Polarization-dependent photomagnetic effect in α-Fe_2O_3:Eu, Ga crystals

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The results of a detailed investigation of the polarization-dependent photoinduced changes of the magnetic state in hematite crystals doped with enuropium and gallium ions are presented. The method of antiferromagnetic resonance was used. The study of the kinetics of photoinduced changes established that a photosensitive center can be represented by a potential with two minima. The barriers separating different states are determined. The photoinduced change in the anisotropic properties is explained by the appearance and vanishing of anisotropic magnetic centers in nonequivalent crystallographic positions, depending on the polarization of the optical radiation. Spectral investigations of the photomagnetic effect were performed.

1. INTRODUCTION

Under external perturbation the properties of a magnetic material can change reversibly or the material can end up in a metastable state. The final result depends on the conditions of excitation and the electronic structure of the magnet. Excitation by optical radiation can be singled out because in this case selective, directed excitation of the centers responsible for different properties is possible. The change in the properties of the magnet can then depend on the characteristics of the radiation, such as, the power, wavelength, and polarization. Examples are the new photoinduced magnetic state arising in $EuCrO_3$ when the threshold radiation power is reached;[1] the spin-reorientational phase transition in $ErCrO_3$ under irradiation at a wavelength corresponding to excitation of Er ions;[2] and, polarization-dependent photoinduced magnetization in $Y_3Fe_5O_{12}$:Si crystals.[3]

We note that because of the specific nature of the electronic structure of rare-earth ions their individual properties are often found to be responsible for the low-temperature behavior of magnets.[4] Thus the introduction of a fraction of a percent of rare-earth ions into iron garnet radically changes the dynamics of the entire magnetic system, as can be judged by the change in the parameters of magnetic resonance.[5] The optical properties of crystals doped with rare-earth ions are just as diverse and distinct. Thus interesting manifestations of these properties can be expected in magnets of this type in interactions with optical radiation.

In Ref. 6 we reported the observation of a polarization-dependent change of the antiferromagnetic resonance (AFMR) in the weakly ferromagnetic crystal α-Fe_2O_3: Eu, Ga. We determined that this effect is observed at temperatures below 70 K.

In this paper we present the results of detailed investigations of the temperature and angular dependence as well as the dynamics of the polarization-dependent photoinduced changes occurring in hematite crystals doped with europium and gallium ions.

2. EXPERIMENT

For the measurements we employed α-Fe_2O_3:Eu (0.035 at.%), Ga (5 at.%) single crystals, grown by spontaneous crystallization from solution in a melt (bismuth–sodium solvent was used). Gallium ions were introduced in order to lower the temperature of the Morin transition and to extend the temperature range of the weakly ferromagnetic phase. The speciments consisted of 0.1 mm thick wafers with transverse dimensions of approximately 2 mm. The magnetic field was oriented in the plane of the specimen. The optical beam propagated along the C_3 axis of the crystal. The state of the magnetic system was monitored by checking the AFMR parameters.

The measurements were performed on the magnetic resonance spectrometer described in (Ref. 7). The frequency of the microwave radiation was equal to $\omega = 35$ GHz. A system which automatically maintained the resonance field made it possible to study the photoinduced changes as a function of time and the temperature dependences under different perturbations.

The light source was an incandescent lamp. The spectral investigations were performed with the help of an SPM-2 monochromator. The power of the optical radiation was determined with an IMO-2N meter. The polarization of the optical radiation was controlled with an Ahrens polarizer.

The temperature in the cryostat chamber was maintained with an accuracy of 0.1 K.

3. RESULTS

Figure 1 shows the temperature dependence of the resonance field and the width of the AFMR line in α-Fe_2O_3: Eu, Ga. Here the situation is, to some extent, similar to that observed in europium iron garnet.[8] A break is observed in the curve of the resonance field in approximately the same temperature range for different crystals and the linewidth has a maximum. In those cases when we doped hematite crystals with diamagnetic and $3d$ ions the temperature dependence of the resonance field and the linewidth as a rule had a broken form in a wide temperature range and with the exception of the low-temperature maximum, explained by the presence of bivalent iron ions, it was random.[9] The features observed in europium garnet and apparently in the present case also are determined by the contribution of levels from the first excited multiplet (primarily formed from the $^7F_1$ multiplet of a free Eu^{3+} ion).

The character of the irradiation-induced change of the resonance field for an α-Fe_2O_3:Eu, Ga-crystal depends on the angle between the external magnetic field $\mathbf{H}_0$ and the

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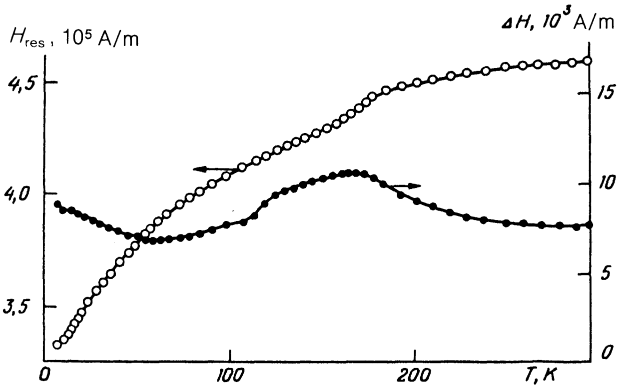

FIG. 1. Temperature dependence of the resonance field and linewidths of AFMR in α-Fe_2O_3:Eu, Ga.

