Photoinduced optical anisotropy of iron borate

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A report is given of an investigation of a new magnetooptic effect—photoinduced linear optical anisotropy (PLOA)—which appears in the basal plane of a magnetically ordered $FeBO_3$ crystal as a result of illumination with unpolarized light in the presence of an external magnetic field sufficient to saturate the magnetic moment in the easy magnetization plane. The magnitude of the PLOA is determined by the presence of the Ni dopant, which is in a low-spin state, and the direction of the anisotropy axis is governed by the orientation of the external field at the moment of illumination. The kinetics of the process of inducing the PLOA depends on the intensity of illumination of the crystal, but is independent of temperature. The results are given of a spectroscopic investigation of the magnitude of the PLOA and of the photosensitivity spectrum, which indicate that an Fe^{3+} host-lattice ion is a component of each of the photosensitive centers and it also acts as the source of the forces that reorient the centers during illumination after a change in the direction of the magnetic field. A study is reported of the storage of optical data on the basis of the new effect. The results are analyzed on the basis of an ordering model for Jahn-Teller distortions at the impurity ions by interaction with the spin-orbit distortions of the photoexcited Fe^{3+} ions. A comparison of the calculations with the experimental angular dependences of the PLOA shows good agreement with the selected model.

Magnetooptic effects in magnetically ordered crystals have been investigated quite thoroughly and classified on the basis of the orientation of the spin system relative to the direction of propagation of light. The Faraday and Cotton-Mouton effects investigated experimentally and theoretically have found extensive applications in optical radiation processing devices and they are used as the basis of methods employed in physics research on domain structures, magnetic parameters, and energy spectra of magnetic materials.[1-5] Nevertheless, it is known that a change in the polarization of electromagnetic radiation propagating in high-symmetry crystalline media may be due to the presence of anisotropic centers of different kinds, which lower the local symmetry. Induced ordering of such centers in cubic crystals gives rise to birefringence and dichroism.[6] These effects have been found first in alkali halide crystals with color centers.[7] Such centers form because of the presence of heterovalent impurities, exhibit anisotropy of the absorption and refraction of light, and have several orientations relative to the crystallographic axes. Illumination of such crystals with linearly polarized light induces a preferred direction of the orientation of the anisotropy axes of the color centers, and the macroscopic optical properties become anisotropic. In magnetic materials such effects occur in yttrium iron garnet doped with silicon, in which linear dichroism sets in after illumination with linearly polarized light or after cooling in a magnetic field.[8] These effects have been interpreted as the localization of an "excess" electron at the site of an Fe ion with a local symmetry axis C_3 corresponding either to a minimum of the absorption of light of given polarization plane azimuth or to a minimum of the anisotropy energy for a given direction of the field. The orientations of the induced dichroic axis and of the uniaxial magnetic anisotropy axis can be al-tered by rotating the plane of polarization of the incident light. The appearance of an excess electron at the site of a magnetically active ion is due to the compensation of the charge of the heterovalent impurity Si^{4+}. In addition to the effects induced by the anisotropic interaction, magnetic materials also exhibit effects induced by unpolarized light.[9,10] The ensuing physical phenomena have been the subject of many discussions and there is as yet no agreed interpretation.[11,12] Media whose properties are affected by illumination with unpolarized light include iron borate, for which photoinduced changes in the magnetic susceptibility[13] and in the magnetoacoustic resonance frequency[14] have been reported and an anisotropy of the optical properties induced by unpolarized light has been observed for the first time.[15] We shall report the results of comprehensive investigations of a photoinduced linear optical anisotropy (PLOA) and consider a model of anisotropic-centers, based on spectroscopic and orientation measurements, and the mechanism of ordering of these centers, based on the interaction of lattice distortions around a photoexcited host-lattice iron ion with distortions around impurity ions characterized by a degenerate orbital state. The results are given of a comparison of model calculations with experimental orientational dependences, which demonstrates that a qualitative agreement is obtained.

EXPERIMENTAL METHOD AND SAMPLES

When light propagates in a medium with linear optical anisotropy, the linear polarization of this light is transformed into an elliptic polarization with the ellipticity proportional to the birefringence and with the azimuth of the major axis of the polarization ellipse rotated by an angle

proportional to a linear dichroism. We determined these effects by a polarimetric method with modulation of the azimuth of the plane of polarization, which enabled us to measure the ellipticity and azimuth with high accuracy. The apparatus used to determine these effects was automated and improved,[16] so that the dependences of the recorded quantities on external actions could be recorded by an X-Y plotter at low intensities of the measuring beam under enhanced angular resolution conditions. Samples were placed in a cryostat on a heat sink with a variable temperature 78–350 K. The cryostat had only warm windows which transmitted the measuring monochromatized beam $(0.4$–$1.1\,\mu)$ and the main light beam with an intensity of ~ 0.1 W/cm^2 on the surface of the samples. Two systems of Helmholtz coils created in the plane of the sample a magnetic field up to 150 Oe, whose vector could be oriented along any direction in the basal plane without altering the field intensity. The investigated samples were nominally pure and Ni-doped single-crystal iron borate plates with linear dimensions 2–4 mm and $d = 30$–$60\,\mu$ thick. Single crystals of FeBO$_3$ are rhombohedral antiferromagnets (D^{6}_{3d}) exhibiting a weak ferromagnetism with a Curie temperature $T_C = 343$ K. In the transparency window of this compound there are two absorption maxima due to the $^6A_1 \rightarrow {}^4T_1$ and $^6A_1 \rightarrow {}^4T_2$ transitions in the Fe^{3+} ion in the crystal field.[17] Previous investigations revealed photoinduced changes in the magnetic susceptibility[13] and in the magnetoacoustic resonance frequency[14] at $T = 77$ K. These effects are weak in nominally pure crystals prepared under different conditions and they vary from sample to sample. This may be due to the presence of some accidental impurities in the undoped samples. Special investigations[18] have shown that the photosensitivity increases on increase in the Ni content so that we carried out our measurements mainly on the doped crystals. In view of the absence of direct methods for the determination of low impurity concentrations, we did not determine the concentration dependences of the effect and its characteristics, but simply noted that an increase in the Ni impurity concentration increased the induced optical anisotropy. A linear optical anisotropy was found for the propagation of light along a direction close to the principal symmetry axis, which was perpendicular to the plane of the sample. In this case one could show that the anisotropy could be described simply by the planar form of the symmetric part of the permittivity tensor.[19] Rotation of the plane of polarization and ellipticity of the beam should be related in the following way to the components of the permittivity tensor:

