

where $A_{100} = 0.291$ for BPII and $A_{110} = 0.175$ for BPI, while ϵ is the scalar order parameter characterizing the local orientation ordering of the molecules in the cubic structures of BP. The theory predicts a universal temperature dependence of ϵ for LC phases:¹⁰

$$\epsilon = \frac{3\beta B_\phi + [\beta^2 B_\phi^2 + 96\gamma T_\phi a_1 (T_\phi - T)]^{1/2}}{16\gamma T_\phi} \quad (5)$$

where $BO^2 = 1.031$, $FO^2 = 1.164$, $BO^5 = 1.017$, $FO^4 = 1.132$, T_ϕ is the temperature of the phase transition from the isotropic liquid to the BP, and α_1, β, γ are the coefficients in the expansion of the free energy in powers of the order parameter. Figure 4b shows the temperature dependence of the scalar order parameter, determined by expression (4) from the experimental values of $\epsilon(\tau, 2)$. The continuous curve is the theoretical dependence of the scalar order parameter obtained from (5) by selection of the parameters β/γ and a_1/γ . For the curve shown in Fig. 4b, $\beta/\gamma = 0.34$, $a_1/\gamma = 0.012 \text{ K}^{-1}$. We see that the value of the local orientational order remains practically unchanged in the phase transition BPI-BPII.

The narrow diffraction peak in thick specimens in the region of the maximum of the main reflection (Fig. 1e), not previously observed in a BP of a LC may be due to diffraction with Fourier harmonic $\epsilon(\tau, -2)$ (not natural). The narrow half-width of the additional peak is evidence of the good quality of the crystal. An estimate of the region of coherent scattering¹¹ from the width of the additional peak reveals that it is about $10^2 \mu\text{m}$, i.e., it corresponds to the thickness of the single crystal. From the intensity of the narrow-band peak we can estimate the value of the modulus of the Fourier harmonic $\epsilon(\tau, -2) \approx 4 \cdot 10^{-4}$. We must emphasize that this is the upper limit of the esti-

mate $\epsilon(\tau, -2)$, since the narrow-band peak may arise with negligible violations of the ideality of the translational order in BP (e.g., with bending of the planes of the cubic lattice through an angle of about 1°). We can assert that $\epsilon(\tau, -2)$ constitutes not more than 1/50 of the Fourier harmonic $\epsilon(\tau, 2)$. The small value of $\epsilon(\tau, -2)$ indicates the correctness of the application of the two-beam approximation in the dynamic theory of diffraction and of allowing for Fourier harmonics of only one type $\epsilon(\tau, 2)$ in Landau's theory of phase transitions.

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Dechiralization of cholesteric liquid crystals due to the action of ionizing radiation

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The authors have studied the influence of ionizing radiation on the spectra of selective reflection of light by cholesteric liquid crystals (CLC)—derivatives of cholesterol. They show that, under the influence of γ -(⁶⁰Co) and proton ($E_p = 70 \text{ MeV}$) irradiation with doses of up to 200 kGr, in the derivatives of cholesterol there is a marked change in the spectra of selective reflection of light, which is due to the formation of radiation-induced impurities. The presence of these impurities, in the first place, reduces the temperature range of existence of the CLC, and, in the second place, alters the effective twisting capacity of the molecules, leading to dechiralization of the system as a whole.