electric-field vector **E** of the light wave. When the crystal is irradiated with light whose **E** vector is parallel to the constant magnetic field (i.e., $\mathbf{E}\|\mathbf{H}_0$) the resonance field increases ("recording" effect). The process develops in time along the curve shown between the points 1 and 2 in Fig. 2 and δH_{res} reaches the value of δH_m. If the light is then switched off, relaxation is observed to some new value δH_r, which at a given temperature remains throughout the entire observation time, with $\delta H_r \approx (0.7\text{–}0.8)\ \delta H_m$ (segment 2–3). If $\mathbf{E}\|\mathbf{H}_0$ holds when the light is switched on at the point 3, then the shift of the resonance field once again returns to the value δH_m. If, however, radiation with polarization $\mathbf{E}\perp\mathbf{H}_0$ is switched on at the point 3, then the shift of the resonance field decreases to zero along the curve 3–4, different from the curve 1–2 ("erasing" effect). We especially call attention to the fact that at low temperatures the sections 1–2 and 3–4 are fit quite well with a double-exponential dependence of the form $\delta H_{res} = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ (each with its own set of parameters), while the segment 2–3 corresponds to one exponential.

The temperature dependences of the resonance field for different conditions of irradiation are presented in Fig. 3. Curve 1 corresponds to a crystal which has never been irradiated. When light with polarization $\mathbf{E}\perp\mathbf{H}_0$ is switched on, the magnitude of the resonance field decreases. As the temperature changes, both with illumination and after the illumination is switched off, we obtain the curve 2. Correspondingly, the curves 4 and 3 give the temperature behavior of the resonance field directly in the case of irradiation with $\mathbf{E}\|\mathbf{H}_0$ and after light with this polarization is switched off. The photoinduced state that arises does not depend on the past history, but rather is determined exclusively by the relative orientation of **E** and $\mathbf{H}_0$. The effect of the light is observed at temperatures $T < T_f = 70$ K, and an inflection point is present in the region $T = 20$–25 K on the temperature curves of the resonance field. If the crystal is once again cooled from temperatures $T > T_f$, then curve 1 is obtained again. We note that at temperatures $T < T_f$ weak temperature hysteresis occurs which depends on the rate of cooling—the more rapidly the temperature changes, the greater the hysteresis. For this reason, all curves were obtained with the specimen heated at the same rate. Irradiaiton with unpolarized white light also increases the resonance field by an amount less than $0.1\delta H_m$.

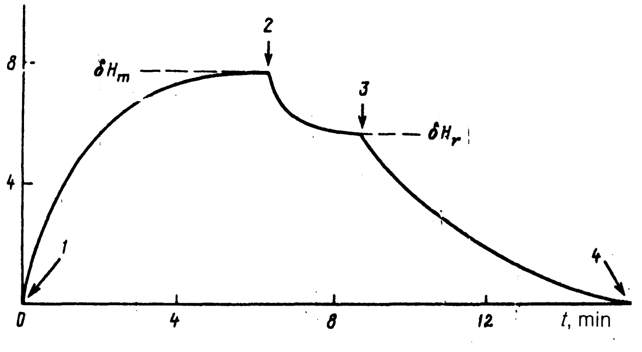

FIG. 2. Time dependence of the resonance field as a function of the polarization of the optical radiation: 1 → 2—$\mathbf{E}\|\mathbf{H}_0$, 2 → 3—light is switched off, 3 → 4—$\mathbf{E}\perp\mathbf{H}_0$. Irradiation with white light, $S = 100$ mW/cm^2. $T = 10$ K.

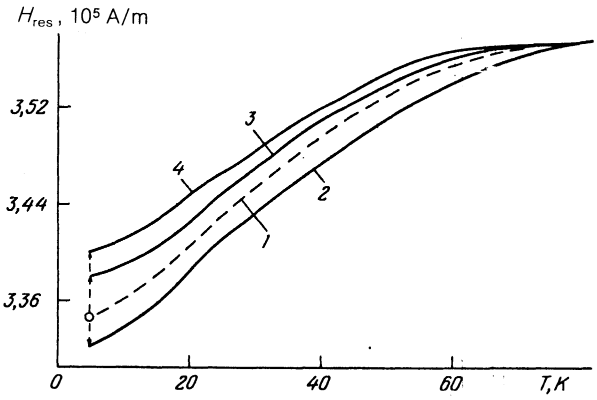

FIG. 3. Temperature dependence of the resonance field. 1) starting crystal, 2) during and after irradation with $\mathbf{E}\perp\mathbf{H}_0$, 3) after irradiation with $\mathbf{E}\|\mathbf{H}_0$, 4) during irradation with $\mathbf{E}\|\mathbf{H}_0$. Irradiation with white light, $S = 100$ mW/cm^2.

The temperature dependence of the parameters A_i and τ_i, presented, respectively, in Figs. 4a and 4b, was obtained for the case $\mathbf{E}\|\mathbf{H}_0$. One can see from Fig. 4 that as the temperature increases the amplitudes A_1 and A_2 drop to zero and the times τ_1 and τ_2, corresponding to the "fast" and "slow" exponentials, remain finite and tend toward one another. The greatest change in the times τ_1 and τ_2 as a function of the temperature occurs at temperatures $T < 15$ K. We note on the curves 2 and 3 (Fig. 4a) in the neighborhood of $T = 20$–25 K the presence of a feature which coincides with the point of inflection on the curves in Fig. 3.