$$\Phi = \frac{\omega d}{cn}\left(\frac{\varepsilon_{xx}'' - \varepsilon_{yy}''}{2}\sin 2\theta - \varepsilon_{xy}''\cos 2\theta\right),$$

$$\chi = \frac{\omega d}{cn}\left(\frac{\varepsilon_{xx}' - \varepsilon_{yy}'}{2}\sin 2\theta - \varepsilon_{xy}'\cos 2\theta\right), \quad (1)$$

where ε_{ij}' and ε_{ij}'' are the real and imaginary components of the symmetric part of the permittivity tensor in the laboratory coordinate system in which the z axis coincides with the direction of propagation of the light and the x axis lies along the horizontal direction of the magnetic field; θ is the azimuth of the plane of polarization of the incident light relative to the x axis. Since the information on the optical anisotropy obtained from birefringence measurements is generally the same as that deduced from the dichroism and the experimental determination of the dichroism is easier, we shall generally consider the dependences of the PLOA on the external parameters on the basis of the dichroism measurements.

EXPERIMENTAL RESULTS

The magnitude of the effects representing the optical anisotropy induced by magnetic order in crystals is usually governed only by the orientation of the spin system relative to the plane of polarization of the measuring light. However, in the case of iron borate it has been found for the first time that linear optical anisotropy may be altered by interaction with unpolarized light.[15] Figure 1 shows the time dependence of the influence of light on the optical anisotropy of FeBO$_3$ at 78 K. The experimental geometry is shown in the inset, where the direction of propagation of the measuring beam is represented by the wave vector $\mathbf{k}$ and the initial orientation of the plane of polarization is represented by the vector $\mathbf{E}$. A signal proportional to the ellipticity of the measuring beam was recorded. On application of a magnetic field along the x axis and then along the y axis (at moments $t = 0$ and 2 min) a polarimeter recorded the ellipticity due to the magnetic linear birefringence. When a crystal was illuminated $(t = 6$ min) in the presence of a magnetic field, the ellipticity changed by δ and this photoinduced change was much slower than simply in the case of switching of the magnetic field and tended to a saturation value which remained constant after the end of the illumination $(t = 8$ min). When the field was switched back to the x axis $(t = 9$ min), the change in the ellipticity represented the magnetic linear birefringence. Illumination in this field $(t = 10$ min) resulted in relaxation to a new value of the ellipticity such that the magnitude of the relaxed component was twice as high as the previous value. A second illumination $(t = 18$ min) in H_y restored the initial ellipticity obtained by first illumination in the same field. Reversal of the sign of the applied field did not alter the values of the magnetic linear birefringence Δ and of the induced linear anisotropy δ. The magnitude of the
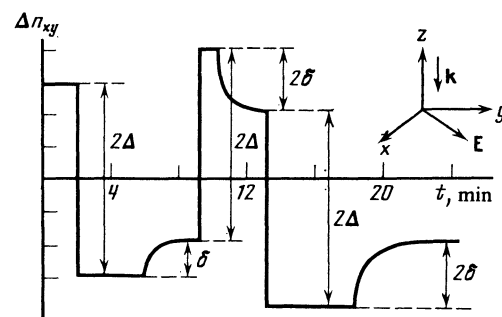

FIG. 1. Time dependence of the ellipticity, proportional to Δn_{xy}. Magnetic fields H_x and H_y are applied respectively at $t = 0$, 9 min and $t = 2$, 13 min. Illumination of the crystal is started at $t = 6$, 10, and 18 min, but stopped during relaxation; Δ is the magnetic linear birefringence; δ is a quantity representing the photoinduced optical anisotropy.

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magnetic linear birefringence in the investigated samples was $\Delta \sim 1.5 \times 10^{-4}$, whereas the photoinduced birefringence depended on the concentration of nickel oxide in the initial charge and for 0.1% of nickel it amounted to $\delta \sim 0.5 \times 10^{-4}$. The photoinduced anisotropy was practically saturated in $t \sim 3$ min at the illumination intensity employed in these experiments. When the duration of illumination was reduced, there was a corresponding fall of the induced birefringence, but there was no duration threshold.

It follows from the results of Fig. 1 that illumination of $FeBO_3$ crystals induces an additional optical anisotropy, which does not influence the magnetic birefringence. Since after the first illumination the value of δ was half the value during subsequent illuminations, the centers responsible for the induced anisotropy were clearly disordered before the illumination and became ordered by the first illumination, whereas subsequent illuminations caused their reorientation. The sign of δ was opposite to the sign of the Cotton-Mouton effect when measurements were made in magnetic fields with the same orientation.