INTRODUCTION

Chiral structures are traditional and very interesting objects of investigation in optics. The simplest examples of such structures are cholesteric liquid crystals (CLC) for which the spiral twisting of the supermolecular structure causes selective transmission and reflection of light, and also gigantic optical activity. As established on the basis of

copious experimental material, the pitch of the spiral of the CLC is very sensitive to various external actions — electromagnetic field, temperature, pressure, etc.¹ However, there have been practically no investigations of the changes of the optical properties of CLC under the influence of such an important factor as ionizing radiation (IR). The importance of such investigations is due not only to possible practical applications but also to the

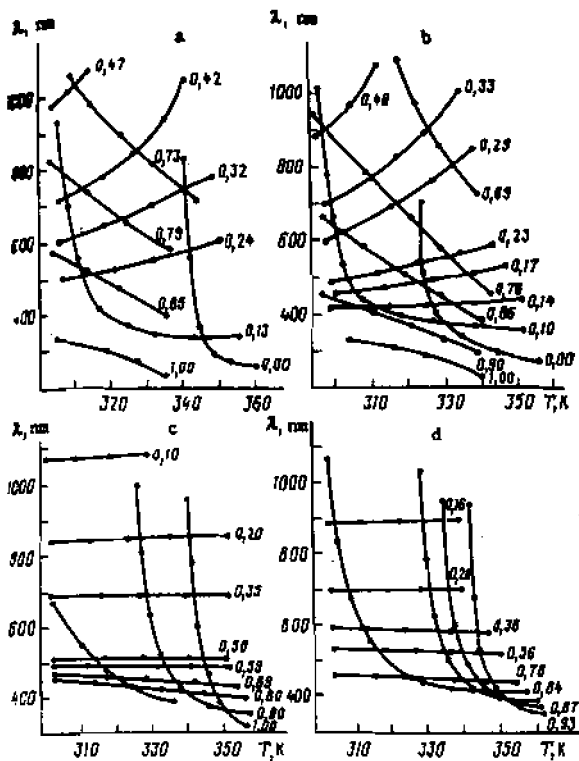


FIG. 1. Temperature dependences of wavelength λ of selective reflection in mixtures of CP + CC (a, b) and CP + CF (c, d). a, c) mixtures of nonirradiated components; b) CP irradiated with protons to a dose of 145 kGr; d) CF irradiated with γ -quanta to a dose of 100 kGr.

general problem of elucidating the influence of IR on chiral structures both at the macrostructural and at the molecular level.

The aim of our work was to fill this gap. We studied the temperature dependences of the wavelengths of selective reflection of CLC and their alterations under the influence of IR. For the initial and irradiated substances, and also for radiation-induced impurities, we determined the so-called molecular twisting forces, which are a quantitative measure of the chirality of the CLC. We measured how the degree of dechiralization of the CLC depends on the dose of IR.

EXPERIMENTAL METHOD

We studied two-component mixtures of three derivatives of cholesterol: cholesteryl formate (CF), cholesteryl pelargonate (CP), and cholesteryl chloride (CC). The choice of mixtures as objects of investigation was prompted, in the first place, by their wide practical applications, and, in the second place, by the necessity of determination of the molecular forces of twisting, the concept of which is based on the laws of change of the wavelength of selective reflection with concentration.² In this article we give data for two mixtures: CP + CC and CF + CP. As the irradiated component in the CP + CC mixture we used CP (the CC was not irradiated), and in the CF + CP mixture we first irradiated the CF. Irradiation of only one component pursued the aim of a more reliable estimation of the changes in CLC due to IR.

The substances were irradiated with 70 MeV protons in a V-240 isochronous cyclotron to a dose

of 145 kGr and with γ -quanta in a K100,000 (⁶⁰Co) apparatus to a dose of 100 kGr (Grey(Gr) = J/kg).

Measurements of the selective reflection spectra vs the temperature and dose of radiation were made in an SF-16 spectrophotometer in the wavelength range 200-1200 nm. For the planar-oriented specimens the thickness of the CLC layer was 15 μ m. Thermostabilization (to within 0.1°C) was effected by a special unit which could also vary the temperature at 0.5-5°C/min.

Before presenting the experimental results it seems pertinent to make one remark. In the region of selective reflection of light in the transmission spectrum of a planar layer of CLC we observe a minimum which coincides in wavelength with the maximum of the selective reflection.² Therefore to simplify with the maximum of the selective transmission minimum, but in describing and discussing the results we use the term "selective reflection."