Figures 5a and 5b show A_i and τ_i as a function of the polarization angle relative to the direction of the external magnetic field. In this case, each new value on curve 3 was obtined afer "erasing" the preceding value with radiation with $\mathbf{E}\perp\mathbf{H}_0$ (in Ref. 6 this dependence was obtained by systematically changing the polarization angle with the external magnetic field oriented along the difficult direction of magnetization in the basal plane of the crystal). Here, as $\theta \to \pi/2$ the quantities A_1 and A_2 approach zero, while τ_1 and

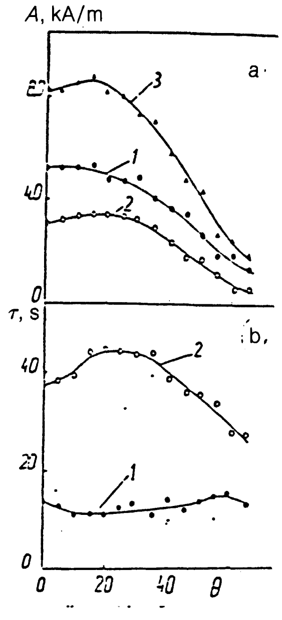

FIG. 4. Temperature dependences of the parameters of photoinduced shifts of the resonance field with a double-exponential approximation, $\delta H_{\text{res}} = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. a) 1—$A_1$, 2—$A_2$, 3—$A_0$; b) 1—$\tau_1$, 2—$\tau_2$.

τ_2 tend toward one another. In all cases, under conditions of "recording," the "fast" exponential has the larger coefficient factor, while under the conditions of "erasing" the situation is reversed—the "slow" exponential has the higher preexponential factor.

The parameters of the curves showing the time dependence, which correspond to the sections 2–3 in Fig. 2 in the case when the temperature varies, are given in Fig. 6. This dependence will be discussed below.

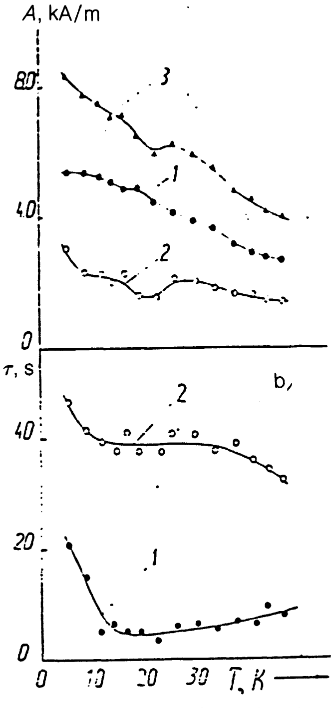

FIG. 5. Parameters of the photoinduced shifts of the resonance field as a function of the angle θ between E and H_0 with a double-exponential approximation $\delta H_{\text{res}} = A_0 + A_1 \exp(-t/\tau_{11}) + A_2 \exp(-t/\tau_2)$. a) 1—$A_1$, 2—$A_2$, 3—$A_0$; b) 1—$\tau_1$, 2—$\tau_2$.

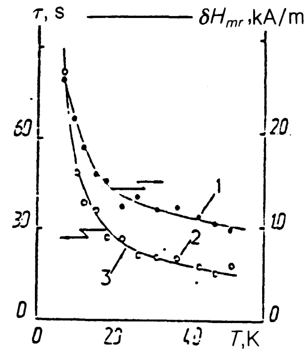

FIG. 6. Temperature dependence of the parameters of the shift of the resonance field for the section 2→3, Fig. 2, with approximation with a single-exponential dependence, $\delta H_{\text{res}} = \delta H_{mr} \exp(-t/\tau)$. 1—$\delta H_{mr}$, 2—$\tau$ (experiment), 3—τ (calculation).

Recording curves were obtained for different optical pumping powers (Fig. 7). Increasing the power of the optical radiation shortens the time to saturation, primarily as a result of the decrease in τ_1. The quantity δH_m does not depend on the radiation power.

4. DISCUSSION

We first note that in this case we associate the polarization-dependent photomagnetic effect to photosensitive complexes containing europium ions. This assertion is indirectly supported by the fact that when α-Fe_2O_3 crystals are doped with europium ions low-temperature anomalies attributed to Fe^{2+} are not observed in the AFMR parameters. Evidently, in α-Fe_2O_3:Eu, Ga the oxygen deficit is compensated by the appearance of Eu^{2+} ions. In contrast to the previously studied hematite crystals doped with diamagnetic and 3*d* ions, here photoinduced changes of an entirely different character are observed in the AFMR, the effect exists in different temperature intervals, and the sign of the shift in the resonance field is different.