The influence of an external magnetic field on the induced optical anisotropy was studied by recording the field dependences of the linear magnetic birefringence of samples in different states. The dependences of Δ on the external field applied along the x or y axes to an unilluminated sample, a sample previously illuminated in a field H_y and a sample illuminated in a field H_x, are plotted in Fig. 2 (curves a, b, and c, respectively). The illumination duration was selected such that the induced anisotropy δ reached saturation ($t \geqslant 3$ min). It is worth noting the following observation, which can be deduced from Figs. 2b and 2c. When a crystal is illuminated in saturating fields the value of Δ in the absence of a magnetic field is finite and larger than δ in saturating magnetic fields ($H > 100$ Oe). This means that the optical anisotropy after illumination includes a contribution of the spin system of the crystal, which creates a domain structure characteristic of the uniaxial magnetic anisotropy. This anisotropy is induced by illumination of a magnetically saturated crystal.[14] Moreover, we can see that the value of δ in saturating magnetic fields in independent of the field. Reversal of the sign of the external field gives rise to field dependences which are symmetric relative to the ordinate in Fig. 2. Measurements of δ as a function of the intensity and sign of a magnetic field applied during illumination showed that its value became saturated on saturation of the spin system and
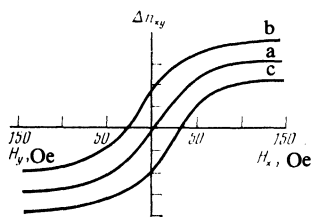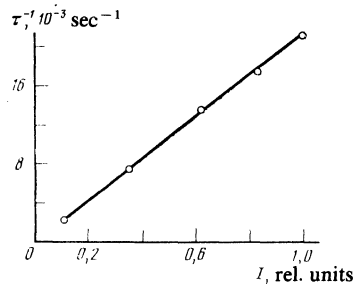

FIG. 3. Dependence of the rate of formation of the PLOA (proportional to τ^{-1}) on the intensity of the exciting light.

is an even function of the external field direction. In other words, the value of δ was governed by the degree of homogeneity of the spin system, and illumination induced a linear optical anisotropy which we shall call the photoinduced linear optical anisotropy (PLOA).

Measurements of the relaxation time (τ) of the PLOA showed that the relaxation depends on the intensity of illumination of the sample. Figure 3 shows the dependence of τ^{-1} on the illumination intensity. This was determined using a nonselective detector and normalized to the nominal emissivity of the illumination source. Clearly, the rate of the buildup of the PLOA, proportional to τ^{-1}, increases linearly on increase in the intensity. It should be pointed out that at low values of the illumination intensity the PLOA no intensity threshold. Hence, the buildup the PLOA is a quantum property and is governed by the number of events with of light absorption by a crystal. This is supported by experiments involving pulsed illumination with low-intensity light, which demonstrate that the pulsed PLOA is cumulative and reached saturation after a certain number of pulses (dependent on the duration and intensity), it value. Attempts to alter the rate of PLOA buildup by varying the sample temperature showed that, within the limits of experimental error, there was no influence of temperature. An important parameter of thermal relaxation of the PLOA was the activation energy governing the heights of the potential barriers that have to be overcome by anisotropic centers under thermal excitation conditions. This energy was determined by the method of linear variation of the sample temperature, which was preferable to isothermal measurements because of the higher precision and greater convenience. Figure 4 shows the dependences of the change in the linear dichroism on the temperature varied at a rate of $dT/dt = 0.7$ K/min. Curve 1 was obtained for a previously unilluminated sample in a magnetically saturated state, curve 2 was obtained after illumination in a field oriented along the x axis, and curve 3 represents a sample illuminated in a field oriented along the y axis. It is clear from Fig. 1 that the value of the PLOA relaxed to the linear magnetic dichroism at $T = 130$ K. The calculated activation energy $E_u = 0.23$ eV agreed well with this kinetic parameter of the photoinduced change in the magnetic susceptibility.[13]

The transition to the PLOA characterized by $\delta = 0$, observed on heating at $T = 130$ K, was not a phase transition because at intermediate temperatures of $78 < T < 130$ K the
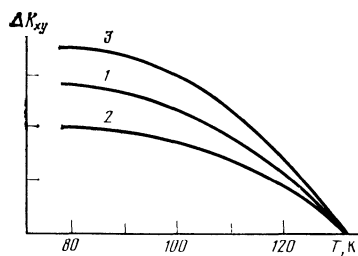

FIG. 2. Magnetic-field dependences of the ellipticity, proportional to the magnetic linear birefringence Δn_{xy} of an unilluminated crystal (a) and of a crystal subjected to a preliminary illumination field H_y (b) and H_x (c).

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FIG. 4. Temperature dependences of the rotation of the plane of polarization proportional to the linear dichroism ΔK_{xy} of unilluminated samples 1 and of samples illuminated in fields H_x (2) and H_y (3). Measurements were carried out in a field oriented along the x axis.
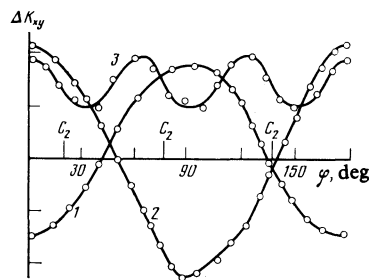

FIG. 5. Angular dependences of the photoinduced linear dichroism 1 and of the magnetic linear dichroism 2. A magnetic field is rotated and the azimuth of the plane of polarization is $\theta = \pi/4$. Curve 3 is a plot of δ (PLOA) in the case when the angle between the plane of polarization and the external field is kept constant at $\theta' - \varphi' = \pi/4$.

value of δ relaxed in isothermal experiments from values corresponding to curves 2 and 3 to a value represented by curve 1 and the relaxation time depended exponentially on temperature. Therefore, the ordering of the anisotropic centers which altered the optical anisotropy and which appeared on illumination with unpolarized light was a metastable effect at $T = 78$ K, and disappeared at higher temperatures. Moreover, curve 1 was reproducible during cooling and heating, whereas curves 2 and 3 could be obtained only after illumination of a sample.