EXPERIMENTAL RESULTS

The family of temperature dependences of the wavelength λ of the maximum of selective reflection over a wide range of concentrations is shown in Fig. 1 (mixtures CP + CC and CF + CP). As it follows from Fig. 1, the overall course of the $\lambda(T)$ dependences in systems with an irradiated component is analogous to the case of an unirradiated mixture. In particular, for CP-CC mixtures with rise of the concentration C of CC the inclination of the dependence $\lambda(T)$ changes twice: when $0 \leq C \leq 0.2\lambda(T)$ it monotonically decreases, when $0.2 \leq C \leq 0.6$ it monotonically increases, and finally, when $0.6 \leq C \leq 1\lambda(T)$ it again decreases.

Moreover, as seen from a more detailed comparison, the behavior of $\lambda(T)$ in the two types of mixture manifests quantitative differences: On irradiation, the $\lambda(T)$ curves shift to lower temperatures, owing to the fall in the phase transmission temperatures as a result of formation of radiation-induced impurities in the system.^{3,4} However, it

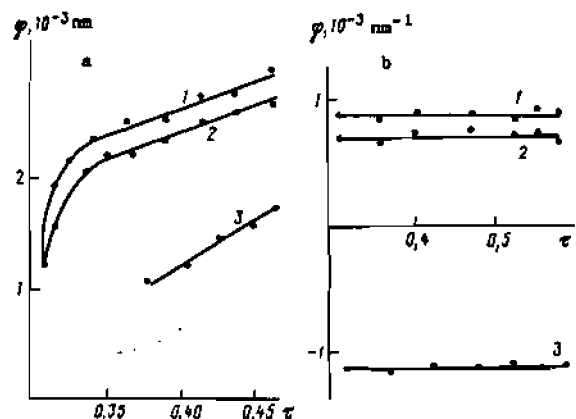


FIG. 2. Dependences of values of effective twisting forces on parameter τ ($\tau = 0.22 T/T_1 \eta(T/T_1)$ (Ref. 11)), where T_1 is the temperature of the phase transition of cholesterol to an isotropic liquid, $\eta(T/T_1)$ is the order parameter.²² a) Nonirradiated CP (1), irradiated with protons to a dose of 145 kGr (2), radiation-induced impurities (3); b) nonirradiated CF (1), irradiated with gamma quanta to a dose of 100 kGr (2), radiation-induced impurities (3).

seems impossible to explain the change in the course of the $\lambda(T)$ dependences in the irradiated mixtures purely on account of the change in the phase transition temperatures.³ This is easy to verify if we reckon that the curves of $\lambda(T)$ in Fig. 1 cannot be compared with one another by a simple transfer along the temperature axis, because as a result of irradiation there is a change in the slope of the $\lambda(T)$ curve. In fact, this means that as a result of irradiation there has been a change in the actual twisting capacity of the irradiated component; a quantitative measure of this is the molecular force of twisting ϕ .

The molecular forces of twisting are determined from the shape of the curve of the reciprocal of the wavelength of selective reflection of the mixture vs the concentration of the components²:

$$\lambda^{-1} = C\phi_1 + (1-C)\phi_2 + C(1-C)\phi_{12}$$

where ϕ_1 and ϕ_2 are, respectively, the molecular forces of twisting of the first and second components, respectively, ϕ_{12} is a parameter representing the mutual influence of the components of the mixture, and C is the concentration of the first (irradiated) component, usually expressed in units by weight (as shown in Ref. 6, the law $\lambda^{-1}(C)$ is better satisfied with a set of weight concentrations). As it follows from the expression, the effective molecular twisting forces are determined by extrapolation of the dependence $\lambda^{-1}(C)$ to the values $C = 0$ and $C = 1$.

