions (3.9)–(3.14), (3.19), and (3.20), the equivalent Fourier harmonics can be interrelated and all these Fourier harmonics can therefore be expressed in terms of one of them. Fourier harmonics corresponding to vectors $\hat{\tau}$ transforming into one another under the symmetry operations contained in the space group of the crystal are said to be equivalent. Moreover, it turns out that for equivalent Fourier harmonics the components (modes) of the expansion (3.21) with fixed m can be expressed in terms of one of these components. The totality of these equivalent modes will be denoted below by the symbol $[hkl; m]$. Symmetry considerations do not, however, yield any relations between nonequivalent Fourier harmonics, for example, Fourier harmonics with different $|\tau|$. Therefore, in general, an infinite number of parameters is required in order to determine the structure of the blue phase.

Experiment shows, however, that actually only a small number of parameters is important. Thus two reflections (100) and (110) (and reflections equivalent to them) are observed for BP II (the probably group is O^2) and three reflections (110), (200), and (211) (and reflections equivalent to them) are observed for BP I (the group O^8). Polarization measurements show^{26,27,38} that modes with $m = 2$ make by far the greatest contribution to the observed reflections. Including only the enumerated modes, with the help of (3.17) and (3.21)–(3.23) we obtain the following expressions for the functions $f_i(\mathbf{r})$, determining in accordance with (3.8) the spatial structure of the order-parameter tensor $\hat{\varepsilon}(\mathbf{r})$:

$$\begin{aligned} f_1(x, y, z) &= \varepsilon(100; 2)(C_z - C_y) \\ &\quad + \varepsilon(110; 2)[2C_yC_z - C_x(C_y + C_z)], \\ f_2(x, y, z) &= -\varepsilon(100; 2)S_x \\ &\quad + \varepsilon(110; 2)[\sqrt{2}S_x(C_y - C_z) - S_yS_z]; \end{aligned} \quad (3.24)$$

for O^2 and

$$\begin{aligned} f_1(x, y, z) &= \varepsilon(110; 2)(2S_yC_z - S_xC_y - S_zC_x) \\ &\quad + \varepsilon(200; 2)(C_{2z} - C_{2y}) \\ &\quad + (2/3)\varepsilon(211; 2)[2\sqrt{6}(C_{2z}S_xC_y - C_{2y}S_zC_x) \\ &\quad - 2S_{2x}C_yS_z + S_{2y}C_zS_x \\ &\quad + S_{2z}C_xS_y], \quad (3.25) \\ f_2(x, y, z) &= \varepsilon(110; 2)[S_zC_y - \sqrt{2}(C_xC_y + S_xS_z)] \\ &\quad - \varepsilon(200; 2)S_{2x} \\ &\quad + (2/3)\varepsilon(211; 2)[-\sqrt{6}(S_{2z}S_xS_y + S_{2y}C_zC_x) \\ &\quad - 5S_{2x}S_yC_z - 2C_{2z}C_xC_y \\ &\quad + 2C_{2y}S_zS_x], \end{aligned}$$

for O^8 , where the notation $C_x = \cos(2\pi x/d)$, $S_x = \sin(2\pi x/d)$, etc. was introduced. For reasons of symmetry the coefficients $\varepsilon(hkl; 2)$ in expressions (3.24) and (3.25) are real. Their absolute values and signs must be determined either experimentally or theoretically. In the next

section it will be shown how the theory of phase transitions, aside from symmetry considerations, also restricts the number of nonzero parameters in the expansions (3.17) and (3.21) and specifies the structure of the blue phase.

c) Phase transitions (Landau's theory)

1) The free energy and characteristic modes

As mentioned already, liquid crystals are distinguished by the large variety of phase transitions. Landau's theory is currently most widely used to describe these transitions theoretically. The comparative simplicity of this theory, the small number of free parameters (which can be measured experimentally), and the nontriviality and diversity of its predictions make this theory very attractive and interesting. We shall therefore begin our description of phase transitions in the blue phase with Landau's theory.

We shall study the isotropic-liquid-liquid-crystal phase transition, in which the order parameter is the tensor $\hat{\varepsilon}(\mathbf{r})$ introduced above. The corresponding theory for the isotropic-liquid-nematic-cholesteric transition was developed by de Gennes,⁷⁶ while Brazovskii, Dmitriev, and Filev^{33,34} and Hornreich and Shtrikman⁵⁵⁻⁶⁶ developed the theory for the isotropic-liquid-blue-phase-cholesteric transition. Brazovskii and Dmitriev showed that depending on the ratio of the parameters in Landau's expansion of the free energy the isotropic-liquid-liquid-crystal phase transition can correspond both to a direct isotropic-liquid-cholesteric transition and to a transition through intermediate phases that are linked to the observed blue phases. It is significant that the intermediate phases exhibit a three-dimensional spatial modulation of the order parameter and are realized for cholesterics with a quite short pitch. Developing this approach, Alexander¹⁷ and Hornreich and Shtrikman⁵⁵⁻⁶¹ specified the structure of the intermediate phases and showed that several intermediate phases with a cubically symmetrical order-parameter field can be realized in a narrow temperature interval between the isotropic liquid and the cholesteric.

We shall now give a detailed exposition of the corresponding theoretical results. The expansion of the free energy in powers of the order parameter and its derivatives has the following form^{33,76}:

$$F = F_0 + F_2\{\hat{\varepsilon}\} + F_3\{\hat{\varepsilon}\} + F_4\{\hat{\varepsilon}\}, \quad (3.26)$$

where F_0 is independent of $\hat{\varepsilon}$, while F_2 , F_3 , and F_4 contain second, third, and fourth powers of $\hat{\varepsilon}$:

$$F_2 = \frac{1}{2} \int d\mathbf{r} \left[a \text{Sp}(\hat{\varepsilon}^2) + c_1 \left(\frac{\partial \varepsilon_{jk}}{\partial x_i} \right)^2 + c_2 \left(\frac{\partial \varepsilon_{ij}}{\partial x_i} \right)^2 + 2c_1 q_C e_{ij} e_{il} \frac{\partial \varepsilon_{jl}}{\partial x_k} \right], \quad (3.27)$$

$$F_3 = \beta \int d\mathbf{r} \text{Sp}(\hat{\varepsilon}^3), \quad (3.28)$$

$$F_4 = \gamma \int d\mathbf{r} [\text{Sp}(\hat{\varepsilon}^2)]^2. \quad (3.29)$$

In (3.26)–(3.29) as is usual in Landau's theory, the coefficient a is proportional to $T - T_c$ where T_c is the temperature of the absolute instability of the isotropic liquid

relative to a transition into the nematic phase with $q_C = 0$, $\beta = 0$, and the coefficients c_1 , c_2 , q_C , β , γ are assumed to be independent of T . These coefficients have the following physical significance: c_1 and c_2 are the elastic moduli of the liquid-crystalline phase; q_C is inversely proportional to the cholesteric pitch ($q_C \neq 0$ only in systems consisting of molecules with left-right asymmetry); the finite value of the coefficient β is linked to the physical nonequivalence of the states with $\hat{\varepsilon}$ and $-\hat{\varepsilon}^1$; γ ensures that the system is stable relative to an increase in $\hat{\varepsilon}$. The presence of a term in (3.27) with first derivatives (the so-called Lifshitz invariant) leads to the appearance of spatially nonuniform structures (cholesterics and blue phases).

At a fixed temperature T a structure that minimizes F is realized. This structure could be determined by writing Lagrange's equations corresponding to the functional (3.26) for $\hat{\varepsilon}(\mathbf{r})$, but this procedure yields a complicated system of nonlinear equations whose general solution is unknown⁶¹ [expression (3.26) is easily minimized only in the case $q_C = 0$; the corresponding structure (nematic) is obtained as a limiting case of the cholesteric in the limit $q_C \rightarrow 0$, and we shall not take the time to study it].

Because of this difficulty, in order to find the minimum of the functional (3.26) we shall first find the structure of the order parameter that minimizes its quadratic part $F_2\{\hat{\varepsilon}\}$. Using the Fourier expansion of the tensor $\hat{\varepsilon}(\mathbf{r})$ (3.17) and the expansion of $\hat{\varepsilon}^\tau$ in terms of the basis tensors (3.21) we find that the quadratic part can be diagonalized in the representation used,

$$F_2\{\hat{\varepsilon}\} = \sum_{\tau, m} \left\{ a + \left[c_1 + \frac{c_2(4-m^2)}{6} \right] \tau^2 - mc_1 q_C |\tau| \right\} \times |\varepsilon(\tau, m)|^2, \quad (3.30)$$

and the contribution of each component $\varepsilon(\tau, m)$ (i.e., of each normal mode) can be easily analyzed separately. The energy of each mode (the coefficient in front of $|\varepsilon(\tau, m)|^2$) is given by the expressions

$$\left. \begin{aligned} \delta_0(\tau) &= a + \left(c_1 + \frac{2c_2}{3} \right) \tau^2, \\ \delta_{\pm 1}(\tau) &= a + \left(c_1 + \frac{c_2}{2} \right) \tau^2 \mp c_1 q_C \tau, \\ \delta_{\pm 2}(\tau) &= a + c_1 \tau^2 \mp 2c_1 q_C \tau, \end{aligned} \right\} \quad (3.31)$$

where $\tau = |\tau|$. It follows from the condition of stability relative to the formation of structures with large τ that

$$c_1 > 0, \quad c_1 + \frac{2}{3} c_2 > 0. \quad (3.32)$$

From (3.31), under the condition (3.32), it also follows that the mode with $m = 2$ has the lowest energy (for definiteness we assume that $q_C > 0$); in this case

$$\delta_{2 \min} = \delta_2(\tau = q_C) = a - c_1 q_C^2. \quad (3.33)$$

It thus appears that the minimum of the free energy (3.24) should correspond to a structure in which only the mode with $m = 2$ is represented. Such a structure, however, by no means corresponds to the minimum of the cubic term $F_3\{\hat{\varepsilon}\}$ in (3.26). This is linked to the fact that structures with

$m = 2$ are substantially biaxial, while $F_3\{\hat{\varepsilon}\}$ reaches a minimum in uniaxial structures.¹¹⁶ To verify this, we diagonalize the tensor $\hat{\varepsilon}$ in the expression (3.28) for $F_3\{\hat{\varepsilon}\}$. Then

$$F_3\{\hat{\varepsilon}\} = 3\beta\varepsilon_1\varepsilon_2\varepsilon_3, \quad (3.34)$$

where $\varepsilon_1, \varepsilon_2, \varepsilon_3 = -\varepsilon_1 - \varepsilon_2$ are the eigenvalues of the tensor $\hat{\varepsilon}$ [see (3.4)]. Minimizing (3.32) under the condition that $\text{Sp}(\hat{\varepsilon}^2) = \text{const}$, we obtain

$$(\varepsilon_2 - \varepsilon_1)(\varepsilon_1 - \varepsilon_3) = 0. \quad (3.35)$$

The two solutions of (3.35), $\varepsilon_2 = \varepsilon_1$ and $\varepsilon_3 = \varepsilon_1$, evidently correspond to uniaxial structures, while the solution $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 0$ does not correspond to a minimum of $F_3\{\hat{\varepsilon}\}$.

The considerations presented above, though they are not entirely accurate, show that there is a contradiction between the square and cubic terms in the free energy: these terms reach their minima in different structures, and together they produce a minimum of the free energy for some compromise structure. The particular structure that appears as a result of the compromise depends on the value of q_C .

For small q_C ($q_C \ll \beta^2/\gamma$, i.e., a large pitch of the helix) the minimum of (3.24) is achieved in a one-dimensional helical structure (cholesteric), in which the mode with $\tau = 0$, $m = 0$ is present together with the mode $m = 2m$, $\tau = q_C$. When $q_C \gg \beta^2/\gamma$ the cubic structure with the space group O^5 , in which the modes [110; 2] are determining, is most advantageous.⁶¹ These modes make a negative contribution to the cubic term $F_3\{\hat{\varepsilon}\}$, which lowers the total free energy. For intermediate values of q_C structures in which the modes [100; 2] (the group O^2) of the modes [200; 2] and [211; 2] (the group O^8) are represented together with the modes [110; 2] are advantageous. These sets of spatial harmonics, further decreasing the free energy because of the cubic term, compensate the loss in the quadratic term appearing because of the fact that for harmonics with different τ $\delta_2(\tau)$ cannot be minimized simultaneously for all τ [see (3.31), (3.33)].