The symmetry properties of the anisotropic centers responsible for the PLOA were determined by recording the orientational dependences of the photoinduced ellipticity and dichroism on the angle between the twofold symmetry axis and the external field applied in the basal plane during illumination. These dependences were obtained for the case when the azimuth of the transmission axis of a polarizer was kept constant at an angle $\pi/4$ to the twofold axis, and also in the case when the azimuth of the polarizer was rotated along with the field in such a way that the angle between the external field and the plane of polarization of the measuring beam was $\pi/4$. Such measurements made it possible to determine the orientation of the indicatrix of the PLOA relative to the external magnetic field and to compare the characteristic directions in a crystal with the induced optical anisotropy. The results of these measurements are presented in Fig. 5, where curve 1 represents the behavior of the PLOA in the former case and curve 3 represents the behavior in the latter case. Since the first dependence was found to have a period π and was described well by a harmonic function, the intersection of the indicatrix of the induced optical anisotropy and the basal plane was an ellipse with major-axis orientation governed by the direction of the external magnetic field. The orientation of the major axes of the PLOA relative to the axes of the indicatrix of the linear magnetic birefringence was determined from the dependence of the phase shift due to the Cotton-Mouton effect on the angle between the external magnetic field and the C_2 axis (curve 2 in Fig. 5). Since this dependence was shifted in phase by $\pi/2$ relative to curve 1, we concluded that the "fast" axes of the magnetic birefringence and PLOA indicatrices were oriented at an angle 90° relative to one another. In the latter case the result was a constant value modulated slightly by a dependence the $\cos 6\varphi$ type with zeros of the latter along the C_2 axes. On the

basis of symmetry considerations, this dependence can be linked to the change in the tilt of the antiferromagnetic vector relative to the basal plane.

The nature of the centers responsible for the PLOA and their composition were studied by recording the photosensitivity spectra of the investigated samples. The ground state of the nickel impurity ions was identified and the influence of nickel on the host matrix ions was studied by recording the absorption spectra of crystals characterized by different values of the PLOA. Figure 6 shows the spectral dependences of the absorption coefficient of a nominally pure $FeBO_3$ crystal 1 with the PLOA amounting to 10^{-6} and of a nickel-doped crystal in which the induced optical anisotropy was two orders of magnitude greater. The results indicated that the main changes in the spectrum due to doping occurred in the region of the absorption edge. We included in Fig. 6 a curve 3 representing between the spectral dependences of the difference $K_2 - K_1$ between the two absorption coefficients. The last curve represents the change produced in the crystal energy spectrum by the presence of the impurity ions. Curve 3 varies monotonically and increases in the ultraviolet region. A comparison of curve 3, representing the spectral dependence of the absorption of the impurity ions, with the spectrum of the isomorphous Al_2O_3:Ni crystal[20] readily revealed a correlation between them. Since in the case of aluminum oxide the nickel ion was identified as Ni^{III} in a low-spin
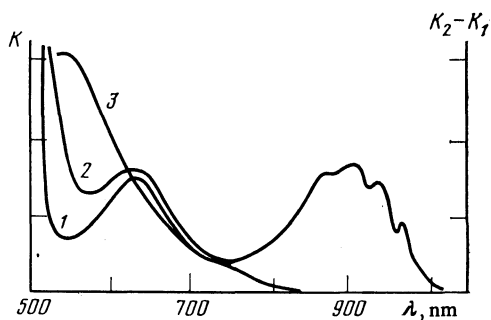

FIG. 6. Spectral dependences of the absorption coefficient K of nominally pure samples (1) and of samples doped with Ni(2), and the difference between these dependences shown on an enlarged scale.
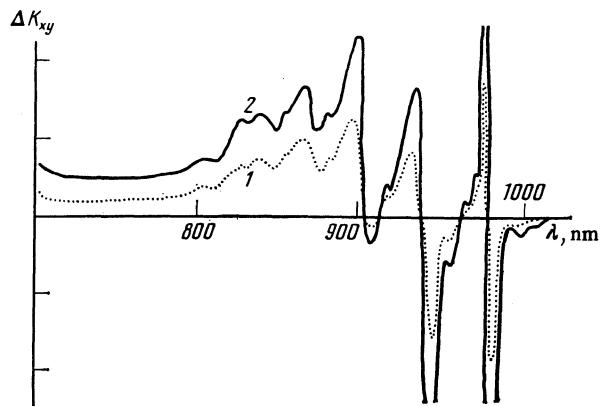
FIG. 7. Spectral dependences of the photoinduced (1) and magnetic (2) linear dichroism.

FIG. 9. Photograph of a crystal in polarized light. A transparency with the word $FeBO_3$ was projected first on the sample.

state, we concluded that the iron borate lattice also contained nickel in the trivalent state, replacing the iron ion, and the crystal field for the nickel impurity was strong. This is usually true of oxygen-containing compounds.[21] Moreover, if we assume that the state of the impurity is Ni^{2+}, then in the near infrared there should be characteristic transitions,[22] but none have been observed.

Identification of the energy levels responsible for the PLOA and attribution of these levels to specific ions were carried out on the basis of the spectra of the photoinduced and magnetic linear dichroism, represented respectively by curves 1 and 2 in Fig. 7. Curve 2 agrees well with the corresponding dependence for a nominally pure crystal,[23] i.e., although doping did alter the optical density in accordance with Fig. 6 (curve 3), it had practically no influence on the magnitude of the magnetooptic effects. A comparison of curves 1 and 2 shows that throughout the investigated spectrum the photoinduced effect is an additive correction to the magnetic linear dichroism, so that the PLOA occurs on the same levels as the magnetooptic effects, i.e., it is due to the presence of the Fe^{3+} ions.