The quantities ϕ_1 , ϕ_2 , ϕ_{12} were determined by approximation of dependence (1) by the method of least squares. The temperature dependences ϕ_1 , ϕ_2 are given in Fig. 2 for CP and CF, respectively. As seen from Fig. 2, in CP and CF under the influence of IR there is a reduction of the effective molecular twisting forces. It is logical to treat this as the result of formation of radiation-induced impurities in the system, with values ϕ^{imp} lower than in the initial molecules. The values of ϕ^{imp} for the impurities can also be estimated if we use the above method for the same irradiated component and consider it as a mixture of molecules of the initial substance with known ϕ and "defective" molecules characterized by some integral parameter ϕ^{imp} .

The correctness of this approach is confirmed, firstly, by the results in Refs. 3 and 4, which indicate the stability of the radiation-induced impurities. Secondly, the introduction of the concept ϕ^{imp} is also based on the circumstance that the value of ϕ^{imp} is practically independent of the impurity concentration (dose of radiation)⁴: For example, when the dose is changed from 110 to 190 kGr, ϕ^{imp} for CP deviates from the values in Fig. 2 (dose 145 kGr) by less than 10%.

To determine ϕ^{imp} we used a linear variant of approximation (1), in which we put $\phi_{12} = 0$, and determined the concentration of radiation-induced impurities by the method in Ref. 3. In particular, for CP with a dose of 145 kGr the impurity concentration is approximately 15%. The obtained temperature dependences ϕ^{imp} are also shown in Fig. 2. From Fig. 2 we see that the value of ϕ^{imp} in CP irradiated with a dose of 145 kGr is about half as great as ϕ for the initial CP, and in CF ϕ^{imp} changes sign at a radiation dose of 100 kGr.

DISCUSSION OF RESULTS

Thus, as a result of the action of IR in derivatives of cholesterol, the magnitudes of the effective molecular twisting forces decrease. Let us consider the possible causes of this effect.

As shown in Ref. 3, irradiation leads to breakdown of the CLC molecules, resulting in the formation of radiation-induced impurities in the system. A change in the chemical structure of the molecules of cholesterol derivatives under the influence of IR can occur either in the steroid nucleus or in the alkyl and isopropyl chains. Leder⁷⁻⁹ studied the influence of the chemical structure of molecules of cholesterics on the magnitude of the twisting force. In these articles it was shown that the effective twisting force increases⁷ with increasing length of the alkyl chain of the compounds of the homologous series of aliphatic esters of cholesterol. In Ref. 8 Leder obtained interesting results of an investigation of the reciprocal effective wavelengths in relation to the length d of the radical R (Fig. 1). It was shown that the reciprocal effective wavelengths in relation to d lie on a straight line both for right-handed and for left-handed cholesterics. This straight line can be analytically expressed by the equation $\lambda^{-1} = 7.5d + 15.6$. Cholesterics in which d is less than 2.08 Å are right-handed, while cholesterics with d greater than 2.08 Å are left-handed. In other words, with variation of d both the absolute values and the signs of the effective twisting forces may alter.

A second important factor determining the spiral twisting is the structure of the steroidal skeletons of the molecules of cholesterol derivatives, in particular, the position of the double bond $C=C$ (Fig. 1). For example, in Ref. 9 it was shown that there is a marked tendency toward increase in the "rightness" of cholesterics when the double bonds in positions 7-8 and 5-6 disappear or this bond is displaced to position 8-14. Now let us consider what types of structural changes in the molecules can bear responsibility for a change in the spiral twist under irradiation.