Parametrization of the free energy. Before we present the expressions for the free energies of different phases, it is convenient to put Eqs. (3.26)–(3.29) into dimensionless form in order to decrease the number of parameters in them. There are six parameters in all ($a, c_1, c_2, q_C, \beta, \gamma$), but by selecting the units of measurement of the free energy, temperature, and length the expression (3.26) can be represented in a form with three dimensionless parameters t, κ and c_2/c_1 :

$$\begin{aligned} f = & \frac{1}{4} \sum_i \left\{ t + 4\kappa^2 \left[1 + \frac{c_2}{6c_1} (4 - m^2) \right] \right. \\ & \times \left(\frac{\pi}{dq_C} \right)^2 (h^2 + k^2 + l^2) \\ & \left. - 2\kappa^2 m \frac{\pi}{dq_C} \sqrt{h^2 + k^2 + l^2} \right\} \mu_i^2 \\ & + \sum_{i, j, n} f_3^\Phi(i, j, n) \mu_i \mu_j \mu_n \\ & + \sum_{i, j, n, s} f_4^\Phi(i, j, n, s) \mu_i \mu_j \mu_n \mu_s, \end{aligned} \quad (3.36)$$

where d is the size of the unit cell,

$$\begin{aligned} f = & \frac{F}{\beta^4/36\gamma^3}, \quad t = \frac{12\gamma}{\beta^2} a, \quad \kappa^2 = q_C^2 \xi_1^2, \\ \xi_1^2 = & \frac{12\gamma}{\beta^3} c_1, \quad \mu_i = \frac{\sqrt{6N_i\gamma}}{\beta} \varepsilon(hkl; m) \end{aligned} \quad (3.37)$$

[we dropped in (3.36) the term that does not depend on $\hat{\varepsilon}$]. We emphasize that the summation in (3.36) extends not over separate modes, but rather over different sets of equivalent modes, which are enumerated by the index i , and the number N_i in the definition of μ_i represents the number of modes contained in this set. The coefficients $f_3^\Phi(i, j, n)$ and $f_4^\Phi(i, j, n, s)$ in (3.36) are simply numbers that determine the contribution to the free energy, for a given space group Φ , associated with the interaction between modes with different i, j, n , and s . These numbers are obtained from the cubic and quartic terms, respectively, by summing the contributions from all equivalent modes; in addition, because of the integration in (3.28) and (3.29) over \mathbf{r} only those combinations of modes for which $\tau_i + \tau_j + \tau_n = 0$ and $\tau_i + \tau_j + \tau_n + \tau_s = 0$ contribute to f_3^Φ and f_4^Φ , respectively. Because of the enormous number of such combinations the summation can be carried out analytically only in the simplest cases when only one or at most two nonequivalent Fourier harmonics are included.^{61,62}

Thus the expression for the free energy depends only on three parameters: the dimensionless temperature t ; the parameter κ , characterizing the "degree of twisting of the helix"; and, the ratio of the elastic moduli c_2/c_1 . The cases $\kappa \ll 1$ and $\kappa \gg 1$ correspond precisely to small and large q_C , discussed above.

2) Structural characteristics

The equilibrium values of the period d of the structure formed and of the quantities μ_i are determined from the condition that f assumes its minimum value. Since the value of the period enters only into the quadratic part of (3.36), from the condition $\partial f/\partial d = 0$ we obtain an expression for d :

$$d = \frac{4\pi}{q_C} \frac{\sum_i [1 + (1/6)(c_2/c_1)(4 - m^2)] (h^2 + k^2 + l^2) \mu_i^2}{\sum_i m \sqrt{h^2 + k^2 + l^2} \mu_i^2}. \quad (3.38)$$

The expression (3.38) is also useful for analyzing the results of experimental measurements, since its right and left sides contain quantities which can be measured independently, making it possible to check the self-consistency of the measurements. We emphasize, however, that (3.38) is a consequence of the assumption that cubic and quartic terms in the expression for the free energy do not contain derivatives; this assumption is by no means obvious. In addition, the existence of three different elastic moduli and not two, as in (3.27), in cholesterics apparently indicates that it is desirable to include such terms.

The problem of finding the equilibrium values of μ_i is more difficult. The coefficients f_3^Φ and f_4^Φ in (3.36) can in principle be calculated for the group T^4 (as the group with the lowest symmetry among those studied) for a very large set of μ_i , and the equilibrium values μ_i can then be deter-

mined by minimizing the quartic polynomial obtained. The values of μ_i found in this manner determine which of the cubic groups corresponds to the minimum of the free energy with fixed values of the parameters $t, \kappa, c_2/c_1$ (the group T^4 is a subgroup of all cubic groups, and the values of μ_i for it can therefore correspond to groups of higher symmetry). This program requires, however, quite long numerical calculations and has thus far not been implemented. It should be noted that the procedure described above, generally speaking, does not give an absolute minimum of the free energy; but it does permit finding the minimum among several valid structures of blue phases. The calculations can be simplified by using available experimental data, which show that in blue phases only some μ_i have an appreciable magnitude. Focusing on these data, we shall proceed from the general expressions for the free energy to expressions for the specific structures containing a finite number of nonequivalent modes.

2.1) Cholesteric.^{2,61} This is a one-dimensional structure consisting of one mode with $\tau = 0$ and $m = 0$ (we denote it by the amplitude μ_0) and two equivalent modes with $\tau = \pm 4\pi/p$, $m = 2$ and amplitude μ_C . The equilibrium value of p is determined from (3.38) $p = 2d = 4\pi/q_C$ and is independent of μ_0, μ_C . The free energy of the cholesteric has the form

$$f_C = \frac{1}{4} t \mu_0^2 + \frac{1}{4} (t - \kappa^2) \mu_C^2 + \mu_0^3 - 3\mu_0 \mu_C^2 + (\mu_0^3 + \mu_C^2)^2. \quad (3.39)$$

Minimizing the expression (3.39) with respect to μ_0 and μ_C we find that the temperature of the transition of their isotropic phase into the cholesteric phase t_{IC} and the equilibrium values of μ_0 and μ_C for $t \ll t_{IC}$ are given by the relations

$$t_{IC} = \begin{cases} \frac{1}{2} \left[1 + \kappa^2 + \left(1 + \frac{\kappa^2}{3} \right)^{3/2} \right], & \text{if } \kappa \leq 3, \\ \kappa^2, & \text{if } \kappa \geq 3, \end{cases} \quad (3.40)$$

$$\mu_0 = \frac{1}{48} [9 - \kappa^2 + \sqrt{(9 - \kappa^2)^2 + 72(\kappa^2 - t)}],$$

$$\mu_C = \sqrt{3\mu_0^2 + \frac{1}{6} \kappa^2 \mu_0}. \quad (3.41)$$

The transition is a first-order one when $\kappa < 3$ and a second-order one when $\kappa \geq 3$, since in the last case the cubic term vanishes for the cholesteric structure (at the minimum of f_C). The change in entropy is given by the relations

$$\Delta S_{IC} = \begin{cases} \frac{1}{4} \left[2 + 3 \left(1 + \frac{\kappa^2}{3} \right)^{1/2} - \left(1 + \frac{\kappa^2}{3} \right)^{3/2} \right], \\ 0, \end{cases}$$

$$\text{if } \kappa \leq 3, \quad (3.42)$$

$$\text{if } \kappa \geq 3.$$

The point of the second-order transition, however, as we shall see below, is not reached because of the transition into the blue phase. We note that in a nematic (i.e., when $\kappa = 0$)

$$t_{IN} = t_{IC} \Big|_{\kappa=0} = 1, \quad \Delta S_{IN} = \Delta S_{IC} (\kappa = 0) = 1, \quad (3.43)$$

and the relations (3.43) give an idea of the above-chosen (3.37) scale of measurement of the temperature and en-

ropy, and therefore of the free energy also.

As already pointed out above, the cholesteric structure, generally speaking, is biaxial and the parameter η [see (3.5)] is given by the relation

$$\eta_C = 1 - \frac{4}{1 + (\sqrt{3} \mu_C / \mu_0)}. \quad (3.44)$$

The biaxiality is maximum at $t = t_{IC}$ and increases with κ , but numerically it is quite small. Thus for $\kappa^2 = 0.5$ and $t = t_{IC}$, $\eta_C \approx 0.04$ (see Refs. 124–126 for a more detailed discussion).

2.2) Blue phases. Since the structure (structures) of the blue phase has not been finally established, we shall study several of the most probable structural models of this phase. The phase O^5 , which must correspond to the asymptotic limit $\kappa \rightarrow \infty$ (this phase has apparently not yet been observed experimentally), has the simplest structure. This phase has only one set of equivalent harmonics [110; 2] (we denote the corresponding amplitude by μ_2). It follows from (3.38) that $d = 2\sqrt{2}\pi/q_C$ and the free energy for O^5 has the form⁶¹

$$f_{O^5} = \frac{1}{4} (t - \kappa^2) \mu_2^2 - \frac{23\sqrt{2}}{32} \mu_2^3 + \frac{499}{384} \mu_2^4. \quad (3.45)$$

Minimizing f_{O^5} with respect to μ_2 we find the temperature t_{1O^5} of the transition from the isotropic phase into the O^5 phase (the transition is always a first-order one), the jump in the entropy at the point of the transition ΔS_{1O^5} , and the equilibrium value of μ_2 for $t \leq t_{1O^5}$:⁶¹

$$\left. \begin{aligned} t_{1O^5} &= \frac{1587}{1996} + \kappa^2, \\ \Delta S_{1O^5} &= 2^5 \cdot 3^2 \cdot 23^2 / 499^2 \approx 0.612, \\ \mu_2 &= \frac{225\sqrt{2} + \sqrt{15074 + 95808(t_{1O^5} - t)}}{998}. \end{aligned} \right\} \quad (3.46)$$

The phase O^5 is locally biaxial; but, unlike a cholesteric, the biaxiality parameter η varies from point to point.

2.3) The phases O^2 and O^8 . For values of $\kappa \sim 1$ and when two or three nonequivalent modes are included the structures of O^2 and O^8 are energetically more advantageous than O^5 . The group O^2 includes, together with the modes [110; 2], the modes [100; 2] [accordingly, we write $\mu(110; 2) = \mu_2$ and $\mu(100; 2) = \mu_1$]. From (3.36) we obtain the following expression for the free energy f_{O^2} :⁶¹

$$f_{O^2} = \frac{1}{4} \left[t + 4\kappa^2 \left(\frac{\pi^2}{d^2 q_C^2} - \frac{\pi}{dq_C} \right) \right] \mu_1^2$$

$$+ \frac{1}{4} \left[t + 4\kappa^2 \left(\frac{2\pi^2}{d^2 q_C^2} - \frac{\sqrt{2}\pi}{dq_C} \right) \right] \mu_2^2$$

$$+ \frac{3(4+3\sqrt{2})}{8} \mu_1^2 \mu_2 - \frac{23\sqrt{2}}{32} \mu_2^3 + \frac{13}{12} \mu_1^4$$

$$+ \frac{139-12\sqrt{2}}{48} \mu_1^2 \mu_2^2 + \frac{499}{384} \mu_2^4. \quad (3.47)$$

The equilibrium values of the spatial period and of the quantities μ_1 and μ_2 can be obtained from (3.47) by numerical minimization. For example, at $t = 1$ and $\kappa = 1$ $\mu_1 \approx 0.577$, $\mu_2 \approx -0.323$, $d \approx 1.13 (2\pi/q_C)$. Detailed numerical calculations show that in spite of the temperature dependence of μ_1 and μ_2 , the ratio μ_2/μ_1 and therefore the ratio of the size of the unit cell d to the pitch of the spiral p are virtually

independent of t and κ . It is interesting to note that the numerically computed ratio μ_2/μ_1 is close to the value obtained by minimizing the cubic part in (3.47) holding $\mu_1^2 + \mu_2^2$ fixed [i.e., in other words, when minimizing $\text{Sp}(\hat{\varepsilon}^3)$ holding $\text{Sp}(\hat{\varepsilon}^2)$ fixed].