As a first step we study in greater detail the kinetics of photoinduced shifts of the resonance field. Since exponential relaxation occurs after optical radiation with $\mathbf{E} \| \mathbf{H}_0$ is

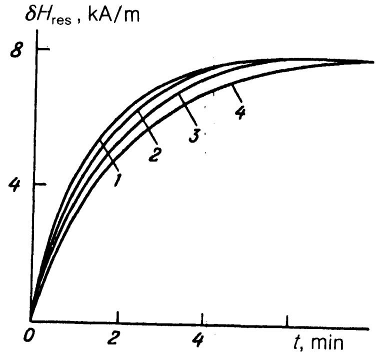

FIG. 7. Time dependence of the shift of the resonance field for different optical pumping powers ($\mathbf{E} \| \mathbf{H}_0$). $S = 150$ (1), 125 (2), 100 (3), and 75 mW/cm^2 (4). Irradiation with white light, $T = 10$ K.

switched off, the irradiation-induced state of the magnetic subsystem is not the ground state, but most likely a metastable state. It also follows from the data in Figs. 2 and 3 that under irradiation with polarization $\mathbf{E}\perp\mathbf{H}_0$ the system is transferred into a state with a lower energy. The double-exponential character of the time dependence observed when the optical radiation is switched on can be explained with the help of a general three-level model of a photosensitive center. We distinguish below the transformations of a center which are caused by irradiation with a different polarization by numbering the transformations, and we shall speak about states $|i\rangle$ of a center and the occupation numbers n_i of these states. In addition, for the time being we neglect the characteristics of the energy spectrum of a photosensitive center which correspond to different states and which ultimately are responsible for the magnetic properties of the center and the selection rules for optical transitions. Figure 8 shows the energy diagram of a hypothetical photosensitive center. On the basis of such a model of centers in the k th crystallographic position the occupation number of the states as a function of time will be described by the system of kinetic equations

$$\frac{dn_i^k}{dt}=\sum_{i\neq j} d_{ij}^k n_j \qquad (i, j=1, 2, 3), \tag{1}$$

where n_j^k is the occupation number of the jth state of the center at the position k and d_{ij} is the probability of a transition between the states i and j (taken with a " + " if the number of particles in the level increases and a " − " if the number of particles decreases). If photosensitive centers are not generated but are only recreated by the radiation, then

$$\sum_i n_i^k=N^k, \tag{2}$$

where N^k is the total number of photosensitive centers in the k th position. This condition appears to be correct, since with increasing optical power the maximum photoinduced shift δH_m does not change but rather only the time to saturation changes (see Fig. 6). It is reasonable to conjecture that optical radiation gives rise directly only to the transitions $|1\rangle\rightarrow|3\rangle$ and $|2\rangle\rightarrow|3\rangle$, and for this reason the probabilities d_{13} and d_{23} are functions of the frequency ν, the intensity I, and the polarization θ of the optical radiation, and the temperature T [i.e., for example, $d_{13}=d_{23}\ (\nu, I, \theta, T)$] and the transitions $|3\rangle\rightarrow|1\rangle$ and $|3\rangle\rightarrow|2\rangle$ are nonradiative. Transitions between the states $|1\rangle\rightarrow|2\rangle$ are thermodynamically equilibrium transitions, so that

$$d_{12}=C\exp(-\Delta_1/k_BT), \quad d_{21}^k=C\exp(-\Delta_2^k/k_BT), \tag{3}$$

where $\Delta_1=E_\Delta-E_1$ and $\Delta_2^k=E_\Delta-E_2^k$. It is conjectured that all probabilities d_{ij}, except for d_{21}, are identical for all crystallographic positions. Otherwise the time dependence will not have a double-exponential form, even at low temperatures, but rather a sum of $2l$ exponentials, where l is the number of nonequivalent positions.

The solution of the system (1) has the form

$$n_i^k(t)=A_{0i}+A_{1i}\exp(-t/\tau_1)+A_{2i}\exp(-t/\tau_2). \tag{4}$$

Explicit expressions for the coefficients A_i and the relaxation times τ_i are presented in the Appendix.

Without knowing the specific structure of the energy levels in the states $|1\rangle$ and $|2\rangle$ corresponding to the potential wells in Fig. 8 we cannot make a quantitative comparison between calculation and experiment. However some information about the properties of a center can still be extracted. If it is assumed that, as is usual for optical transitions, the relaxation time of the state $|3\rangle$ is not more a few microseconds,[10] then after the light is switched off only transitions between the states $|1\rangle$ and $|2\rangle$ come into play (since now $n_3=0$). For this case the population of the state $|2\rangle$ of a center in the k th position acquires the form

$$n_2^k(T, t)=n_{02}^k+\delta n_2^k\exp[-t/\tau_r(T)], \tag{5}$$

where n_{02}^k is the equilibrium population, which depends on the temperature of the system. For our model we have

$$1/\tau_r(T)=C\{\exp(-\Delta_1/k_BT)+\exp(-\Delta_2/k_BT)\}. \tag{6}$$

This dependence fits the experimental points well for $C=0.058\ \mathrm{s}^{-1}$, $\Delta_1/k_B=70$ K, and $\Delta_2/k_B=11$ K (see Fig. 6, curve 2) for temperatures $T<35$ K; at higher temperatures the experimental points lie aboe the values given by this expression.

The assumption that the barrier heights Δ_2 have the same value for all nonequivalent positions makes it impossible to explain the magnitude of the residual shift δH_r of the resonance field after the light with $\mathbf{E}\|\mathbf{H}_0$ is switched off. This suggests that there exist centers which at a given temperature do not relax to the state $|1\rangle$ but rather are found in a state of the form $|2\rangle$ and are transferred into the state $|1\rangle$ only as a result of irradiation with $\mathbf{E}\perp\mathbf{H}_0$.