The rate of the photoinduced process depends on the illumination wavelength, so that in the case of a constant illumination intensity the value of τ^{-1} may be regarded as a measure of the photosensitivity and used to determine the spectral dependence of this sensitivity. Figure 8 shows the spectral dependence of $\tau^{-1}(\lambda)$, which is well correlated with the quantity representing the kinetics of the photoin-
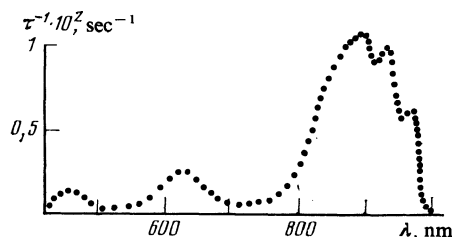

FIG. 8. Spectral dependence of the rate of formation of the PLOA, reflecting the photosensitivity of the samples.
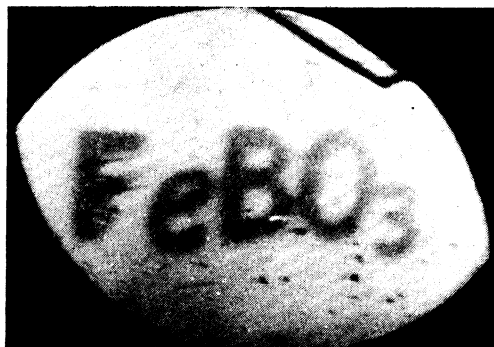
duced change in the magnetic susceptibility.[13]

A comparison with the absorption spectrum in Fig. 6 shows that maxima of the curve in Fig. 8 occur at the positions of the absorption bands. A slight discrepancy from the results of Ref. 13 is clearly due to the different role of the surface absorption of light in the change in the magnetic susceptibility and in the induced optical anisotropy. Moreover, it is clear from both dependences that the greatest changes in these properties occur as a result of optical excitation corresponding to the absorption band due to the $^6A_1 \rightarrow {}^4T_1$ transition. It follows from the results that the Fe^{3+} host-lattice ions supply the energy used in the ordering or reorientation of the anisotropic centers responsible for the PLOA.

It follows from these results that PLOA can be used to store optical data in iron borate crystals because the action of unpolarized light results in "memorization" of the spatial distribution of the intensity in the form of changes in the optical anisotropy. This possibility was first pointed out in Ref. 24 and multitone optical data storage was achieved using PLOA.[25] The tone variations were achieved by two methods: spatial variation of the intensity in the cross section of the exciting light beam and spatial variation of the orientation of the magnetic field during illumination. Observation of a crystal in crossed nicols revealed that the parts of a sample exposed earlier showed greater changes in the initial linear polarization of the transmitted light and appeared brigher than the unilluminated parts. When the directions of the PLOA axes were altered by an external magnetic field during illumination of different parts (keeping exposure the same), the phase shift during retrieval of the data was different and, therefore, the degree of bleaching was different. By way of illustration, Fig. 9 shows the photograph (obtained in crossed nicols) of a crystal on the surface of which a transparency with the word $FeBO_3$ was projected beforehand. An analysis of the quality of the image and its parameters indicated that the effect in question can be used to develop new principles for optical data storage.

DISCUSSION OF RESULTS

In a model-free description of the PLOA we shall use experimental observations from which it follows that the

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magnitude of the effect depends mainly on the orientation of the antiferromagnetic vector at the moment of illumination and represents an additive correction to the magnetooptic linear anisotropy. Then, the symmetric part of the permittivity tensor ε_{ij}^s can be represented by a superposition of expansions in terms of the components of the antiferromagnetic vector l_i during measurements and l_i' during illumination:

$$\varepsilon_{ij}{}^s = \alpha_{ijkn} l_k l_n + \beta_{ijkn} l_k' l_n', \qquad (2)$$

where α and β are tensors which are symmetric in respect of index pairs and correspond to the point symmetry of the crystals. Then, in accordance with Eq. (1), the photoinduced birefringence or dichroism can be described as follows in the laboratory coordinate system

$$\delta = \beta_1 \sin 2(\varphi' - \theta) + \beta_2 q \sin 3(\varphi' + \varphi_0) \sin(\varphi' + 2\theta), \qquad (3)$$

where

$$\varphi_0 = 0, \quad \theta - \varphi' = \frac{\pi}{4}, \quad \delta = \beta_1 + \frac{\beta_2 q}{2} \sin 6\varphi';$$

β_1 and β_2 are the phenomenological constants describing the PLOA; φ' is the azimuth of the ferromagnetic vector during illumination; θ is the azimuth of the plane of polarization of the measuring beam (both azimuths are measured relative to the x axis); q is the angle representing the tilt of the antiferromagnetic vector relative to the basal plane. Before illumination, the crystal is characterized by $\beta_1 = \beta_2 = 0$ and the optical anisotropy corresponds to the Cotton-Mouton effect. Illumination of the samples results in a light-induced ordering of the anisotropic centers and we then find that $\beta_1 \neq 0$ and $\beta_2 \neq 0$. It is clear from Fig. 1 that after the first illumination we have $\beta \approx 0.3\Delta$ (for an Ni concentration 0.1%). A comparison of the orientational dependences in Fig. 5 with Eq. (3) also shows that the agreement is good. In fact, if $\theta = $ const, the angular dependence of Eq. (1) is a harmonic function with a period π, whereas at $\theta - \varphi' = $ const it should take the form of a constant component modulated by a harmonic function with a period $\pi/3$. We can readily see that the depth of modulation is governed by the photoinduced change in the tilt of the antiferromagnetic vector relative to the basal plane, i.e., illumination of a crystal alters the longitudinal component of the antiferromagnetic vector, and the magnitude of this component for undoped samples is governed by the ratio of the fourth- and second-order magnetic anisotropy constants. Therefore, the model of the PLOA should describe also the illumination-induced change in the magnetic anisotropy of these crystals.