In the O^8 phase, taking into account the modes $\mu(110; 2) \equiv \mu_2, \mu(200; 2) \equiv \mu_4$ and $\mu(211; 2) \equiv \mu_6$, the expression for the free energy has the form

$$\begin{aligned}
 f_{O^8} = & \frac{1}{4} \left[t + 4\kappa^2 \left(\frac{2\pi^2}{d^2 q_C^2} - \frac{\sqrt{2}\pi}{dq_C} \right) \right] \mu_2^2 \\
 & + \frac{1}{4} \left[t + 8\kappa^2 \left(\frac{2\pi^2}{d^2 q_C^2} - \frac{\pi}{dq_C} \right) \right] \mu_1^2 \\
 & + \frac{1}{4} \left[t + 4\kappa^2 \left(\frac{6\pi^2}{d^2 q_C^2} - \frac{\sqrt{6}\pi}{dq_C} \right) \right] \mu_6^2 \\
 & - \frac{5}{8} \mu_2^3 + \frac{3}{8} (3 + 2\sqrt{2}) \mu_2^2 \mu_4 \\
 & - 1.3058 \mu_2^2 \mu_6 - 3.039 \mu_2 \mu_4 \mu_6 + 0.1012 \mu_2 \mu_6^2 - 2.1456 \mu_4 \mu_6^2 \\
 & - 0.4219 \mu_6^3 + \frac{449}{384} \mu_2^4 - \frac{24 + 17\sqrt{2}}{48} \mu_2^3 \mu_4 - 0.3420 \mu_2^2 \mu_6 \\
 & + \frac{151 + 12\sqrt{2}}{48} \mu_2^2 \mu_4^2 + 0.1436 \mu_2^2 \mu_4 \mu_6 + 2.2905 \mu_2^2 \mu_6^2 \\
 & + 1.7339 \mu_2 \mu_4^2 \mu_6 + 2.1643 \mu_2 \mu_4 \mu_6^2 + 0.5539 \mu_2 \mu_6^3 \\
 & + \frac{13}{12} \mu_1^4 + 3.2802 \mu_1^2 \mu_6^2 + 0.9817 \mu_4 \mu_6^3 + 1.3125 \mu_6^4 \quad (3.48)
 \end{aligned}$$

[we obtained the coefficients in (3.48), describing the interaction of the modes μ_2 and μ_4 with μ_6 , numerically].³⁾ Numerical minimization of the expression (3.48), for example, for $t = 1$ and $\kappa = 1$ gives $\mu_2 \approx -0.494$, $\mu_4 = -0.374$, $\mu_6 = 0.246$, $d = 1.29(2\sqrt{2}\pi/q_C)$ and shows that, as in the O^2 phase, the ratios μ_4/μ_2 , μ_6/μ_2 and d/p are almost independent of t and κ .

Thus Landau's theory allows the calculation of the values of the parameters determining the structure of the blue phases. These parameters can be measured directly in optical experiments, and their measured values (see below) are close to the values obtained above from Landau's theory.

The results of numerical calculations of the energy of different phases can be used to construct the phase diagram in the t - κ (temperature-chirality) plane (Fig. 15).

In the approximation used above (small number of harmonics), however, the phase diagram is not very reliable. This is linked to the fact that the values of the free energies of different phases are numerically very close in wide intervals of t and κ . Because of this circumstance the existence of modes with low amplitude which are not included in (3.45), (3.47), and (3.48) can substantially change the position of the boundaries between the phases in the t - κ diagram (at the same time, the relative amplitude of the strong modes remains virtually unchanged). The question of whether or not Landau's theory gives a quantitative description of the phase diagram of blue phases therefore remains open.

d) The disclination theory

Besides the foregoing description of the blue phase based on Landau's theory, an alternative approach based on more specific physical models of the structure of the blue

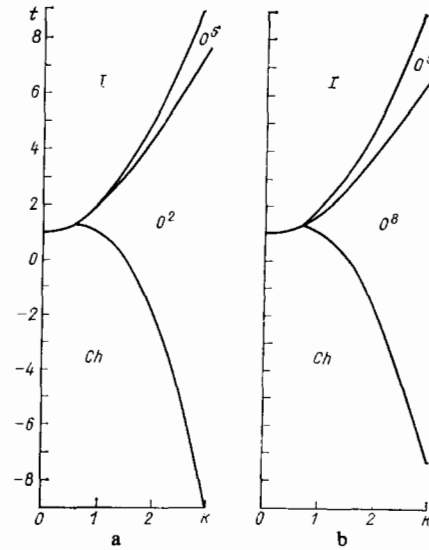


FIG. 15. Phase diagram (a), calculated using Landau's theory (the isotropic phase, O^2 , O^5 , O^8 , and the cholesteric are studied). Since the energy of the O^2 phase is only negligibly lower than that of O^8 , the diagram (b), obtained with the O^2 phase excluded, is also shown. Harmonics with $m = 2$ up to (220) were included in constructing the diagrams.

phase was proposed in Refs. 64–66 and 78. In this approach it is assumed at the outset that the blue phase is locally uniaxial and its structure can be described with the help of the director \mathbf{n} . The main difference between the structure of the blue phase and that of the cholesteric consists of the fact that at each point the cholesteric is twisted in only one direction perpendicular to the director, while in the blue phase local twisting occurs in two directions perpendicular to the director, i.e., a double twisting occurs. Since the existence of double twisting is incompatible for topological reasons with the continuity of the director field, linear defects in the field of the director, called disclinations, arise in the blue phase. The physical arguments in favor of such a structure are clear. Because the helical structure is energetically advantageous and because of the fact that there is nothing to distinguish one of the directions perpendicular to the director, the local minimum of the elastic energy corresponds to double twisting of the director. We shall now show that the same conclusion also follows from the theory of elasticity of liquid crystals.

For a uniaxial crystal with a tensorial order parameter (3.1) the elastic part of the free-energy density (3.27) can be rewritten in a one-constant approximation in the form⁶⁶

$$F_e = \frac{K}{2} \left[\left(\frac{\partial n_j}{\partial x_i} + q_C e_{ijk} n_k \right)^2 - q_C^2 \right], \quad (3.49)$$

where K is Frank's modulus of elasticity ($K = c_1 S^2$). For a cholesteric the local change in the director can be written in the form $\mathbf{n} = (1, q_C z, 0)$, where $|q_C z| \ll 1$, and in this case $F_e = 0$. If, however, the twisting occurs in two directions z and y , then locally $\mathbf{n} = (1, qz, -qy)$. It is easy to verify that in the last case the minimum of (3.49) appears at $q = q_C$ and is equal to $-Kq_C^2/2$, i.e., the double twisting is locally favored. What are the structural consequences of the fact that the double twisting is energetically favored locally? Because

of the incompatibility of the continuity of the director field with the double twisting of the director in a macroscopic sample, as noted above, the discontinuity is accompanied by sharp changes (disclinations) in the orientation of the director, and in the corresponding regions the local elastic energy increases rapidly. For this reason, energy considerations (referring to the total elastic energy) indicate that the structure with double twisting of the director can be realized if the corresponding energy gain (compared with the energy of the usual cholesteric ordering) is greater than the energy loss due to disclinations. In the opposite case, cholesteric ordering of the director must be realized. The drop in the energy of disclinations as the temperature approaches the point of the transition into the isotropic phase, combined with a sharp increase in the gain in energy from the double twisting as the pitch of the helix decreases (q_C increases), suggests that for small-pitch cholesterics the double twisting of the director can be energetically advantageous near the temperature of the transition into the isotropic liquid. The quantitative theory of the described model, developed in Refs. 64 and 66, completely confirmed the qualitative considerations presented above and produced structural models of the blue phase consisting of cubic lattices of linear disclinations in the director field.

The following expression for the elastic energy of a liquid crystal is the starting point in Refs. 65 and 66:

$$F_e = \frac{K_{11}}{2} (\operatorname{div} \mathbf{n})^2 + \frac{K_{22}}{2} (\mathbf{n} \operatorname{rot} \mathbf{n} + q_C)^2 + \frac{K_{33}}{2} [\mathbf{n} \operatorname{rot} \mathbf{n}]^2 + \frac{K_{22} + K_{24}}{2} \operatorname{div} [(\mathbf{n} \nabla) \mathbf{n} - \mathbf{n} \operatorname{div} \mathbf{n}], \quad (3.50)$$

which in the one-constant approximation ($K_{11} = K_{22} = K_{33} = K$, $K_{24} = 0$) reduces to (3.49). The expression (3.50) differs from the usual expression^{1,2} in that it contains the last term,⁷⁹ which has the form of a total divergence. It is this term that yields the gain in energy in the case of double twisting. The usual argument that this term does not make a contribution to the volume energy, since it reduces to an integral over the surface, does not work in this case because the integration over the surface includes also an integration over the surface of singular lines (disclinations). In the blue phase the disclinations have a finite volume density, and the integration over their surface gives a contribution to the total energy which is proportional to the volume.

To find the structure of the blue phase the expression (3.50) was minimized numerically.^{65,78} As a result, it was shown that the elastic energy (3.50) plus the energy of the disclinations has a stable minimum for structures with the spatial symmetry O^2 , O^5 , and O^8 in a small temperature interval near the point of the transition into the isotropic liquid (see Fig. 13).^{65,78} The fact that, as calculations showed, only a small number of spatial Fourier harmonics of $\hat{\varepsilon}(\mathbf{r})$ have an appreciable magnitude in these structures deserves special mention.⁷⁸

The energy of the nucleus of the disclinations, which is assumed to be strongly temperature dependent, was taken into account in a model fashion. This allowed a qualitative explanation of the phase diagram of blue phases (including also transitions between the phases O^2 and O^8), the tempera-

ture dependence of the density of the blue phase and its lattice spacing, as well as the large (~ 30) magnitude of the ratio of the latent heats of the isotropic-liquid-blue-phase and blue-phase-cholesteric transitions.

The model described gives a deeper understanding of the physical factors responsible for the blue phase in Landau's theory. It is clear that the existence of a blue phase in this theory also follows from the fact that the complicated (non-one-dimensional) change in the order parameter as a function of the coordinate is advantageous [the expressions (3.49) and (3.50) follow from (3.27) in the one-constant approximation]. Moreover, it can be shown that in the case of a biaxial order-parameter tensor, in contrast to the uniaxial tensor (director) studied above, the local minimum of the elastic part of the free energy (3.27) is achieved with local rotation of each of the three principal axes of the tensor $\hat{\varepsilon}(\mathbf{r})$ as a function of \mathbf{r} .

In the case of a biaxial order-parameter tensor, in spite of the complicated nature of its spatial variations, discontinuities in the order-parameter field can be avoided in a complicated structure in which not only do the principal axes of the tensor $\hat{\varepsilon}(\mathbf{r})$ rotate as a function of the coordinate, but the principal values of the tensor also vary in space.

It is interesting to note that the calculation described above based on the Landau theory of the structures of the blue phase for the groups O^2 and O^8 gives results which are in good agreement with those of the disclination model. Indeed, it turns out that in most of the volume of the unit cell the tensorial order parameter corresponds to a prolate ellipsoid (i.e., for example, $\varepsilon_1 > 0$, while $\varepsilon_2 < 0$ and $\varepsilon_3 < 0$). In addition, the local biaxiality η [see (3.5)] is small and of the same order of magnitude as in the cholesteric (Fig. 16). For this reason, the blue phase can be described approximately with the help of the director $\mathbf{n}(\mathbf{r})$ in the corresponding part of the volume. In comparatively small regions (approximately 3% of the volume) the tensor $\hat{\varepsilon}(\mathbf{r})$ corresponds to an oblate ellipsoid ($\varepsilon_1 < 0$, while $\varepsilon_2 > 0$ and $\varepsilon_3 > 0$), and these regions can be compared with the core of the disclinations

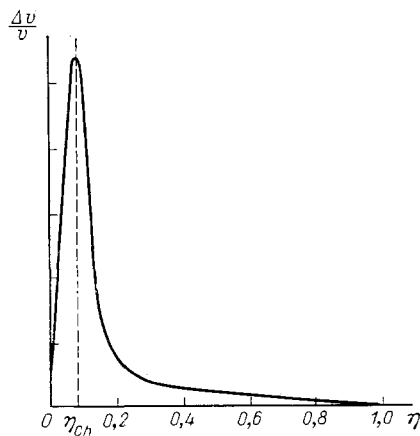


FIG. 16. Computed distribution of the biaxiality parameter η over the volume of the unit cell. The relative fraction of the volume corresponding to different values of η is plotted along the ordinate axis. $t = 1$, $\kappa = 1$, η_{ch} is the biaxiality parameter for the cholesteric (3.44).

studied in the disclination theory. These "disclinations" lie along a third-order axis (see Fig. 13). The expressions (3.24) and (3.25) make possible a detailed study of the structure of the core of the disclinations. In particular, it turns out that in the O^8 structure the core of the disclinations has approximately the shape of a cylinder with a radius $R \approx 0.037 d$ (if it is assumed that the lattice spacing $d = 3000 \text{ \AA}$, then a completely reasonable value of the order of 100 \AA is obtained for R). For structures with the O^2 and O^5 symmetry the corresponding analysis with the help of Landau's theory shows that the core of the disclinations does not have a constant transverse radius but is rather spindle-shaped; in addition, the order parameter vanishes at the tips of the spindles.