An attempt to model the behavior of the system under the assumption that radiation with polarization $\mathbf{E}\|\mathbf{H}_0$ excites only centers from the state $|1\rangle$ (i.e., $d_{23}=d_{31}=0$) and radiation with $\mathbf{E}\perp\mathbf{H}_0$ excites only centers from the state $|2\rangle$ ($d_{13}=d_{32}=0$), gave relaxation times that are very far from the experimental values. Thus we arrive at the conclusion that the effect observed under irradiation is the result of competition between the "direct" $|1\rangle\rightarrow|3\rangle\rightarrow|2\rangle$ and "re-

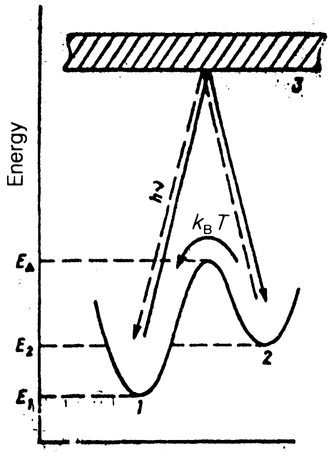

FIG. 8. Model of a photosensitive center.

verse" $|2\rangle \to |3\rangle \to |1\rangle$ optical transitions of a photosensitive center. Additional information about the magnitudes of the photoinduced changes in the resonance field as a function of the direction of polarization can be obtained by analyzing the spectral dependence of the photosensitivity; this dependence is presented in Fig. 9.

The experimental data were obtained as follows. In order to obtain the curve 1 the specimen was first irradiated with white light with polarization $\mathbf{E}\perp\mathbf{H}_0$. Then radiation from a different source and having the required wavelength and polarization $\mathbf{E}\|\mathbf{H}_0$ was passed through a monochromator and directed onto the specimen, and the maximum shift of the resonance field was determined. Then the wavelength was changed and all measurements were repeated. In order to obtain the curve 2 the operations were performed in a different order. First, the specimen was irradiated with white light with polarization $\mathbf{E}\|\mathbf{H}_0$. After the maximum change in the resonance field was achieved the light was switched off and the system was allowed to relax. After the system relaxed, radiation at the required wavelength and with polarization $\mathbf{E}\perp\mathbf{H}_0$ was switched on and the induced change was recorded.

It is clear from Fig. 9 that at each wavelength the magnitude of the shift in the resonance field under irradiation with polarization $\mathbf{E}\perp\mathbf{H}_0$ is larger than in the case of the polarization $\mathbf{E}\|\mathbf{H}_0$. This, as well as the existence of a small shift under irradiation with unpolarized light, imposes restrictions on the transition probabilities. The optical absorption spectrum of this crystal in the range 1–2.5 μm has the form of a weak, wide line. Dichroism of optical absorption is not observed at liquid-nitrogen temperatures, so that it can be assumed that $d^{\|}_{13} + d^{\|}_{23} = d^{\perp}_{13} + d^{\perp}_{23}$ (the superscripts indicate the polarization of the radiation). Under this condition, in order to understand the presence of a shift in the resonance field under irradiation with unpolarized light, the following conditions must be satisfied: $d^{\|}_{31} > d^{\perp}_{31}$ and $d^{\|}_{32} > d^{\perp}_{32} + d_{21}$.

A central question in the study of photoinduced changes of the magnetic properties of a crystal is the question of the nature of the photosensitive center and the interactions responsible for these properties. In the present case we call attention to the following facts. The temperature T_f for an α-Fe_2O_3:Eu, Ga crystal falls in the temperature range where anomalies are observed in the electric properties of nonstoichiometric EuO_x crystals.[11] In the latter case the anomalies are explained by the existence of magnetic impurity centers, consisting of a trivalent europium ion and an electron, captured in the field of an oxygen vacancy. In this case, the electron weakly bound on the oxygen vacancy can be quite strongly delocalized. For EuO_x the singularities of the electric properties are associated with the reconstruction of the impurity magnetic center and are of an activational character. The temperature dependence of the resistivity has a point of inflection at a temperature of about 25 K. This inflection is explained by the change in the carrier density, which depends on the number of active centers.

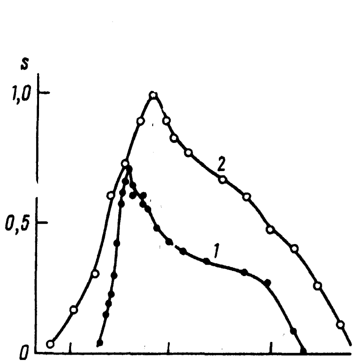

FIG. 9. Spectral dependence of the shift of the resonance field, normalized to the maximum shift for light with polarization $\mathbf{E}\|\mathbf{H}_0$ (1) and for light with polarization $\mathbf{E}\perp\mathbf{H}_0$ (2).

In the case of α-Fe_2O_3:Eu, Ga crystals the EuO_x data can also be used for choosing a model of a photosensitive center. The present experiments can be interpreted on the basis of a model in which the photosensitive center is a complex consisting of an oxygen vacancy and a bivalent europium ion, exchange-coupled with the matrix. Such a state corresponds to the state $|1\rangle$ in Fig. 8.