Since the magnitude of the PLOA depends on the presence of the Ni impurity ions, it is clear that doping creates centers at positions of symmetry lower than the point symmetry of the crystal, so that such centers have several crystallographically equivalent positions. The nonuniform population of these positions by the centers gives rise to preferred directions and, consequently, creates an optical anisotropy. A symmetry analysis makes it possible to establish the positions of the ions forming centers with such properties. We can readily show that several crystallographically

equivalent positions in the unit cell of iron borate have the oxygen-ion and general positions.[26]

Since the nickel ion is identified in the Ni^{III} state (Fig. 6), there are at least two mechanisms of formation of anisotropic centers.

1) An impurity ion may behave as an interstitial impurity in the general position in the lattice and diffuse between equivalent positions as a result of interaction with light. However, this is in conflict with the activation energy ~ 0.23 eV, which in the case of ion diffusion should be greater than 1 eV. Moreover, such a center should have a dipole moment because of the loss of the point of symmetry and it therefore may respond to an anisotropic external action, such as polarized illumination, contrary to our experiments.

2) It is known that an Ni^{III} ion in an octahedral environment is a Jahn-Teller ion.[27] In this case the oxygen octahedron experiences tetragonal distortions along one of the cubic axes and the orientations of the distortion axes are independent of the direction of spin of this ion because of the absence of the first-order spin-orbit coupling. Cooperative ordering of the orbitals of the Jahn-Teller ions is not very likely because of the low concentration of these ions, so that the symmetry of the crystal as a whole remains rhombohedral.

Ordering of the Ni^{III} orbitals can be brought about by interaction with the orbitals of the photoexcited Fe^{3+} ions, the lowest states of which are triplets with a strong spin-orbit coupling. There are three types of such interaction[28]: electron-vibrational, quadrupole-quadrupole, and exchange. As a result of these interactions the populations of the orbitals of the Ni^{III} ions and, therefore, the orientations of the tetragonal distortions of the octahedra are governed by the directions of the spins of the host lattice ions in the photoexcited state because of the spin-orbit coupling of the latter, since the phototransition of the Fe^{3+} ion is due to an orbital state corresponding to the direction of its spin. Such ordering of the orbitals of the Ni^{III} ions results in correlated distortions of the host lattice, which reduce the symmetry of this lattice and create optical anisotropy. If the energy barriers separating the three configurations of the Jahn-Teller distortions are greater than the thermal energy, the ordered state of the orbitals of the Jahn-Teller ions remains "frozen-in" and remembers the orientation of the spins of the host lattice during illumination. Heating alters the Jahn-Teller effect from static to dynamic and this results in a uniform distribution of the axes of the Jahn-Teller distortions along the three directions and disappearance of a preferred direction. In accordance with this model optical anisotropy forms at the levels of the Fe^{3+} host lattice ion with the ligand environment deformed by the ordered Jahn-Teller distortions. Therefore, the PLOA spectrum should be correlated with the spectrum of the Cotton-Mouton effect, and the photosensitivity spectrum with the absorption spectrum. This is indeed observed experimentally (Figs. 7 and 8).

The orientational dependences of the PLOA will be described by a calculation based on a simple model of an anisotropic distribution of the Jahn-Teller distortions under the conditions of the static Jahn-Teller effect. We shall assume

that C_0 is the concentration of the Jahn-Teller centers in a crystal. In the case of the static effect there are three orientations of the distortion axes in a crystal and these are parallel to the cubic axes of an octahedron. In the case of an equiprobable distribution, the concentration of the centers with distortions along each orientation is $C_0/3$. Since we are interested only in the anisotropy of the distribution, we shall introduce quantities $n_p = C_p - C_0/3$ representing the deviation of the concentrations of the various types of distortions from the equiprobable form. A local deformation along each of the tetragonal axes can be represented by

$$\lambda_{ij}{}^x = \begin{pmatrix} \lambda_{11} & 0 & 0 \\ 0 & \lambda_{22} & 0 \\ 0 & 0 & \lambda_{22} \end{pmatrix}, \quad \lambda_{ij}{}^y = \begin{pmatrix} \lambda_{22} & 0 & 0 \\ 0 & \lambda_{11} & 0 \\ 0 & 0 & \lambda_{22} \end{pmatrix},$$

$$\lambda_{ij}{}^z = \begin{pmatrix} \lambda_{22} & 0 & 0 \\ 0 & \lambda_{22} & 0 \\ 0 & 0 & \lambda_{11} \end{pmatrix}. \tag{4}$$

From Eq. (4) we can readily separate the anisotropic parts by assuming that $\lambda_{11} = \lambda_{22} + \Delta\lambda$. Then, the average deformation of a crystal due to the presence of local deformations can be written in the form

$$\lambda_{ij} = \sum_{p=1}^{3} n_p \lambda_{ij}{}^p. \tag{5}$$

When light is absorbed, lattice distortions due to the strong LS coupling appear around a photoexcited ion. We can allow for them by using the fact that the immediate environment of such an ion has almost perfect cubic symmetry so that the distortions can be represented by magnetostrictive deformations of the cubic lattice (accurate within isotropic terms):

$$u_{ii} = -\frac{B_1}{c_{11}-c_{12}} \alpha_i{}^2, \quad u_{ij} = -\frac{B_2 \alpha_i \alpha_j}{c_{44}}. \tag{6}$$