Thus the two theories of the blue phase, which have thus far been developed in greatest detail, produce very similar results. They actually differ only by the degree to which the corresponding models are specified and by the methods used to obtain the results. In Landau's theory the modes responsible for the minimum of the elastic energy are sought first, and then the structures which minimize the total free energy (i.e., actually structures with minimum local biaxiality) are constructed from these modes. In the disclination theory, on the other hand, local uniaxiality is assumed at the outset, and then the structures which minimize the elastic energy are sought. It is therefore not surprising that the results obtained are similar.

To check the predictions of the theories described here experimentally, the structure of the blue phase must be related to its properties, primarily its optical properties. The following sections of this review are devoted to this question.

4. OPTICAL PROPERTIES

The experimentally observed peculiarities of the optics of blue phases and cholesterics are linked to the diffraction of light by the periodic structure of these phases, and their optical properties have many common features. It turns out that because of the absence of birefringence the theoretical description of the optics of the blue phase is even somewhat simpler than that of the cholesterics, and is analogous to the theory of diffraction of x rays in ordinary crystals, differing from the latter only by its polarization properties.^{57,67,68}

As is well known, a crystal diffracts radiation if the wavelength of the light in the crystal and the direction of propagation of the light satisfy the Bragg condition $2d_\tau \sin \theta_B = \lambda$, where d_τ is the spacing corresponding to the reciprocal-lattice vector τ , while $2\theta_B$ is the scattering angle. It is convenient to rewrite this condition in the vector form

$$\tau^2 + 2\kappa_0\tau = 0, \quad (4.1)$$

where κ_0 is the wave vector of the wave incident on the crystal (including the index of refraction of the crystal $\kappa_0^2 = (2\pi/\lambda)^2 = \epsilon_0\omega^2/c^2$). The wave vector of the diffracted wave κ_τ is given by the relation $\kappa_\tau = \kappa_0 + \tau$. The relation (4.1) is purely geometrical in nature and determines only the position of the regions of diffraction (reflections) corresponding to different τ . The use of (4.1) for the identification of experimentally observed reflections imposes strin-

gent restrictions on the possible structures of the blue phase, in particular, its possible space groups.^{26,27,43} Here the situation is analogous to the x-ray diffraction structural analysis, which is used to determine the symmetry of the crystal under study and the orientation of the crystallographic axes from the observed aggregate of reflections.

More detailed information on the structure of blue phases, as will be evident below, is contained in the intensities and polarization properties of the reflections and their frequency (or angular) width.

a) Kinematic theory

We shall begin our study of the optical properties of blue phases with the simplest kinematic approximation; the results for cholesterics are given in Refs. 1, 6, and 80. This approximation neglects multiple scattering of light and attenuation of the primary beam due to scattering in the sample and can be used to describe scattering in small perfect samples, in which the intensity of the scattered beam is much lower than that of the incident beam.

In the kinematic approximation the intensity of the reflections I_τ and the coefficient of reflection R are proportional to the square of the corresponding Fourier harmonic $\hat{\epsilon}^\tau$:

$$R(\mathbf{e}_0, \mathbf{e}_d) = \frac{I_\tau}{I_0} = |\mathbf{e}_d^* \hat{\epsilon}^\tau \mathbf{e}_0|^2 R_\tau, \quad (4.2)$$

where I_0 is the intensity of the wave incident on the crystal, $|\mathbf{e}_d^* \hat{\epsilon}^\tau \mathbf{e}_0|^2$ is the polarization-structure factor (see below), and the factor R_τ depends on the dimensions and shape of the crystal and determines the angular and frequency width of the reflection. For example, for a crystal shaped in the form of a plane-parallel plate with a thickness L the factor R_τ has the form $R_\tau = \{\sin^2[\alpha \kappa_0^2 L / (2(\kappa_\tau \cdot \mathbf{s}))]\} / |b| \alpha^2 \epsilon_0^2$, where $\alpha = (\tau^2 + 2\kappa_0\tau) / 2\kappa_0^2$, $b = (\kappa_0 \cdot \mathbf{s}) / (\kappa_\tau \cdot \mathbf{s})$, and \mathbf{s} is the normal to the surface of the sample. The quantity R_τ reaches a maximum at $\alpha = 0$, i.e., when (4.1) holds, and at the maximum $R_\tau \sim L^2$; the angular and frequency width of the reflection is proportional to L^{-1} .

The expression (4.2) demonstrates an important property of light scattering in the blue phase. Namely, its strong, quite complicated, and informative polarization dependence, which distinguishes light scattering in the blue phase from the diffraction of x rays (in the latter case the structural information contained in the polarization characteristics is almost never used). The polarization dependence of R and the information on the structure of the crystal is contained in the polarization-structure factor $|\mathbf{e}_d^* \hat{\epsilon}^\tau \mathbf{e}_0|^2$, which describes the diffraction scattering of the wave with polarization \mathbf{e}_0 into the wave with polarization \mathbf{e}_d . If the polarization of the diffracted wave is not analyzed, then the factor $|\mathbf{e}_d^* \hat{\epsilon}^\tau \mathbf{e}_0|^2$ must be summed over all polarizations \mathbf{e}_d , after which the coefficient of reflection assumes the form

$$R(\mathbf{e}_0) = (|\mathbf{A}_\tau|^2 - \kappa_\tau^2 |\mathbf{A}_\tau|^2) R_\tau, \quad (4.3)$$

where $\mathbf{A}_\tau = \hat{\epsilon}^\tau \mathbf{e}_0$.

When the incident wave is polarized, the diffracted wave is also completely polarized, and its polarization vector is given by the expression

$$\mathbf{e}_\tau = [A_\tau - \kappa_\tau (\kappa_\tau A_\tau) \kappa_\tau^{-2}] |A_\tau - \kappa_\tau (\kappa_\tau A_\tau) \kappa_\tau^{-2}|^{-1} \quad (4.4)$$

[we note that the expression (4.2) reaches a maximum when $\mathbf{e}_d = \mathbf{e}_r$].

We shall study in greater detail the polarization properties of scattering in the blue phase.⁶⁷ Near the point where the Bragg conditions hold for a definite reflection corresponding to the reciprocal lattice vector τ , the polarization properties of the scattering, as follows from (4.2)–(4.4), are determined by the form of the Fourier harmonic $\hat{\varepsilon}^\tau$. It is convenient to introduce the characteristic polarization vectors $\mathbf{e}_{0\sigma}$ (where $\sigma = 1, 2$), which are the characteristic vectors of the operator $\varepsilon_{ij}^{\tau*} \varepsilon_{mj}^\tau (\delta_{mi} - \kappa_{rj} \kappa_{rm} / \kappa_r^2)$ in (4.3) and the corresponding polarization vectors $\mathbf{e}_{r\sigma}$ [see (4.4)]. The expression (4.3) assumes its maximum and minimum values precisely for the eigenpolarizations, and the diffraction scattering from each eigenpolarization $\mathbf{e}_{0\sigma}$ proceeds only into the corresponding eigenpolarization of the diffracted wave $\mathbf{e}_{r\sigma}$, since $(\mathbf{e}_{r2}^* \hat{\varepsilon}^\tau \mathbf{e}_{01}) = (\mathbf{e}_{r1}^* \hat{\varepsilon}^\tau \mathbf{e}_{02}) = 0$. The polarization-structure factor for the eigenpolarizations is equal to $|F_\sigma|^2$, where

$$F_\sigma = (\mathbf{e}_{r\sigma}^* \hat{\varepsilon}^\tau \mathbf{e}_{0\sigma}). \quad (4.5)$$

The simple kinematic approach presented above permits describing and understanding many qualitative features of the optical properties of the blue phase. In the general case of an arbitrary ratio of the components with different m the eigenpolarizations determined by the polarization vectors $\mathbf{e}_{0\sigma}$, $\mathbf{e}_{r\sigma}$ in the expansion (3.21) are elliptical and depend on the ratios of the different components $\hat{\varepsilon}^\tau$ and their Bragg angle θ_B . In what follows, reflections with elliptical eigenpolarizations will be called chiral reflections, since for them the coefficients of reflection for right- and left-polarized light differ; chiral reflections are labelled in Table I by the letter c . The eigenpolarizations for nonchiral reflections are linear.

In the particular case when only one term with $m = 2$ or $m = -2$ is present in the expansion (3.21), light with the eigenpolarization which is the same as in the cholesteric (in the kinematic approximation) undergoes maximum diffraction scattering. For this polarization (we denote it by \mathbf{e}_{0+}) the ratio of the axes of the polarization ellipse (lying in the scattering plane and perpendicular to it) is equal to $\sin \theta_B$, while the direction of rotation on the polarization ellipse is to the right for $m = 2$ and to the left for $m = -2$. The diffracted wave in this case has the same eigenpolarization independent of the polarization of the incident wave. Light with orthogonal polarization in this case is not diffracted, while the polarization-structure factor in (4.3) is equal to $|\varepsilon(\tau; \pm 2)|^2 (1 + \sin^2 \theta_B)^2 |\mathbf{e}_0^* + \mathbf{e}_0|^2 / 4$. For $\theta_B = \pi/2$ (backwards diffraction) in the case under study only the right- or only the left-circularly polarized light, respectively, is diffracted. The experimentally observed polarization characteristics of scattering, as already mentioned, provide evidence for the fact that the amplitude of modes with $m = 2$ (or $m = -2$) is much higher than that of other modes.

If unpolarized light undergoes diffraction scattering in the blue phase, then the scattered beam is in the general case

partially polarized. With the help of the formulas (4.2)–(4.5) we obtain the following expression for the degree of polarization of the scattered beam P_r (when the incident beam is unpolarized)

$$P_r = \frac{||F_1|^2 - |F_2|^2|}{(|F_1|^2 + |F_2|^2)^{-1}}. \quad (4.6)$$

The polarization, represented in the reflected beam, is described by the vector \mathbf{e}_{r1} if $|F_1| > |F_2|$ and \mathbf{e}_{r2} if $|F_2| > |F_1|$. In a particular case the scattered beam can be completely polarized even when the incident beam is unpolarized. For this it is necessary that the light with one of the characteristic polarizations not be diffraction-scattered, i.e., one of the amplitudes F_1 or F_2 must vanish. This situation occurs, for example, in the case studied above, when only the component with $m = 2$ or -2 appears in (3.21).

Thus far, in applying the kinematic formulas to the description of the polarization properties, we implicitly assumed that the same is perfect. A real sample can consist of separate small perfect blocks with the axes of separate blocks oriented randomly. We shall briefly discuss the physical picture of diffraction by imperfect crystals of the blue phase and methods for describing it theoretically. A qualitative feature of imperfect crystals is that the waves diffracted by different blocks are not coherent with respect to one another and generally speaking have different polarization. In the general case, this leads to partial depolarization of the diffracted beam, even when the incident beam is completely polarized. The polarization state of partially polarized beams is described with the use of Stokes parameters⁸¹ (or, which is equivalent, the polarization tensor^{80–83}); the three Stokes parameters and the intensity of the wave form a four-vector. The interaction of an arbitrarily polarized wave with the crystal can be described by the so-called Mueller matrices⁸² (real 4×4 matrices), which transform the four-vector of the incident wave into the four-vector of the diffracted (or transmitted) wave. The convenience of such a description is linked to the fact that the Mueller matrices for noncoherently scattering blocks simply add, which, for example, enables averaging over orientations of the blocks in a simple manner. The elements of the Mueller matrices are expressed in terms of quadratic combinations of Fourier harmonics $\hat{\varepsilon}^\tau$ of the form $\varepsilon_{ik}^{\tau*} \varepsilon_{lm}^\tau$, and in the kinematic approximation the elements of the Mueller matrices are directly proportional to $\varepsilon_{ik}^{\tau*} \varepsilon_{lm}^\tau$. Mueller matrices therefore contain all information on the interaction of light with the crystal, with the exception of information on the phase of $\hat{\varepsilon}^\tau$. Specific expressions for the Mueller matrices in the case of the blue phase with random orientation of separate blocks are presented in Refs. 57 and 68. The use of Mueller matrices also permits unifying the study of polarization properties.³⁸

We note that the kinematic approximation can be used to describe optically thick imperfect crystals of the blue phase, in a manner similar to the way this is done for cholesterics^{60,80,83} and for diffraction of x rays.⁸⁴