Before continuing our model analysis of the effect, we wish to point out the following. As one can see from Fig. 9, the photosensitivity spectra of the α-Fe_2O_3:Eu, Ga crystal for radiation with different polarization, which are interpreted as transitions according to the schemes $|1\rangle \to |3\rangle \rightsquigarrow |2\rangle$ ($\mathbf{E}\|\mathbf{H}_0$) and $|2\rangle \to |3\rangle \rightsquigarrow |1\rangle$ ($\mathbf{E}\perp\mathbf{H}_0$), are similar in form and cover a wide region between 1.0 μm and 2.5 μm. Our photosensitivity spectrum is similar to the spectra for transitions between states of mixed electronic configurations. The available data are insufficient for determining unequivocally the structure of the photosensitive center. Nonetheless the following variants are possible. As a result of a transition of the Eu^{2+} ion into an optically excited state the environment of the ion becomes distorted, and after optical relaxation of the photoelectron the bivalent europium ion ends up in a state different from the starting state. The scheme of the transformations of the center is as follows:

$$\underbrace{Eu^{2+} + O}_{\text{stage}} + h\nu \underset{\perp}{\overset{\|}{\rightleftarrows}} \underbrace{(Eu^{2+})^* + O^*}_{\text{stage } |2\rangle} \text{ (photodeformation).}$$
$$|1\rangle$$

This ultimately results in a change of the positions of the magnetic sublevels of the gound multiplet. [An example of effects of this type is photo-induced EPR in $BaF_2:Tm^{2+}$ (Ref. 12)]. It is also possible that, as in the case of nonstoichiometric EuO_x crystals irradiated with polarization $\mathbf{E}\|\mathbf{H}_0$, a magnetic center is formed that can be regarded as *F*-center, interacting with rare-earth ion. The schemes for the "direct" and "reverse" transitions are as follows:

$$\underbrace{Eu^{2+} + O + h\nu}_{\text{stage } |1\rangle} {}^{\|}\!\!\rightarrow \underbrace{Eu^{3+} + e}_{\text{stage } |2\rangle},$$

$$Eu^{3+} + e + h\nu^{\perp} \rightarrow Eu^{2+} + O.$$

Reference 13 contains data implying that the optical absorption spectrum of an *F* center participating in such a photochromic center can occupy a region of several thousand inverse centimeters, and for oxide compounds it falls within the range of wavelengths of interest to us.

Both possibilities indicated above equally make it possible to organize photoinduced restructuring of an impurity center, and this in turn will change the magnetic state of the center and (or) the interaction of the center with the matrix.

From what has been said above it follows that the change in the anisotropy of magnetic properties and also the time dependence of the induced changes are related to the existence of magnetic impurity centers in nonequivalent crystallographic positions, the heights of the energy barriers for which depend on the orientation of the external magnetic field.

Our investigation of the anisotropy of the AFMR field in α-Fe_2O_3: Eu, Ga at low temperatures gave the following results. When the crystal is cooled in the absence of a field the anisotropy of the resonance field is hexagonal to a high degree of accuracy. Cooling in a magnetic field equal to the resonance field results in distortion of the hexagonal anisotropy. Figure 10 (part a, circles) shows the dependence of the resonance field on the orientation of the external magnetic field in the basal plane of the crystal with cooling in a field oriented along the easy axis. Figure 10 also shows (part a, solid line) the phenomenological approximating curve $H_{\rm res}$ for anisotropy fields of sixth and second orders, respectively, $H_6 = 38$ A/m and $H_2 = 13$ A/m. After irradiation with light with $\mathbf{E} \| \mathbf{H}_0$ in a magnetic field and relaxation after the light was switched off the anisotropy in the basal plane changed. The anisotropy fields took on the values, respectively $H_6 = 42$ A/m and $H_2 = 3$ A/m. (The following values were used to obtain the fit: $H_D = 1.7 \cdot 10^6$ A/m, $H_E = 7.4 \cdot 10^8$ A/m, $\omega/\gamma = 10^6$ A/m, and $H_\Delta^2 = 7.2 \cdot 10^5$ A/m^2. Here all the notation is standard.)[5] Figure 10 (part b, dots) shows the experimental data on the difference of the resonance fields before irradiation ($H_{\rm res}$) and after irradiation ($H^*_{\rm res}$) as well as the curve (solid line) of $\delta H = H_{\rm res} - H^*_{\rm res}$, obtained as the difference of the corresponding approximating curves.

If it is assumed that the same impurity magnetic centers are responsible for the thermomagnetic and photosensitive parts of the anisotropy, then a consistent description of the time and angular dependences is possible on the basis of an approach in which the host hematite crystal is regarded as a two-sublattice easy-plane weak ferromagnet that is exchange-coupled with the anisotropic impurity centers dissolved in it. In this description the free energy of the crystal has the form

$$U = F_Z + F_D + F_E + F_A + F_I, \tag{7}$$

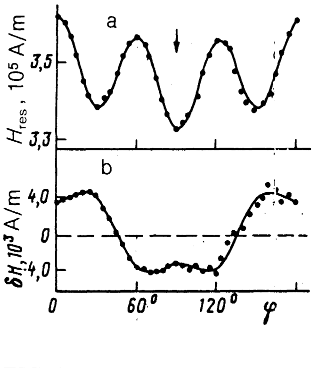

FIG. 10. a) Angular dependence of the resonance field and b) photoinduced shift of the resonance field. The dots are the experimental points, the solid line is the theoretical approximation, and the arrow indicates the direction of $\mathbf{H}_0$ on cooling and irradiation of the specimen; $T = 10$ K.

where F_z is the Zeeman energy, F_D is the Dzyaloshinskii interaction, F_E is the intersublattice exchange interaction, F_A is the magnetic anisotropy energy in the basal plane, and F_I is the energy of the photosensitive impurity centers.