The density of the thermodynamic potential can be represented, including only the terms of interest to us, by

$$H = H_0 + {}^1\!/_2 c_{ijkl} u_{ij}\lambda_{kl} + (kT/C_0 V) \sum_{p=1}^{3} n_p{}^2, \tag{7}$$

where H_0 is the density of the free energy obtained allowing for the Jahn-Teller effect; $c_{ijkl} u_{ij}\lambda_k$ is the elastic energy of the interaction of the Jahn-Teller centers with the photoexcited centers; the last term represents the configuration entropy. Minimizing Eq. (7) with respect to n_p, subject to the condition

$$\sum_{p=1}^{3} n_p = 0,$$

we obtain

$$n_1 = -\frac{\Delta\lambda B_1 C_0 V}{12kT} (1-3\alpha_1{}^2), \quad n_2 = -\frac{\Delta\lambda B_1 C_0 V}{12kT} (1-3\alpha_2{}^2),$$

$$n_3 = -\frac{\Delta\lambda B_1 C_0 V}{12kT} (1-3\alpha_3{}^2), \tag{8}$$

where B_1 is the magnetoelastic constant of the iron ion in an excited state; α_i are the direction cosines of the antiferromagnetic vector in the cubic coordinate system. After transition to the rhombohedral structure with the z axis along the C_3 symmetry axis, we find that if we ignore the squares of the longitudinal component of the antiferromagnetic vector, then

$$n_{1,2} = -\frac{\Delta\lambda B_1 V}{12kT} C_0 \left[\frac{1}{2}\cos 2\varphi' \pm \frac{\sqrt{3}}{2}\sin 2\varphi' - 6q\sin 3(\varphi'-\varphi_0) \right.$$

$$\left. \times \left(\sqrt{\frac{1}{18}}\cos\varphi' \pm \sqrt{\frac{1}{8}}\sin\varphi' \right) \right]. \tag{9}$$

Here φ' is the angle between the direction of the magnetic field in the basal plane and the x axis in the laboratory coordinate system during illumination; φ_0 is the angle between the x axis and the symmetry axis C_2; q represents the tilt of the antiferromagnetic vector relative to the basal plane: $l_z = q\sin 3(\varphi' + \varphi_0)$. It follows from Eq. (9) that the concentration of the Jahn-Teller centers with the appropriate directions of distortions depends on the orientation of the antiferromagnetic vector, so that the average deformation of a crystal is governed by the direction of the magnetic field in the basal plane during illumination. The additional components of the permittivity tensor dependent on the deformation can be expressed in terms of the photoelastic constants p:

$$\varepsilon_{ij}{}^\Phi = p_{ijkl}\lambda_{kl}. \tag{10}$$

Bearing in mind that the ellipticity and rotation of the major axis of the polarization ellipse due to linear optical anisotropy in the basal plane can be represented by Eq. (1), we obtain from Eqs. (5), (8), and (9) that

$$\delta = \frac{\omega d}{cn} \frac{(p_{11}-p_{12}+\sqrt{2}\,p_{14})\Delta\lambda^2 B_1 V}{3kT} C_0 \left[\frac{1}{4}\sin 2(\theta-\varphi') \right.$$

$$\left. -\frac{q}{2}\sin 3(\varphi'-\varphi_0)\sin(\varphi'+2\theta) \right], \tag{11}$$

whereas if $\varphi_0 = 0$ and $\theta = \varphi' + \pi/4$, then

$$\delta = \delta_0 [{}^1\!/_4 - {}^1\!/_4 q\sin 6\varphi']. \tag{11a}$$

An analysis of the above expression shows that if $\theta = $ const, the phase shift due to the PLOA can be represented in practice by a single harmonic function of the azimuth of the external magnetic field during illumination, with a period π because $q \ll 1$. However, if the azimuth of the plane of polarization of the measuring light beam is altered so that it follows the orientation of the field, the experimental dependence has a constant component modulated by a harmonic function with the period $\pi/3$ in accordance with Eq. (11a), i.e., the above analytic expression is in qualitative agreement with the experimental orientational dependence of the PLOA (curves 1 and 3 in Fig. 5) and satisfies the phenomenological expression (3). The smaller number of parameters in Eq. (11), compared with Eq. (3), is due to the fact that Eq. (11) is derived ignoring the trigonal distortions of the immediate environment of the Jahn-Teller ions. We

shall now estimate the order of magnitude of the PLOA by substituting typical values in Eq. (11). The volume of a unit cell is $V \sim 10^{-23}$ cm^3, the photoelastic constants are $p \sim 10$, the Jahn-Teller distortions are $\Delta\lambda \sim 10^{-1}$–$10^{-2}$, the magnetoelastic constant is $B \sim 10^9$–10^{10} erg/cm^3, the thickness of the investigated crystal is $d \sim 10^{-2}$ cm, and the impurity concentration is $C_0 \sim 10^{-3}$; then, for optical wavelengths of $\sim 10^{-4}$ cm, we find that the phase shift is $\delta \sim 10^{-2}$–10^{-3}, in good agreement with the experimental value of the PLOA.