1) Circular and linear dichroism

Thus far we have been talking about selective reflection of light by the blue phase. Naturally, a maximum in the in-

tensity of the reflected light is accompanied by a minimum in the transmitted intensity. This, as has been pointed out, is also used to study the blue phase experimentally.^{26,43,85} In particular, the method of measuring circular dichroism,^{43,95} which depends on the difference in the coefficients of transmission T_{\pm} of left (-) and right (+) polarized light and is defined by the ratio

$$D_c = (T_+ - T_-) (T_+ + T_-)^{-1} \quad (4.7)$$

is informative. Assuming that the sample is nonabsorbing, in the kinematic approximation it is easy to express the quantity D_c in terms of the reflection coefficient R_{\pm} for right (left) polarized light (4.3). Namely, since $R_{\pm} = (1 - T_{\pm}) \ll 1$,

$$D_c \approx \frac{1}{2} (R_- - R_+). \quad (4.8)$$

From (4.3) and (4.8), assuming that only the mode with $m = \pm 2$ is present in $\hat{\epsilon}^r$ [see (3.21)], an expression can be obtained for the wavelength-integrated circular dichroism from each separate reflection:

$$\int D_c d\lambda \sim |\epsilon(\boldsymbol{\tau}; \pm 2)|^2 (1 + \sin^2 \theta_B) (\sin \theta_B)^{-1}. \quad (4.9)$$

In addition to circular dichroism, linear dichroism D_l of diffraction origin, associated, analogously to (4.8), with the difference of the coefficients of reflection (and transmission) for two orthogonal linear polarizations (for example, for polarization parallel to the plane formed by the vectors $\boldsymbol{\kappa}_0$ and $\boldsymbol{\tau}$ and perpendicular to it), also occurs in the blue phase. It is significant that the circular and linear dichroisms depend differently on the components of the tensor $\hat{\epsilon}^r$ and on the Bragg angle, and their combined measurement gives additional information on $\hat{\epsilon}^r$. If only the component with $m = 2$ (or with $m = -2$) contributes to $\hat{\epsilon}^r$, then $\bar{D}_l = \cos^2 \theta_B D_c / 2 \sin \theta_B$ and linear dichroism is absent in backward diffraction reflection ($\theta_B = \pi/2$).

We emphasize that the presence of diffraction linear dichroism is not inconsistent with the cubic symmetry of the crystal. From symmetry considerations it follows only that linear dichroism is absent only when light propagates precisely along the third- and fourth-order axes. Physically this is linked to the mutual compensation of linear dichroism from different reflections. However, even with a small (of the order of the angular width of the reflection) deviation from the third- or fourth-order axis, this compensation breaks down, and an appreciable linear dichroism can be observed. We note that linear dichroism, unlike circular dichroism, does not occur in unoriented samples. It is significant that in the kinematic approximation both circular and linear dichroism are equal to the sum of the dichroisms from separate reflections, while in the dynamic theory this, generally speaking, does not happen.

b) Optics of perfect samples

1) Basic equations

It was assumed above that scattering within a separate perfect region of the blue phase is small. However, it is now possible to obtain samples with quite large perfect re-

gions,^{41,43,85} for which the kinematic approximation presented above may be unsatisfactory, because in this approximation multiple scattering, which is especially important in the case of thick ($L \gg (\boldsymbol{\kappa}_0 s) / \boldsymbol{\kappa}_0^2 |F_{\sigma}|$) samples, is neglected. Because of the complicated form of the dielectric permittivity tensor the exact analytic solution of Maxwell's equations, i.e., multiple scattering is taken into account exactly, cannot be obtained. We shall therefore describe below the optics of perfect samples of the blue phase based on the approximation known as the dynamic theory of diffraction, analogous to the manner in which this is done in the case of cholesterics.^{6,80}

In this theory under the conditions of diffraction [i.e., when the Bragg-Wolf conditions (4.1) hold, at least approximately] the field of the light wave in the blue phase $\mathbf{E}(\mathbf{r}, t)$ is represented as a superposition of two plane waves with the wave vectors \mathbf{k}_0 and $\mathbf{k}_r = \mathbf{k}_0 + \boldsymbol{\tau}$:

$$\mathbf{E}(\mathbf{r}, t) = (\mathbf{E}_0 e^{i\mathbf{k}_0 \mathbf{r}} + \mathbf{E}_r e^{i\mathbf{k}_r \mathbf{r}}) e^{-i\omega t}. \quad (4.10)$$

From Maxwell's equations, using the expansion (3.17) and $\hat{\epsilon}(\mathbf{r})$, we arrive at the following system of equations for the amplitudes \mathbf{E}_0 and \mathbf{E}_r ⁶⁷:

$$\begin{aligned} \left(1 - \frac{\boldsymbol{\kappa}_0^2}{\boldsymbol{\kappa}_0^2}\right) \epsilon_0 \mathbf{E}_0 + \hat{\epsilon}^{-\boldsymbol{\tau}} \mathbf{E}_r &= 0, \\ \hat{\epsilon}^{\boldsymbol{\tau}} \mathbf{E}_0 + \left(1 - \frac{\boldsymbol{\kappa}_r^2}{\boldsymbol{\kappa}_0^2}\right) \epsilon_0 \mathbf{E}_r &= 0, \end{aligned} \quad (4.11)$$

where $\boldsymbol{\kappa}_0^2 = \epsilon_0 \omega^2 / c^2$. It turns out that it is easier to solve the system (4.11) for the blue phase than the corresponding problem for the cholesteric, which is a consequence of the absence of birefringence in the blue phase. In particular, the eigenpolarizations of the solutions of the system (4.11) coincide with the above-discussed eigenpolarizations $\mathbf{e}_{0\sigma}$, $\mathbf{e}_{r\sigma}$, found in the kinematic approximation. In the eigenpolarizations the equations (4.11) separate into two uncoupled systems of two equations. Expanding the amplitude of the wave in terms of the eigenpolarizations ($\mathbf{E}_0 = \sum_{\sigma=1}^2 E_{0\sigma} \mathbf{e}_{0\sigma}$, $\mathbf{E}_r = \sum_{\sigma=1}^2 E_{r\sigma} \mathbf{e}_{r\sigma}$), we obtain

$$\begin{aligned} \left(1 - \frac{\boldsymbol{\kappa}_0^2}{\boldsymbol{\kappa}_0^2}\right) \epsilon_0 E_{0\sigma} + F_{-\sigma} E_{r\sigma} &= 0, \\ F_{\sigma} E_{0\sigma} + \left(1 - \frac{\boldsymbol{\kappa}_r^2}{\boldsymbol{\kappa}_0^2}\right) \epsilon_0 E_{r\sigma} &= 0, \end{aligned} \quad (4.12)$$

where the quantities F_r are defined in (4.5), $F_{-\sigma} = (\mathbf{e}_{0\sigma}^* \hat{\epsilon}^{-\boldsymbol{\tau}} \mathbf{e}_{r\sigma})$.

We call attention to the fact that the dynamic system (4.12) is completely equivalent to the corresponding system in the theory of diffraction of x rays. The detailed results of the dynamic theory of diffraction of x and γ rays can therefore be used to describe the diffraction of light in the blue phase.⁸⁶⁻⁸⁸ The difference in the description of the diffraction of light in the blue phase is associated only with the polarization properties. In the x-ray case the dynamic system has the form (4.12) in the linear eigenpolarizations π and σ , lying in the scattering plane and perpendicular to it, respectively, while for the blue phase the eigenpolarizations in the general case are elliptical and depend on the direction of propagation of the light beams.⁶⁷

We note here that the polarization characteristics of the interaction of light with the blue phase differ from those for the case of a cholesteric. In a cholesteric, when light propagates at an angle to the cholesteric axis, the eigenpolarizations change in the region of selective reflection (with respect to angle or frequency), whereas in the blue phase the polarization characteristics of the eigenwaves remain almost unchanged in the entire region of selective reflection (to the extent of the relative narrowness of the reflections).

2) Reflection and transmission of light

Making use of the noted analogy between the optics of the blue phase and the diffraction of x rays, we present immediately the final 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 the layer (Fig. 17). We shall also expand the amplitudes of the wave incident on the crystal E^e , the wave diffracted by the crystal E^r , and the wave transmitted by the crystal E^t in terms of the eigenpolarizations: $E^e = \sum_{\sigma=1}^2 E_{\sigma}^e e_{0\sigma}$, $E^r = \sum_{\sigma=1}^2 E_{\sigma}^r e_{r\sigma}$, $E^t = \sum_{\sigma=1}^2 E_{\sigma}^t e_{0\sigma}$. Then, for Bragg geometry ($b < 0$, see Fig. 17a).

$$E_{\sigma}^r = E_{\sigma}^e F_{\sigma} (\alpha + i\Delta \operatorname{ctg} l)^{-1} e_0^{-1}, \quad (4.13)$$

$$E_{\sigma}^t = E_{\sigma}^e \Delta (\Delta \cos l - i\alpha \sin l)^{-1}, \quad (4.14)$$

while for Laue geometry ($b > 0$, see Fig. 17b)

$$E_{\sigma}^r = E_{\sigma}^e F_{\sigma} \Delta^{-1} e_0^{-1} \sin l, \quad (4.15)$$

$$E_{\sigma}^t = E_{\sigma}^e (\cos l + i\alpha \Delta^{-1} \sin l), \quad (4.16)$$

where $\alpha = (\tau^2 + 2\kappa_0\tau)/2\kappa_0^2$, $\Delta = \sqrt{\alpha^2 + (F_{\sigma}F_{-\sigma}/b\epsilon_0^2)}$, $l = \Delta\kappa_0^2 L/2(\kappa_r s)$, $b = (\kappa_0 s)/(\kappa_r s)$, and s is the inward normal to the surface of the sample. The parameter α characterizes the deviation of the wavelength and (or) the angle of incidence from the values determined by the Bragg-Wolf condition (4.1). Assuming that these deviations are small ($|\alpha| \ll 1$), we find that in terms of the angle of incident θ

$$\alpha = (\theta_B - \theta) \sin 2\theta_B, \quad (4.17)$$

and in terms of the wavelength λ

$$\alpha = (\lambda - \lambda_B) \sin^2 \theta \cdot \lambda_B^{-1}, \quad (4.18)$$

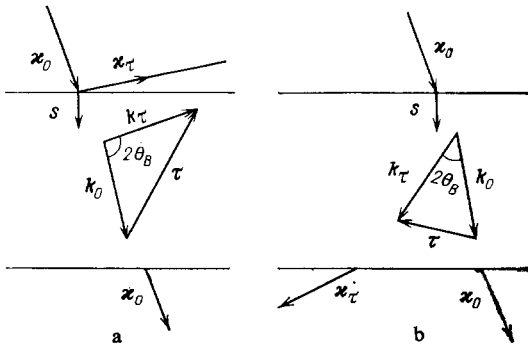


FIG. 17. Diffraction geometry. a) Bragg case, b) Laue case.

where $\lambda_B = 4\pi\sqrt{\epsilon_0} \sin \theta / |\tau|$. The quantity l in (4.13) and (4.14) is the dimensionless thickness of the crystal, while the quantity Δ is proportional to the diffraction correction to the wave vector κ_0 .

The expressions (4.13)–(4.16) completely solve in the two-wave approximation the problem of diffraction of light in the blue phase. For example, the coefficients of reflection for the incident wave with the eigenpolarizations have the form

$$R_{\sigma} = |F_{\sigma}|^2 b^{-1} \sin^2 l (\alpha^2 + \Delta^2 \cos^2 l)^{-1} e_0^{-2}, \quad (4.19)$$

in the Bragg case and

$$R_{\sigma} = |F_{\sigma}|^2 e_0^{-2} b^{-1} \Delta^{-2} \sin^2 l \quad (4.20)$$

in the Laue case.

3) Polarization characteristics

If the incident wave has an arbitrary polarization e^e and the degree of polarization P^e , then the coefficient of reflection is given by

$$R(P^e, e^e) = \frac{1}{2} (1 - P^e) (R_1 + R_2) + P^e (R_1 |e_{01}^* e^e|^2 + R_2 |e_{02}^* e^e|^2). \quad (4.21)$$

In the case of an unpolarized incident beam ($P^e = 0$) the expressions for the degree of polarization of the reflected and transmitted light assume the form

$$P^r = |R_1 - R_2| (R_1 + R_2)^{-1}, \quad (4.22)$$

$$P^t = |R_1 - R_2| (2 - R_1 - R_2)^{-1}.$$

The polarization vector of the reflected beam coincides with e_{01} if $R_1 > R_2$ and with e_{02} if $R_2 > R_1$. The transmitted beam has an additional polarization, i.e., e_{02} when $R_1 > R_2$ and e_{01} when $R_2 > R_1$. In the case when only the single component with $m = 2$ or $m = -2$ is present in $\hat{\epsilon}^r$, the polarization properties coincide with the kinematic properties.