In studying F_I we note that in many oxide compounds (garnets, orthoferrites, etc.) the interaction between the rare-earth and $3d$ ions is of an antiferromagnetic character.[4] The Eu^{2+} ions in the ground state are in the S state and it can be assumed that their interaction with the host matrix is isotropic. If, however, the center transfers into the state $|2\rangle$, then in any of the above cases it will be anisotropic. We assume further that the form of the interaction with the host matrix is identical for all impurity ions, irrespective of the iron sublattice with which the impurity center interacts. This assumption is correct if the impurity centers are uniformly distributed over the volume and the same number of impurity centers interact with each of the two sublattices. In this case the Hamiltonian of the impurity center at the k th position has the following form in a local coordinate system:

$$f_I^k = f_1^k \quad \text{for} \quad f_I^k = f_2^k \tag{8a}$$

depending on the past history of the center (i.e., the polarization of the optical radiation, the temperature, and the orientation of the magnetic field), where

$$f_1^k = E_{ex1}^k + V_1^k, \qquad f_2^k = E_{ex2} + V_2^k. \tag{8b}$$

and $E^k_{ex1,2}$ are the exchange interaction energies of the impurity magnetic centers in the states $|1\rangle$ or $|2\rangle$ interacting with the moment of the iron sublattice and $V^k_{1,2}$ are the anisotropy energies of the impurity centers. The free energy of the entire subsystem of impurity centers can be written as

$$F_I = \sum_k \sum_i (n_1^k \nu_{1i}^k \varepsilon_{1i}^k + n_2^k \nu_{2i}^k \varepsilon_{2i}^k) - ST, \tag{9}$$

where ε^k_{1i} and ε^k_{2i} are the eigenvalues of the Hamiltonians (8b), ν^k_{1i} or ν^k_{2i} are the populations of the ith sublevel of the center in either the state $|1\rangle$ or the state $|2\rangle$ (the numbers n^k_1 and n^k_2 of centers are given by the expressions (4) and fix the distribution of photocenters over the states $|1\rangle$ and $|2\rangle$), and S is the entropy of the impurity subsystem.

For the AFMR field we obtain the expression

$$H_{\rm res} = -\frac{H_D}{2} + \left\{ \frac{H_D^2}{4} + \frac{\omega^2}{\gamma^2} + H_E H_A + H_E H_F \right\}^{1/2}, \tag{10}$$

where H_F is the impurity field and the other notation is standard.

Under the condition (2), H_F has the structure

$$H_F = {\sum_k}' Q^k(\varphi_H) n_2^k, \tag{11}$$

where $Q^k(\varphi_H)$ contains the angular dependence.

It is more convenient to study the anisotropic and kinetic properties using Fig. 11, which shows the impurity centers in different crystallographic positions, projected on the same unit cell (for example, the circle 1 symbolizes the total number of impurity centers located in the corresponding equivalent positions, etc.). It is assumed that the magnetic impurity centers are localized near possible oxygen vacancies. The structure of the center is drawn in the circles schematically.

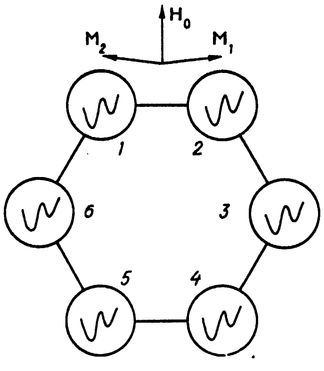

FIG. 11. Diagram of the distribution of impurity centers over inequivalent crystallographic positions projected on the unit cell.

In this picture the anisotropy of the crystal in the basal plane is determined by the anisotropy of the impurity center in the state $|2\rangle$ and the distribution of centers over the states $|1\rangle$ and $|2\rangle$.

Before continuing our discussion of the results we note that for hematite crystals doped with rare-earth ions, at the present time there are no data on the magnitudes of the exchange interactions between the rare-earth ions and the iron ions. However, for different compounds of iron oxides containing some type of rare-earth ions the exchange interaction is, as a rule,[4] anisotropic and does not differ much in magnitude for different crystals. Assuming for simplicity that in the case of α-Fe_2O_3:Eu, Ga the exchange interaction between the europium ion in the k th position and the iron subsystem is of an antiferromagnetic quasi-Ising character, we have in a local coordinate system

$$E_{ex}^{k}=|\lambda|\mathbf{S}_{\mathrm{Eu}}^{z\,k}\,\mathbf{M}_{\mathrm{Fe}}, \tag{12}$$

where $\mathbf{S}_{\mathrm{Eu}}^{z_k}$ is the operator of the z-component of the spin of the Eu ion, λ is the molecular-field constant, and $\mathbf{M}_{\mathrm{Fe}}$ is the magnetization of the iron sublattice.

For estimates we shall use the value of the exchange energy for europium iron garnet, equal to $E_{ex}^{\mathrm{Eu\text{-}Fe}}/k_{\mathrm{B}} \approx 24$ K. We also assume that the contribution of magnetic interactions lowers, in an additive fashion, the position of the bottom of the potential well corresponding to the state $|2\rangle$.