The model of ordering of the Jahn-Teller distortions around impurity ions by interaction with photoexcited host lattice ions thus allows us to describe correctly the orientational dependences of the PLOA and to obtain its magnitude, which is of the same order as the experimental value. Hence, we may assume that the mechanism of the PLOA is indeed governed by the Jahn-Teller ions which, in the investigated range of temperatures, may give rise to a Jahn-Teller glass state[29] or noninteracting static distortions.[30] The transition to the ordered, but metastable, state is initiated by the orbitals of the photoexcited host lattice ions, the population of which is governed by the direction of the antiferromagnetic vector.[31]

The new magnetooptic effect, photoinduced linear optical anisotropy, can be used to store and process optical data, and also to study impurity states in magnetically ordered crystals. It should apparently be pointed out that the effects occurring in YIG and in $Cd_2Cr_2Se_4$ on interaction with unpolarized light are also of Jahn-Teller origin and occur in Fe and Cr ions, which (in a suitable environment) exhibit orbital degeneracy.

[1]J. F. Dillon Jr., J. Appl. Phys. 39, 922 (1968).

[2]A. J. Kurtzig, J. Appl. Phys. 42, 3494 (1971).

[3]G. S. Krinchik and M. V. Chetkin, Usp. Fiz. Nauk 98, 3 (1969) [Sov. Phys. Usp. 12, 307 (1969)].

[4]G. A. Smolenskiĭ, R. V. Pisarev, and I. G. Siniĭ, Usp. Fiz. Nauk 116, 231 (1975) [Sov. Phys. Usp. 18, 410 (1975).

[5]G. B. Scott, D. E. Lacklison, H. I. Ralph, and J. L. Page, Phys. Rev. B 12, 2562 (1975).

[6]P. P. Feofilov and A. A. Kaplyanskiĭ, Usp. Fiz. Nauk 76, 201 (1962) [Sov. Phys. Usp. 5, 79 (1962)].

[7]F. Luty, in: Physics of Color Centers (ed. by W. B. Fowler), Academic Press, New York, 1968, p. 182.

[8]J. F. Dillon Jr., E. M. Gyorgy, and J. P. Remeika, J. Appl. Phys. 41, 1211 (1970).

[9]U. Enz and H. van der Heide, Solid State Commun. 6, 347 (1968).

[10]V. G. Veselago, E. S. Vigeleva, G. I. Vinogradova, V. T. Kalinnikov, and V. E. Makhotkin, Pis'ma Zh. Eksp. Teor. Fiz. 15, 316 (1972) [JETP Lett. 15, 223 (1972)].

[11]V. G. Veselago and R. A. Doroshenko, Tr. Fiz. Inst. Akad. Nauk SSSR 139, 67 (1982).

[12]A. Tucciarone, Physics of Magnetic Garnets (Proc. Intern. School on Physics "Enrico Fermi," Course 70, Varenna, 1977), North-Holland, Amsterdam, 1978, p. 320.

[13]D. E. Lacklison, J. Chadwick, and J. L. Page, J. Appl. Phys. 42, 1445 (1971).

[14]M. H. Seavey, Solid State Commun. 12, 49 (1973).

[15]Yu. M. Fedorov and A. A. Leksikov, Pis'ma Zh. Eksp. Teor. Fiz. 27, 389 (1978) [JETP Lett. 27, 365 (1978)].

[16]A. A. Leksikov, Yu. M. Fedorov, and A. E. Aksenov, Prib. Tekh. Eksp. No. 6, 186 (1982).

[17]R. Wolfe, A. J. Kurtzig, and R. C. Le Craw, J. Appl. Phys. 41, 1218 (1970).

[18]D. E. Lacklison, J. Chadwick, and J. L. Page, J. Phys. D 5, 810 (1972).

[19]Yu. M. Fedorov, A. A. Leksikov, and A. E. Aksenov, Fiz. Tverd. Tela (Leningrad) 26, 220 (1984) [Sov. Phys. Solid State 26, 128 (1984)].

[20]D. S. McClure, J. Chem. Phys. 36, 2757 (1962).

[21]S. Krupička, Physik der Ferrite und der vertwandten Magnetischen Oxide, Wieweg, Brunswick, 1973 (Russ. Transl., Nauka, M., 1976).

[22]R. Newman and R. M. Chrenko, Phys. Rev. 114, 1507 (1959).

[23]Yu. M. Fedorov, A. A. Leksikov, A. E. Aksenov, and I. S. Edelman, Phys. Status Solidi B 106, K127 (1981).

[24]A. A. Leksikov and Yu. M. Fedorov, Pis'ma Zh. Tekh. Fiz. 8, 934 (1982) [Sov. Tech. Phys. Lett. 8, 405 (1982)].

[25]A. A. Leksikov, Yu. M. Fedorov, and A. E. Aksenov, Pis'ma Zh. Tekh. Fiz. 9, 377 (1983) [Sov. Tech. Phys. Lett. 9, 163 (1983)].

[26]Yu. M. Fedorov, Preprint IF SO-122F, Krasnoyarsk, 1980.

[27]E. M. Gyorgy, R. C. Le Craw, and M. D. Sturge, J. Appl. Phys. 37, 1303 (1966).

[28]K. I. Kugel' and D. I. Khomskiĭ, Usp. Fiz. Nauk 136, 621 (1982) [Sov. Phys. Usp. 25, 231 (1982)].

[29]M. A. Ivanov, V. Ya. Mitrofanov, and A. Ya. Fishman, Fiz. Tverd. Tela (Leningrad) 20, 3023 (1978) [Sov. Phys. Solid State 20, 1744 (1978)].

[30]D. M. Hannon, Phys. Rev. 164, 366 (1967).

[31]V. V. Eremenko, I. E. Kaner, Yu. G. Litvinenko, and V. V. Shapiro, Zh. Eksp. Teor. Fiz. 84, 2251 (1983) [Sov. Phys. JETP 57, 1312 (1983)].