Using expressions (4.13)–(4.16), Mueller's matrices, describing the reflection and transmission of a wave in a perfect crystal, can also be obtained.

It should be noted that the expressions presented here were obtained neglecting the reflection of rays at dielectric boundaries, i.e., it is assumed that the average dielectric permittivity of the blue phase coincides with that of the surrounding medium. When the average dielectric properties of the blue phase and of the external medium differ appreciably, reflection by dielectric boundaries can have an observable effect on the characteristics under study. In this case, the dielectric boundaries can be taken into account by well-known methods^{6,80} without any fundamental difficulties.

4) Multiple-scattering effects

The formulas of the dynamic theory (4.13)–(4.16) describe a number of multiple-scattering effects which are absent in the kinematic approximation. Thus the frequency (angular) width of the region of diffraction scattering (see Fig. 8), i.e., the width of the frequency (angular) interval of selective reflection of waves with the eigenpolarizations, is proportional to $|F_{\sigma}|$ for thick samples [see (4.13) and

(4.15)] and it is therefore proportional to the corresponding harmonic in the Fourier expansion of $\hat{\epsilon}(\mathbf{r})$. (We note, however, that in the case of backward diffraction the angular width is proportional to $\sqrt{|F_\sigma|}$. In the Bragg case the region of selective reflection in a thick crystal is given by the inequality $|\alpha| \leq \sqrt{|F_\sigma F_{-\sigma}|/b\epsilon_0^2}$, and in this region the coefficient of reflection R_σ is close to unity.

The dynamic approach also describes the experimentally observed rotation of the polarization plane of light in the blue phase and, in particular, the reversal of the sign of rotation (see Fig. 1). From (4.14) and (4.16) we find (in the case of circular eigenpolarizations $e_{\sigma\sigma}$) the following expression for the angle of rotation φ_t of the polarization plane of the light transmitted through a layer of the blue phase:

$$\varphi_t = \frac{1}{2} \left\{ \left[\arctg \left(\frac{\alpha}{\Delta} \operatorname{tg} l \right) \right]_{\sigma=1} - \left[\arctg \left(\frac{\alpha}{\Delta} \operatorname{tg} l \right) \right]_{\sigma=2} \right\}. \quad (4.23)$$

The point at which the sign of the rotation of the polarization plane changes corresponds to $\alpha = 0$. We also note that in perfect samples of the blue phase, just as in a cholesteric, the angle of rotation of the polarization plane, as follows from (4.23), depends nonlinearly on the sample thickness (see Refs. 6 and 80).

Another effect of multiple scattering are the so-called Pendellösung beats,^{86,87} which are beats in the coefficients of reflection and transmission as well as in the polarization properties of beams as a function of the light frequency (or the angle of deviation from the Bragg condition) for a fixed sample thickness or as a function of the thickness with the remaining parameters held fixed. The period of these dynamic beats is expressed directly in terms of $|F_\sigma|$, which admits an exact determination of these quantities,⁸⁷ independent of the measurement of the absolute scattering intensities.

Another result of the dynamic analysis are the peculiarities of the manifestation of linear birefringence and linear dichroism in the blue phase, whose existence is linked to multiple scattering effects and is not inconsistent with the fact that the structure of the blue phase belongs to cubic space groups. We are talking about diffraction birefringence of waves with eigenpolarizations, which turn out to be circular only for particular directions of propagation of light in the blue phase, just as for propagation of light along the cholesteric axis, while in the general case they are elliptical. The difference in the effective refractive indices Δn of the eigenwaves is proportional to the difference ψ of the phases of the waves with eigenpolarizations passing through the crystal: $\Delta n = \psi(\kappa_0 s)/\kappa_0^2 L$, where the angle ψ is given by the expression (4.23) without the factor 1/2. The existence of a predominant linear component in elliptical eigenpolarizations is manifested precisely as linear birefringence. The characteristic feature of such birefringence is its strong frequency (angular) dependence and the reversal of the sign in the region of selective scattering [when the sign of α in (4.23) changes]. In the particular case when only the component with $m = 2$ or -2 is present in $\hat{\epsilon}^r$, linear birefringence and linear dichroism vanish at $\theta_B = \pi/2$ and grow as

the Bragg angle decreases. For nonchiral reflections the diffraction birefringence is linear and is described in Ref. 67. In the general case, many reflections, and not only one reflection, contribute to the diffraction birefringence; this case requires a special analysis (for diffraction of x rays this problem was solved in Ref. 89).

It may thus be concluded that the experimentally observed small linear birefringence^{42,90} can have a diffraction character, and it cannot be interpreted unconditionally as an argument against the cubic nature of the blue phase. Another qualitative result linked with multiple scattering is the depolarization of light beams even in perfect samples of the blue phase, if the beams have a finite angular (or frequency) width. This is a consequence of the frequency (angular) dependences of the polarization of the diffracted beams discussed above and following from (4.13)–(4.16). As a result, in a perfect sample, even for a completely polarized incident beam (with non-eigenpolarization), because of the nonmonochromaticity and angular divergence the diffracted beams are only partially polarized.⁶⁷ These depolarization effects can, however, be manifested only in samples with a high degree of perfection, since in imperfect samples depolarization is predominantly a result of the lack of coherence of the scattering by separate crystallites.

The observation of dynamic effects by Marcus⁴¹ (see Fig. 8) in selective scattering indicates the practical significance of these effects for the study of blue phases.

Another dynamic effect (bleaching), linked with multiwave diffraction of light in the blue phase, was observed in Ref. 78. The theory of multiwave diffraction in the blue phase has thus far not been developed, but symmetry considerations make it possible to study in some cases the polarization properties for multiwave diffraction also. It should be noted that multiwave diffraction in the blue phase can, in analogy to the case of diffraction of x rays,^{117,118} be used to determine the relative phases of the harmonics $\hat{\epsilon}^r$ in the Fourier expansion of $\hat{\epsilon}(\mathbf{r})$.

c) Pretransitional phenomena in the isotropic phase

Substances having a blue phase also exhibit some optical peculiarities in the isotropic phase in the pretransitional region at temperatures somewhat above the transition temperature. In this region the average order parameter is equal to zero, but fluctuations of the order parameter and therefore of the dielectric permittivity can occur also, leading to scattering of light and manifested also in corrections to the average index of refraction. Because of the chiral asymmetry of the molecules the fluctuations also are right-left asymmetrical, and for this reason the scattering and index of refraction are different for light with right and left circular polarization, which causes rotation of the polarization plane and circular dichroism. We emphasize that all these phenomena are closely interrelated: scattering by fluctuations attenuates a light wave as it propagates in the crystal, i.e., it causes the appearance of an imaginary part in the index of refraction; in its turn, the presence of the imaginary part unavoidably adds (because of the dispersion relations) a fluctuation correction to the real part of the index of refraction. In terms of the

phenomenological language we can say that the isotropic phase near the point of the phase transition is a medium with strong spatial dispersion because of the fact that the characteristic dimension in the system (radius of the fluctuations) is not very small or even comparable to the wavelength of the light.

The unified nature of pretransitional optical phenomena is manifested in the fact that they are all determined by the same quantity: the correlation function of the fluctuations of the order parameter $G_{ij}^{kl}(\mathbf{r}'' - \mathbf{r}') = \langle \varepsilon_{ij}(\mathbf{r}'') \varepsilon_{kl}(\mathbf{r}') \rangle$, where the angular brackets indicate averaging over thermal fluctuations. A peculiarity of substances exhibiting a blue phase is that when the pitch of the helix is small (when $\kappa^2 \gg 1$), one mode with $m = 2$ or $m = -2$ (plane mode) makes the main contribution to the fluctuations, while when $\kappa^2 \lesssim 1$, other modes can also be significant.

The correlation function G_{ij}^{kl} was calculated by Brazovskii and Dmitriev³³ in the Gaussian approximation, i.e., under the assumption that the fluctuations are small and that in the expression for the free energy of the fluctuations terms of order higher than second in $\hat{\varepsilon}$ can be omitted (see also Refs. 2, 34, 76, and 91-94). In this approximation the Fourier component of the correlation function $G_{ij}^{kl}(\mathbf{q})$ has the form

$$G_{ij}^{kl}(\mathbf{q}) = \frac{k_B T}{V} \sum_m \sigma_{ij}^m(\mathbf{q}) \sigma_{kl}^m(-\mathbf{q}) \delta_m^{-1}(\mathbf{q}), \quad (4.24)$$

where σ_{ij}^m and $\delta_m(\mathbf{q})$ are given by (3.23) and (3.31), and k_B is the Boltzmann constant. The physical meaning of the expression (4.24) is quite obvious: the modes for which the energy $\delta_m(\mathbf{q})$ is minimum make the main contribution to the correlation function. As we saw above [see (3.33)], $\delta_m(\mathbf{q})$ reaches a minimum when $|\mathbf{q}| = q_C$ and $m = 2$ (i.e., the plane mode makes the maximum contribution to the correlation function).

Light scattering makes possible direct measurement of the correlation function. The cross section for scattering of a light wave with wave vector κ_0 and polarization vector \mathbf{e}_0 into a wave with the corresponding vectors κ_1 and \mathbf{e}_1 is directly proportional to $G_{ij}^{kl}(\kappa_0 - \kappa_1)$:

$$\sigma = V \left(\frac{\kappa_0^2}{4\pi} \right)^2 G_{ij}^{kl}(\kappa_0 - \kappa_1) e_{1j}^* e_{1k} e_{0l}^* e_{0i}. \quad (4.25)$$

The structure of the correlation function and the contribution of different fluctuation modes to it can be studied by measuring the polarization of the light and the momentum transferred $\kappa_0 - \kappa$ (this question is discussed in detail in the review by Belyakov and Kats⁹¹).

Another method used to study the correlation function consists of studying the rotation of the polarization plane in the isotropic phase.^{44,93,95} Other effects of spatial polarization, linked to fluctuations, can also be observed in this case. Indeed, in an isotropic medium the expression for the Fourier harmonics of the dielectric permittivity tensor is determined by three constants and has the form

$$\varepsilon_{ij}^d(\omega, \kappa) = \varepsilon_{tr}(\omega, \kappa^2) \left(\delta_{ij} - \frac{\kappa_i \kappa_j}{\kappa^2} \right) + \varepsilon_l(\omega, \kappa^2) \frac{\kappa_i \kappa_j}{\kappa^2} + i e_{ijh} \kappa_h \gamma_c(\omega, \kappa^2), \quad (4.26)$$

where $\varepsilon_l = (\kappa \hat{\varepsilon}^d \kappa) / \kappa^2$ and $\varepsilon_{tr} = (\text{Sp} \hat{\varepsilon}^d - \varepsilon_l) / 2$ are the longitudinal and transverse dielectric permittivities; the imaginary part of the pseudoscalar $\gamma_c = -i e_{ijk} \kappa_k \varepsilon_{ij}^d / 2 \kappa^2$ produces circular dichroism, and the real part produces rotation of the polarization plane.

Far from the point of the transition into the blue phase the effects of spatial dispersion are weak, $\varepsilon_{tr} = \varepsilon_l = \varepsilon_0$, and γ_c describes molecular rotation of the polarization plane. Near the transition all three quantities ε_{tr} , ε_l , and γ_c can have singularities. Thus far, however, only the pretransitional behavior of γ_c has been studied theoretically and experimentally.