Cholesteryl pelargonate. As follows from the results obtained by us previously by ESR and IR spectroscopy, under the influence of IR, in CP there is a change in the geometry of the steroid nucleus of the molecule, due to changes in its chemical structure; but there are little or no changes in the structure of the alkyl chain. Analysis of the structure of the steroid nucleus of the molecules of the cholesterol series suggests that the weakest link with respect to irradiation is the double bond in position 5-6 (Fig. 1), joining quadruple and triple carbon atoms; according to many data (see, e.g., Ref. 10), in irradiation of hydrocarbon compounds, dissociation of C-C bonds near quadruple and triple carbon atoms preponderate. The probability of dissociation of these bonds is 5-10 times greater than the probability of dissociation of other types of C-C bonds. As shown by Leder,⁹ change in the structure of the steroid nucleus near bond 5-6 reduces the twisting capacity of CP. For example, if the carbon atoms in positions 5-6 are joined, not by a double bond, as in cholesterol derivatives, but by a single bond, as in the cholestanol series, then the value of ϕ decreases by a factor of 5-10. Consequently, the

reduction in ϕ for CP, experimentally observed by us, is evidently due to radiation-induced changes in the region of the bond 5-6 of the steroid nucleus of the molecule.

Cholesteryl formate. In contrast with CP, the principal consequence of radiolysis of CF, as follows from ESR data and IR spectroscopy, is a change in the formyl termination with formation of COOH groups, with the result that the molecules are joined into dimers by hydrogen bonds.⁴ The dechiralization of CF is evidently due to this circumstance, since the dimers formed may possess a twisting force of opposite sign.

From the above it follows that under the influence of IR there is a marked change in the spectra of selective reflection of CLC, which is due to formation of radiation-induced impurities. These impurities play a double role: In the first place they alter the temperature range of existence of the CLC; and in the second place, they alter the effective twisting capacities of the molecules.

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Influence of forced magnetoelectric convection on the dopant impurity distribution in growth of single crystals by the Czochralski method

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The authors have constructed a mathematical model of the processes of heat and mass transfer in the melt during growth of single crystals by Czochralski's method in a magnetic field with simultaneous passage of an electric current through the melt. They compare the results of numerical and natural experiments. By the method of numerical experiment they determine the optimal technological parameters of the process for which one achieves the smallest scatter of the impurity concentration along the radius of the crystal.

1. INTRODUCTION

In order to analyze the processes of heat and mass transfer in melts, recently increasing use has been made of methods of numerical experiment (NE)-modeling technological processes on a computer. Numerical experiments enable us to obtain fairly accurate estimates of the influence of any particular technological parameter on the source of the process. This type of estimate is very important, because it often enables us to reduce the number of costly natural experiments.

A number of articles have recently been published with descriptions of a mathematical model of Czochralski growth of single crystals under magnetohydrodynamic (MHD) actions.¹⁻³ An obvious consequence of MHD action is reduction of such undesirable phenomena as temperature fluctuations, thermal asymmetry, vibration of the melt, etc.³

An interesting principle, in our view, of action on the melt is described in Ref. 4. Simultaneous transmission of an electric current through the melt and action of a constant magnetic field generates in the melt easily controlled magnetoelectric convection.

The aim of our present work was to investigate the features of a mathematical model of the processes of heat and mass transfer in the melt during growth of single crystals of elemental semiconductors by the Czochralski method in a magnetic field with simultaneous transmission of an electric current through the melt, performance of numerical experiments on the model, comparison of the results of the natural experiment with those of calculation based on various physical parameters, and determination of the paths of minimization of the nonuniformity of the distribution of the impurity along the radius of the single crystal.

2. FEATURES OF MATHEMATICAL MODEL

It is known⁵ that the flow of melt in a crucible during growth of single crystals by the Czochralski method satisfies the Navier-Stokes equation,

$$\begin{aligned} \frac{\partial \mathbf{V}}{\partial t} + (\mathbf{V} \nabla) \mathbf{V} &= R e^{-1} \Delta \mathbf{V} - \nabla p + \mathbf{l}, \\ \frac{\partial T}{\partial t} + (\mathbf{V} \nabla) T &= R e^{-1} P r^{-1} \Delta T, \quad \operatorname{div} \mathbf{V} = 0 \end{aligned} \quad (1)$$