In the absence of the optical radiation and of an external magnetic field, when there is no distinguished direction and all positions in Fig. 11 are equivalent ($N = N_0/6$, where N_0 is the total number of centers), as the temperature decreases from $T > \Delta_1/k_{\mathrm{B}}$ the probabilities for occupying the states $|1\rangle$ and $|2\rangle$ do not differ significantly and it can be assumed that $n_1^k \simeq n_2^k$. As the temperature is further lowered to $T = 4.2$ K this balance changes depending on the rate of cooling. Since the constant C is small, however, the excess centers (with respect to equilibrium) become frozen in the $|2\rangle$ state (here the question is one of finite observation times). The state obtained in this manner is not a thermodynamically equilibrium state, and with time relaxes to equilibrium. Since all positions are equivalent, however, the system exhibits purely hexagonal anisotropy.

If the cooling is conducted in a nonzero magnetic field with fixed orientation, then, as one can see from Fig. 11, for the situation shown, which corresponds to the conditions of the experiment, the positions of types 3 and 6 are equivalent to one another while the positions of types 1, 2, 4, and 5 are equivalent to one another. Since different nonequivalent positions correspond to different barrier heights Δ_2, according to the relation (3) the thermodynamic equilibrium populations of the state $|2\rangle$ for these positions are different. There obviously exists uniaxial anisotropy in the distribution of the population of the state $|2\rangle$ for different positions. In reality, the situation is significantly more complicated, since the explicit form of the structure of the energy levels in each potential well is not known, and it is the form of this structure that determines the temperature and angular dependence of the magnetic contributions.

The dependence of the bottom of the potential well on the magnetic energy makes it possible to understand the time dependence of the changes in the resonance field. In the geometry shown in Fig. 11, for centers in the positions 1, 2, 4, and 5 we have $\Delta_2/k_{\mathrm{B}} \approx 11$ K and in the positions 3 and 6 $\Delta_2/k_{\mathrm{B}} = 11 + E_{ex}/k_{\mathrm{B}} \approx 36$ K. As a result of illumination with light having polarization $\mathbf{E}\|\mathbf{H}_0$, in all positions the states $|2\rangle$ are predominantly populated. After the light is switched off, owing to thermodynamically equilibrium transitions the system tends toward equilibrium. At low temperatures the relaxation time [the expression (6)] is determined by the lower energy barrier, and the section 2–3 in Fig. 2 apparently corresponds to establishment of thermodynamic equilibrium for centers in the positions 1, 2, 4, and 5, the state $|2\rangle$ for the positions 3 and 6 remaining "frozen." As the temperature decreases centers with higher energy barriers contribute to the relaxation time. In reality, this is manifested as a discrepancy between the experimental values of the relaxation times and the approximating curve, $\Delta_2/k_{\mathrm{B}} = 11$ K (Fig. 6), for $T > 35$ K.

5. CONCLUSIONS

It follows from the results of our investigations that the polarization-dependent photoinduced change of the AFMR in α-Fe_2O_3:Eu, Ga is related to the restructuring of photosensitive centers containing europium ions. Analysis of the time-dependent changes of the magnitude of the resonant field shows that a photosensitive center can be described by a model potential having two minima. The energy barriers separating different states of the photocenter were determined. It was established that the optically excited state plays the role of an intermediate state in the restructuring of a magnetic impurity center. The behavior of the angular dependences of the photoinduced changes can be interpreted in terms of the appearance and disappearance of anisotropic magnetic centers in nonequivalent crystallographic positions accompanying selective excitation of the centers.

In conclusion we note that in order to study more thoroughly the energy structure of photosensitive centers the spectral properties of crystals must be studied in greater detail and a microscopic analysis must be performed.

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APPENDIX

$$-\frac{1}{\tau_{1,2}}=\frac{\alpha}{2}\pm\left(\frac{\alpha^2}{4}-\beta\right)^{1/2}=P_{1,2},$$

$$\alpha=(d_{12}+d_{13}+d_{21}+d_{23}+d_{31}+d_{32}),$$

$$\beta=(d_{12}d_{23}+d_{13}d_{21}+d_{13}d_{23}+d_{21}d_{32}+d_{31}d_{12}+d_{31}d_{21}$$
$$+d_{31}d_{23}+d_{12}d_{32}+d_{13}d_{32}),$$

$$n_i(t)=A_0{}^i+A_1{}^i\exp(-t/\tau_1)+A_2{}^i\exp(-t/\tau_2),$$

$$A_0{}^i=K_i/P_1P_2=K_i\tau_1\tau_2,$$

$$A_1{}^i=(n_i{}^0\tau_2+L_i\tau_1\tau_2+K_i\tau_1{}^2\tau_2)/(\tau_2-\tau_1),$$

$$A_2{}^i=(n_i{}^0\tau_1+L_i\tau_1\tau_2+K_i\tau_1\tau_2{}^2)/(\tau_1-\tau_2),$$

$$L_1=n_1{}^0(d_{21}+d_{23}+d_{32})+n_2{}^0d_{21}-Nd_{31},$$

$$K_1=-N(d_{31}d_{21}+d_{31}d_{23}+d_{32}d_{21}),$$

$$L_2=n_2{}^0(d_{12}+d_{13}+d_{31})+n_1{}^0(d_{12}-d_{32})-Nd_{32},$$

$$K_2=-N(d_{12}d_{31}+d_{12}d_{32}+d_{13}d_{32}).$$

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