We shall present quantitative expressions for the fluctuation correction to $\hat{\varepsilon}^d$, obtained under the assumption that pretransitional fluctuations in $\hat{\varepsilon}$ are small.^{33,34,76} As is well known (see Sec. 9 in Ref. 97), in this case $\hat{\varepsilon}^d = \varepsilon_0 + \Delta \hat{\varepsilon}$, where ε_0 is the dielectric permittivity in the absence of fluctuations, and $\Delta \hat{\varepsilon}$ is proportional to $\langle \hat{\varepsilon} \delta E \rangle$, where δE is the local correction to the electric field generated by the fluctuations in $\hat{\varepsilon}$. Using the explicit expression for δE in terms of $\hat{\varepsilon}$,⁹⁸ for the fluctuation correction $\Delta \hat{\varepsilon}$, following Ref. 97, we obtain

$$\Delta \hat{\varepsilon} = \frac{\omega^2}{c^2} \left\langle \hat{\varepsilon}(\mathbf{r}) \int \hat{\Gamma}(\mathbf{r} - \mathbf{r}') \hat{\varepsilon}(\mathbf{r}') \exp[i\kappa(\mathbf{r}' - \mathbf{r})] d\mathbf{r}' \right\rangle, \quad (4.27)$$

where $\hat{\Gamma}(\mathbf{r} - \mathbf{r}')$ is the photon Green's function.⁹⁸ After averaging using (4.24) and the Fourier components of $\hat{\Gamma}(\mathbf{r} - \mathbf{r}')$, we obtain

$$\Delta \varepsilon_{ij} = \frac{\omega^2}{c^2} \lim_{\varepsilon \rightarrow +0} \left[\int d\mathbf{q} G_{ih}^{ij}(\mathbf{q}) \frac{\kappa^2 \delta_{lh} - (\kappa - \mathbf{q})_l (\kappa - \mathbf{q})_h}{\kappa^2 (q^2 - 2\kappa \mathbf{q} - i\varepsilon)} \right]. \quad (4.28)$$

From (4.26) and (4.28) the expressions for ε_{tr} , ε_l and γ_c can be represented in terms of elementary functions of the dimensionless quantities q_C/κ , t , κ^2 and c_2/c_1 . In the general case these expressions are very cumbersome, and different limiting cases have been studied only for γ_c .^{33,34,68-70} Thus for media with a long pitch ($\kappa^2 \ll 1$) the modes $m = \pm 1$ make the main contribution to the rotation of the polarization plane, and

$$\gamma_c = \frac{k_B T q_C}{24\pi \varepsilon_0 \sqrt{c_1 (1 + c_2/2c_1)^3 [a - c_1 q_C^2/4 (1 + c_2/2c_1)]}}. \quad (4.29)$$

In the case of a short pitch in the immediate vicinity of the transition point (when $t - \kappa^2 \ll \kappa^2$), modes with $m = \pm 2$ can make an important contribution to γ_c , and the magnitude and sign of the rotation in this case are strongly dependent on the wavelength.⁷⁰ In addition, in this region the imaginary part of γ_c , which is responsible for the fluctuation-induced circular dichroism, can be significant.⁶⁸

We underscore the fact that the linear dichroism of molecules can also cause the appearance of fluctuation-induced circular dichroism in the isotropic phase (as in the case of cholesterics^{6,80}). Including it in $\Delta \hat{\varepsilon}$ introduces a factor $(1 + i \text{Im} \varepsilon_a / \text{Re} \varepsilon_a)^2$ in expressions (4.27)-(4.29) [see (3.3) for ε_a]. Thus the measurement of circular dichroism in the region of linear dichroism of molecules affords another possibility for studying pretransitional fluctuations.

The above analysis of pretransitional phenomena was based on the assumption that fluctuations are weak. The case of strong fluctuations, which can even change the nature of the transition from the isotropic liquid into the cholesteric and the blue phase,^{2,33,34} are also of great interest, but this question has thus far not been adequately studied.

5. STRUCTURAL STUDIES OF THE BLUE PHASE

In this section we shall discuss the fundamental paths for determining the structure of the blue phase and the practical results achieved in this direction. Studies of the structure of the blue phase (as also, incidentally, structural studies of crystals in general) involve three stages: 1) determination of the translational periodicity of the structure (finding the dimensions of the unit cell); 2) determination of the symmetry properties of the lattice (establishing its space group); and, 3) determination of the unique coordinate dependence of the order parameter $\hat{\epsilon}(\mathbf{r})$ (the electron density in structural studies of ordinary crystals) within the entire unit cell. The stages are listed here in order of increasing complexity, and the solution of the problem at the third stage implies the complete determination of the structure under study.

a) Optical structural analysis

Since optical methods are most informative, we shall study them first. As we saw above, each Fourier harmonic in the expansion of $\hat{\epsilon}(\mathbf{r})$ (3.17) leads to the appearance of a reflection in the scattering of light by the blue phase. The experimental determination of all Fourier harmonics $\hat{\epsilon}^\tau$ followed by reconstruction of $\hat{\epsilon}(\mathbf{r})$ with the help of the formula (3.17) therefore completely solves the question of the structure of the order-parameter field in the blue phase. The expansion (3.17) can formally include an infinite number of harmonics. But, as experiment shows (see, for example, Refs. 43 and 85) only a small number of reflections have appreciable intensity. For this reason, in practice the "optical structural analysis" of the blue phase reduces to the problem of determining a comparatively small number of tensor Fourier harmonics $\hat{\epsilon}^\tau$.

Let us consider what this means. In the most general case, each Fourier component is determined by 12 parameters [this follows from the number of independent (six), in general complex, components of the symmetrical tensor $\hat{\epsilon}^\tau$; here we do not assume that $\text{Sp}(\hat{\epsilon}^\tau) = 0$]. Nonvanishing $\text{Sp}(\hat{\epsilon}^\tau)$ corresponds to taking into account the spatial modulation of the isotropic part of the dielectric susceptibility $\hat{\epsilon}^d$. For the isotropic component the conditions for the existence of reflections are the same as for the component with $m = 0$ (as for x rays⁷⁴). We note that the modulation of the isotropic part of $\hat{\epsilon}^d$ can be linked, for example, to the modulation of the density and is, as a rule, neglected. The number of independent parameters that must be determined experimentally can be decreased by using additional considerations or making additional assumptions in structural studies of the blue phase. For example, the use of the symmetry properties of $\hat{\epsilon}(\mathbf{r})$ in cubic crystals very severely restricts the number of independent parameters of $\hat{\epsilon}^\tau$ for reflections of a particular

type (see Table I). Using the results of the theory of phase transitions in the analysis of the structure of the blue phase also makes it possible to decrease substantially the number of free parameters. Thus, within the framework of Landau's theory, as mentioned in Sec. 3c, in the approximation under study the expansion (3.21) for each $\hat{\epsilon}^\tau$ contains only one nonvanishing term with $m = 2$ (or -2). This theoretical result makes it possible to reduce to two the number of free parameters in the harmonic.

Without making any additional assumptions regarding "optical structural analysis," we assert that the usual measurements of the intensity and polarization characteristics do not permit determining only the phase of $\hat{\epsilon}^\tau$, i.e., only one of the parameters of $\hat{\epsilon}^\tau$. This is linked to the fact that the intensity and polarization characteristics depend on quadratic combinations of $\hat{\epsilon}^\tau$. The remaining parameters in $\hat{\epsilon}^\tau$, however, can in principle be measured. As is well known,⁸² the study of the polarization characteristics of scattering in a fixed geometry makes possible the determination of only seven parameters in $\hat{\epsilon}^\tau$ [this restriction is linked to the transverse nature of light waves; for example, for backwards reflection ($\theta_B = \pi/2$) it is impossible to measure components with $m = \pm 1$]. For this reason, measurements of the intensity of scattering and of the polarization characteristics for two arbitrary orientations of the incident beam are in principle sufficient to determine $\hat{\epsilon}^\tau$, with the exception of the phase.

The above analysis of the structural and symmetry properties of the blue phase and their relationship to the optical characteristics of this phase lead to the following results. 1) The dimensions of the unit cell are determined by the frequency (angular) position of the regions of selective reflection [see (4.1)]. 2) The space group of the structure is determined by the set τ (Miller indices) of observed reflections (regions of selective reflection). Here it should be noted that just as in x-ray structural analysis, in many cases the same collection of observed reflections can correspond to several space groups. The situation is further complicated by the fact that in reality only several reflections with the longest wavelengths are observed, while, for example, simple and body-centered groups differ only starting with the seventh reflection⁴² (in order of increasing $|\tau|$). In such cases additional information must be used in order to unequivocally establish the space group.

b) Polarization measurements and the phase problem

Structural studies of the blue phase reveal additional possibilities for making comparisons with x-ray structural studies. They are associated with the fact that polarization measurements in the optical range have been completely mastered, unlike the x-ray range, where the complexity of polarization measurements virtually precludes the use of the corresponding information. By measuring the polarization characteristics of the reflections it is possible either to establish uniquely the space group or to reduce the number of competing possibilities. Establishing the chirality of definite reflections (i.e., the difference in the scattering of light by opposite circular polarizations) is especially informative.

Thus in the O^5 group the second reflection is nonchiral, in O^2 the third is nonchiral, and in O^8 the sixth is nonchiral (see Table I). In principle polarization measurements allow the separation of all groups, with the exception of T^3 and T^5 (Refs. 67 and 68) (for the groups T^3 and T^5 the polarization properties of the reflections coincide, and only the relative phases of the reflections of separate types differ). The complete determination of the structure under study requires determining $\hat{\varepsilon}^\tau$ for the observed reflections taking into account their relative phases and indicates, in accordance with (3.17), the possibility of reconstructing uniquely the coordinate dependence of the order parameter $\hat{\varepsilon}(\mathbf{r})$. We emphasize again, however, that the usual diffraction measurements, both in the x-ray and optical ranges, including polarization measurements, do not give information on the phases of $\hat{\varepsilon}$, which are required for determining, according to (3.17), the coordinate dependence of $\hat{\varepsilon}(\mathbf{r})$. This "phase problem" is common to all diffraction methods.^{99,100} In practice, however, because of the existence of sources of coherent optical radiation it is much easier to determine the phase in the optical range than in the x-ray range. In particular, the method of recording the interference of the object beam (in our case the diffracted beam) with the coherent reference beam whose phase is known, which is often realized in practice (for example, in recording holograms), can be used.

It should be noted that the determination of $\hat{\varepsilon}(\mathbf{r})$ requires only the relative phases of the Fourier harmonics with different τ . To find these phases, multiwave diffraction in which the Bragg condition (4.1) holds for several τ at the same time and the intensity and polarization of the diffracted wave carry information on the relative phases of the corresponding $\hat{\varepsilon}^\tau$ (in this case sources of coherent radiation are not required) can be used as in the case of x rays.^{117,118}

It is also important to note that the symmetry properties of cubic space groups impose restrictions on the relative phases of harmonics with different τ , and in the case of special reflections [$(h00)$, $(hk0)$, (hkk) , and (hhh)] they also impose conditions on the relative phases of the components for each $\hat{\varepsilon}^\tau$ (see Table I above). The latter is equivalent to the restriction on the relative phases of the quantities $\varepsilon(\tau; m)$ with different m . As a result, for reflections of the form $(h00)$ and $(hk0)$, actually observed in experiments, the phase problem reduces merely to determining the sign of $\hat{\varepsilon}^\tau$, which is much simpler than the general case.

In concluding this section we shall note a specific peculiarity of "optical structural analysis" of the blue phase, which is useful to keep in mind when performing experimental studies. Because of the informativeness of polarization measurements in structural studies it is desirable to use thin samples in order to simplify the interpretation of the measurements. A kinematic description can be used for them, and the polarization characteristics of scattering are independent of the thickness (see Sec. 4), in contrast to thick samples for which a thickness dependence could exist. In the blue phase the azimuthal dependence of the characteristics of selective scattering, i.e., the dependence on the angle of rotation of the sample around the reciprocal lattice vector τ in the Bragg condition (4.1), is informative. In this case the

components $\varepsilon(\tau; m)$ with $m = 0, \pm 1, \pm 2$ and the interference between them are responsible for the modulation of measured quantities with periods of 2π , π , $2\pi/3$, and $\pi/2$ in the azimuthal angle. By measuring this azimuthal dependence of the scattering characteristics (for example, the scattering intensity of two circular and two linear polarizations) it is therefore possible to determine the amplitude and the relative phases of the components $\varepsilon(\tau; m)$ in the expansion (3.21). Of course, samples which are as close as possible to being single-domain must be used here, because, for example, the azimuthal dependence under study simply does not occur in scattering from completely unoriented polydomain samples. Here we call attention to the fact that the polarization characteristics are determined from the results of relative measurements, in accordance with which the polarization of selective scattering is expressed in terms of the relative magnitudes of the components $\varepsilon(\tau; m)$ and their phases and not in terms of their absolute magnitudes. As a result of this, the accuracy with which the relative values of $\varepsilon(\tau; m)$ are determined depends directly on how well multiple-scattering effects have been excluded in the polarization properties (how well the kinematic approximation is satisfied) or how accurately they are included if they are important.

c) Results of structural studies

As already pointed out, the entire program for determining the structure of the blue phase as described above can in principle be implemented based on optical measurements without any additional assumptions or information. The experimental studies performed both in pure substances and in mixtures have produced significant information on the structure of blue phases, but they do not yet provide a unique reconstruction of this structure. With regard to the magnitude of the period in blue phases, all investigators agree that the blue phases are observed in substances (mixtures) with a short cholesteric pitch ($p \lesssim 5000 \text{ \AA}$). It turns out that in all substances studied approximately the same ratio is observed between the maximum wavelength of selective reflection λ_{BP} (in the medium) and the cholesteric pitch: $\lambda_{BP I} \approx 1.4p$, $\lambda_{BP II} \approx 1.2p$. As the temperature is lowered, the period of the blue phases increases—very strongly for BP I and much more weakly for BP II, according to data obtained by Meiboom and Sammon,²⁶ and does not change at all for BP II according to other data.²⁷ According to the theory (see Sec. 3) the period is virtually independent of the temperature and $\lambda_{BP I} \approx 1.3p$, $\lambda_{BP II} \approx 1.13p$. The observed small disagreement between theory and experiment can be attributed, for example, to the fact that the harmonics dropped from $\hat{\varepsilon}^\tau$ in the theory are neglected.

With regard to the space groups of blue phases, here the picture is less clear and different authors have proposed different space groups for the BP I and BP II phases. It is unanimously agreed upon only that BP I and BP II have cubic structures. Most investigators^{26,27,38-41,43,66,78,85} are inclined to believe that the BP I phase has a cubic body-centered lattice (group O^8) and the BP II phase has a simple cubic lattice (O^2). Polarization measurements performed on

oriented samples^{43,85} are especially convincing here, since in this case the orientation of the reciprocal lattice vectors relative to the crystallographic axes has been established. It should be emphasized, however, that because of the finite accuracy of the measurements other possibilities, for example the subgroups of the groups O^2 and O^8 (O^2 has the subgroup T^1 , while O^8 has the subgroups T^5 and T^4), cannot be completely excluded. For example, the only two sets of reflections (100) and (110) observed in BP II, assigned to the group O^2 , can be formally interpreted as the reflections (200) and (220) of any cubic group except O^1 , O^2 , O^3 , and O^4 (see Table I). A larger number of reflections must be measured in order to make a more reliable determination of the group.

The measurements of selective scattering of light in cholesteryl *n*-alkanoates ($3 < n < 18$),⁴² in which one of the phases is assigned to the group O^5 , differ somewhat from the results presented above. It is concluded in Ref. 101, based on the chirality of the third reflection, that the BP II lattice is body-centered. The absence of unanimity regarding the question of the space groups of blue phases is in all probability attributable to the fact that different authors arrive at their conclusions based on a small number of reflections, though, of course, it has not been excluded that in different compounds and mixtures the blue phases have different symmetry. Another factor that could interfere with the identification of the space group is the deviation of the polarization properties of reflections from the theoretically predicted properties because of multiwave effects; in particular, chirality can appear in nonchiral reflections. Phase separation can also make it difficult to identify phenomena occurring in mixtures.¹⁰²

The structure of the compounds studied has not yet been completely determined by optical methods, but additional assumptions make progress possible here. Thus if in accordance with the theory it is assumed that the modes $\varepsilon(\tau; 2)$ make the main contribution, then the ratio of the moduli of the amplitudes of these modes for different harmonics can be calculated from the data on circular dichroism.^{43,85} Assigning to $\varepsilon(\tau; 2)$ the signs following from the theory, $\hat{\varepsilon}(\mathbf{r})$ can be reconstructed from the formulas (3.24) and (3.25) to within a coefficient. We note that for a number of mixtures of cholesteryl nonanoate and cholesteryl chloride these ratios are on the average equal to $|\varepsilon(110; 2)| : |\varepsilon(200; 2)| : |\varepsilon(211; 2)| \approx 1:1:0.33$ for BP I and $|\varepsilon(100; 2)| : |\varepsilon(110; 2)| \approx 2.5$ for BP II^{43,85} and are close to the values following from Landau's theory [we recall that $\varepsilon(\tau; 2)$ and μ_i in (3.47) and (3.48) are related by the relation (3.37)]. The signs of $\varepsilon(\tau; 2)$ can also be determined (i.e., the "phase problem" can actually be solved) experimentally by NMR, which is a very effective and promising method in structural studies of blue phases.^{32,71,103} NMR spectra can contain information on the dielectric permittivity tensor $\hat{\varepsilon}(\mathbf{r})$ and its spatial distribution in the phase under study. For this reason, in particular, NMR data can be used to determine experimentally the phase relations between different Fourier harmonics $\hat{\varepsilon}^\tau$, which, as we have seen, can be determined to within a phase factor comparatively simply from optical measurements.

Using the values of $\hat{\varepsilon}^\tau$ measured by optical methods for calculating the NMR spectra and regarding the phases of these quantities as free parameters, the corresponding phases can be determined from the condition that the measured and computed NMR spectra coincide, and the distribution $\hat{\varepsilon}(\mathbf{r})$ in the structure under study can thereby be completely reconstructed. As an example, Fig. 18 shows the NMR spectra calculated in accordance with Ref. 103 for the O^2 and O^8 groups; in addition, spectra for all combinations of signs of $\varepsilon(110; 2)$, $\varepsilon(200; 2)$, $\varepsilon(211; 2)$ are presented (for O^2 the signs are unimportant). If the signs are the same as those following from Landau's theory, then the spectra for O^2 and O^8 practically coincide and are analogous to the spectra observed experimentally.³² For other signs the spectra for O^8 differ markedly from the observed spectra, which makes the choice of phases in this case unique.

6. CONCLUSIONS

The preceding sections of this review show that in the last few years great progress has been made in the study of the blue phases of liquid crystals, and this work lies at the frontier of modern research not only in the area of liquid crystals, but also the physics of the condensed state as a whole. Here problems are posed and in many cases, as we have seen, solved for the example of liquid-crystalline systems, but the significance of the problems extends beyond liquid crystals in themselves; the results are of general physical interest and are important, for example, for the theory of phase transitions with a complex order parameter and, in particular, the theory of melting, problems of defects in condensed media, hydrodynamics of anisotropic liquids, etc. Here for the time being there are more unsolved questions than questions for which a definite answer can be given.

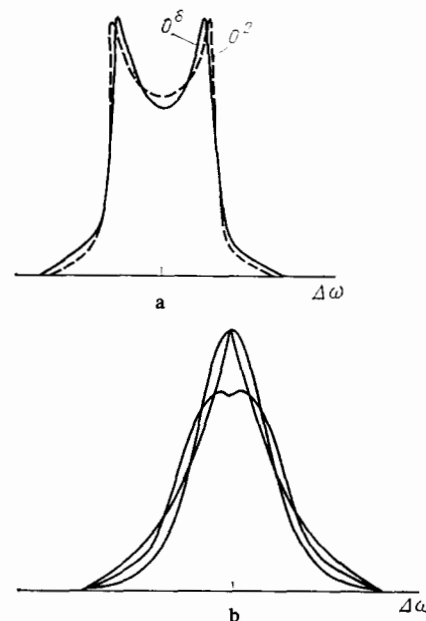


FIG. 18. NMR spectra calculated following Ref. 103. a) Signs of the Fourier harmonics from Landau's theory; b) for the group O^8 with incorrect signs of the Fourier harmonics.

Moreover, the application of new methods to the study of blue phases^{51,52,104} raises new problems. As a result of this, in this review primary attention was devoted to research paths along which most progress has been achieved: symmetry of blue phases, phase transitions in them, and optical properties. Other paths which are no less interesting and important are only mentioned here because they have not yet been adequately researched.

Therefore, in conclusion we shall briefly mention current problems and unsolved questions concerning blue phases.

One of the main problems is the structure of BP III (the fog phase), in which long-range translational order is absent. One possibility is that BP III is a region of strongly developed fluctuations in the isotropic phase^{33,34} [estimates show⁶⁸ that the usual fluctuations (see Sec. 4) cannot explain the magnitude of the circular dichroism observed in this phase]. It is also possible that BP III consists of nuclei of the blue phases BP I or BP II in the isotropic liquid^{48,60} (see Fig. 14). Some modern theories of crystallization suggest an interesting possibility.^{3,105-107} These theories predict that phases without translational order but with long-range orientational order (cubic or icosahedral) can exist between the liquid and crystalline phases; in this case, anisotropy should be observed in light scattering by BP III. Other possibilities have also not been excluded, and BP III must be further studied experimentally and theoretically.

The study of the hydrodynamic and elastic properties of the blue phase are also at the starting stage. Because of their three-dimensional periodic structure blue phases must have an elastic shear modulus, equal in order of magnitude to Kq_c^2 i.e., 10^3-10^4 dynes/cm². Preliminary experiments on unoriented samples have given precisely this value.^{51,52,131} A theory has not yet been advanced for this problem. It is desirable to measure the shear moduli (there are two in cubic crystals) for perfect samples, since it is known that the elastic moduli of crystals are very sensitive to the degree of perfection of the sample. Lattice vibrations in blue phases have not yet been studied and the yield stress of the blue phases has not been determined. These questions are apparently also closely related to the anomalies in the viscosity, which were observed a long time ago in the region of the isotropic-liquid-cholesteric transition (increase in the viscosity by several orders of magnitude and its strong dependence of the rate of shear). It is shown in Ref. 50 that these anomalies are associated with the presence of blue phases and vanish in cases when blue phases do not occur (see Fig. 12). Many uncertainties remain, however, because the viscosity anomalies are observed in some substances in a very large temperature interval of $\sim 15^\circ$.⁵ It would be interesting to study diffusion in the blue phases, since the presence of "disclinations" can strongly affect transport phenomena (diffusion along dislocations occurs in ordinary crystals).

We note that the existence of shear moduli at zero frequency (if they indeed exist) would mean that the blue phase is actually a solid, but a very unique one. Although three-dimensional long-range order in the orientations of the molecules exists in the blue phase, long-range order does not

exist in the arrangements of the centers of gravity of the molecules. The molecules can therefore flow (though with a high friction) through the lattice of the order parameter (an analogous "permeation" process also occurs in the cholesteric structure^{1,5}).

The question of orientation of blue phases by surfaces is very interesting. In some cases the blue phases are apparently oriented so that the vector of the strongest harmonic in the structure would be perpendicular to the surface.⁸⁵

The electrical properties of blue phases have not been adequately studied. Only the untwisting and transition of blue phases into the cholesteric or nematic phases in an external field and field-induced birefringence have thus far been observed.^{48,53,54,122} We note that piezoelectricity can occur in the crystal class T , but should be absent in the class O .⁹⁷ This result, however, was obtained for weak deformations. Since in blue phases small loads can lead to large deformations (because of the smallness of the shear moduli), the question of piezoelectricity deserves a detailed theoretical and experimental study.

More accurate and thermodynamically equilibrium thermal measurements in the isotropic and blue phases, which, in particular, would resolve the question of the role of fluctuations in the phase transitions studied, are extremely desirable.¹³¹ With regard to the best developed optical methods for studying blue phases, here, in analogy to x-ray diffraction,^{117,118} multiwave diffraction effects could be very useful for structural studies (in particular, for determining the phase of the structural amplitude). This question has, however, not yet been studied theoretically or experimentally.

We also point out some general conclusions that can be drawn for other areas of solid-state physics from the results obtained for the blue phase. 1) Lifshitz's invariants in Landau's expansion can lead to three-dimensional (in particular, cubic) structures (this could be important for magnetic materials and ferroelectrics, where an analogous situation can occur). 2) The cubic term in Landau's expansion does not necessarily reach a minimum in body-centered structures, which could be significant for the theory of melting of solids,¹⁰⁸ for the theory of matter in neutron stars,¹⁰⁹ and for cubic smectics (D smectics)¹²⁸ and lyotropic crystals.¹²⁹ 3) Apparently there is a far-reaching analogy between the disclination structure of blue phases and the disclination structure in the lattices of some solids.¹¹⁰ In particular, in both cases disclination-free structures can be constructed in a space with more than three dimensions (on three-dimensional spheres in a four-dimensional space^{111,112}). Constructions of this type are useful for understanding the nature of short-range order in glasses, amorphous solids, and liquids.^{111-113,130} Analogies between the physical properties of the blue phase and colloidal crystals, which have been intensively studied in recent years (see the review of Ref. 114), should also be noted. These include, in particular, the Bragg diffraction of light, elastic moduli comparable to those in the blue phase, analogous phase transitions, anomalies in the viscoelastic properties, etc. There is thus still much left to be done in the study of blue phases. It is, however, significant

that an adequate approach has been found to a problem with an almost 100-year history, and for this reason new progress in the study of this extremely interesting phase state of matter should be expected in the near future.

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¹There is evidence (see the article by Stegemeyer and Bergmann in Ref. 4) that the blue phase was first observed by Reinitzer.

²A more detailed exposition of the results of early studies can be found in Ref. 4 (see also Ref. 6).

³See also the recently published paper of Ref. 127.

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