Orthogonal magnetic "impurity" (Fe^{+3} in *c* positions) in orthoferrite $YFeO_3$

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The field dependence of the impurity lines in yttrium orthoferrite were investigated in magnetic fields up to 140 kOe in the direction of the *c* and *a* axes in the frequency range 75–400 GHz and temperature interval 12–70 K. It is shown that the impurity lines are due to electronic transitions between levels of the $^6S_{5/2}$ multiplet of Fe^{+3} ions occupying yttrium positions. The magnetic moments of these ions are directed opposite to the weak-ferromagnetic moment, i.e., they are practically orthogonal to the magnetic moments of the sublattices of the matrix. Precise measurements of the magnetization from the anomaly in the temperature dependence $\sigma_c(T)$ at low temperatures made it possible to estimate the concentration of these "impurity" ions: $3.5\cdot 10^{-4}$ per formula unit. The anisotropy constants of the impurity ions and the impurity-matrix exchange interaction parameters were determined from the experimental data. The uniaxial anisotropy constant is substantially different from the value predicted by the microscopic theory.

INTRODUCTION

In Refs. 1 and 2, in an investigation of antiferromagnetic resonance (AFMR) in the submillimeter range in yttrium orthoferrite $YFeO_3$ single crystals at low temperatures, additional intense absorption lines at frequencies of about 260 (Refs. 1 and 2) and 270 GHz (Ref. 1) were observed besides the two well-known AFMR modes. In Ref. 1 it was proposed that these lines are produced by impurities. A study of the behavior of the strongest line (260 GHz) in a magnetic field oriented along the *c* axis of the crystal[2] showed that the resonance frequency decreases linearly with increasing field. From this it was concluded that the magnetic moments of the impurity ions are directed antiparallel to the external magnetic field (and, correspondingly, the weak-ferromagnetic moment of the crystal), i.e., almost orthogonal to the magnetic moments of the main matrix. However, repeated x-ray fluorescence analysis of the sample investigated in Ref. 2 showed, with an accuracy of 10^{-5}, that there are no magnetic impurities. In this connection, it was suggested in Ref. 2 that the Fe^{+3} ions, which replace Y^{+3} ions in the *c* positions (the designations of the positions are taken from Ref. 3), can play the role of the "impurity." In what follows we designate these "impurity" ions as $Fe^{+3}(c)$ [in contrast to the ions of the main matrix in the *b* positions—$Fe^{+3}(b)$] and we call them, respectively, impurity ions and matrix ions.

The aim of the present work is to check this conjecture experimentally. To this end, we altered somewhat the experimental conditions, as compared with Ref. 2, increasing the sensitivity of the apparatus and also performing the measurements at different temperatures. This enabled us to observe clearly three additional lines of decreasing intensity, in addition to the two lines reported in Refs. 1 and 2. All five lines formed a group, i.e., their frequencies had the same dependence on the external field. We interpreted them as transitions within the ground-state multiplet of the $Fe^{+3}(c)$ ion ($^6S_{5/2}$ ground state), split into six unequally spaced levels by the exchange interaction with the $Fe^{+3}(b)$ matrix ions, the crystal field, and the external magnetic field. The two lines observed in Refs. 1 and 2 at temperatures below 20 K are explained as transitions between the lower levels of the multiplet ($|-5/2\rangle\leftrightarrow|-3/2\rangle$ and $|-3/2\rangle\leftrightarrow|-1/2\rangle$), which are the strongest transitions.

In addition, precise measurements of the temperature dependence of the spontaneous magnetization in the direction of the *c* axis were performed on the sample. The anomaly observed at low temperatures confirmed the presence of a magnetic impurity that decreases the weak-ferromagnetic moment of the matrix. The concentration of $Fe^{+3}(c)$ ions was estimated from these measurements to be $3.5\cdot 10^{-4}$ per formula unit.

We note that the investigation of such an "impurity" is of interest from several viewpoints. As is well known, in most cases the impurity ions replace ions of the matrix. In our case, however, we are dealing with an "impurity" that differs from the matrix ions not by the type of ion and not even by a change in the valence of the ion, but only by the position of the ion in the crystallographic cell. As far as we know, this is the first experimental study of the resonance modes of an impurity of this type.

Further, the interaction of the matrix with the impurity in our case can be regarded as the analog of the R–Fe interaction, where the system of Fe^{+3} ions, strongly diluted with nonmagnetic yttrium, plays the role of the rare-earth sublattice. The R–Fe interaction in orthoferrites has been studied quite well (see, for example, Ref. 4). It is well known that, in spite of the fact that the symmetry of the position *c* is low (C_s), this position is symmetric with respect to the $Fe^{+3}(b)$ ions. As a result, the interaction with the eight nearest antiferromagnetically ordered $Fe^{+3}(b)$ ions is virtually completely cancelled out. Impurities of this type (called quadrupole impurities) were studied theoretically in Refs. 5–7, after they were discovered experimentally[8] in the antiferromagnetic $FeCl_2$:Fe^{+3}. The distinction in the case of the orthoferrite $Y(c)Fe(b)O_3$:$Fe^{+3}(c)$ is, first, that the impurity and matrix ions have the same valence and, second, the ex-

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change field produced at the position of the impurity, mainly by the canting of the magnetic moments of the matrix owing to the Dzyaloshinskiĭ interaction, is not completely compensated. In addition, as will become evident below, the theory proposed in Refs. 5–7 disagrees with our data.

In the case of a substitution impurity, the magnetic moments of the impurity are usually collinear with the magnetic moment of the sublattice where the substitution occurred. Resonance on impurity ions in the S state in such a situation was observed, for example, in Refs. 9–12 (Mn^{+2} ion, $^6S_{5/2}$ multiplet). Crystals in which the magnetic moments of the impurity were orthogonal to the magnetic moments of the sublattices because of the large anisotropy of the impurity ion [for example, Fe^{+2} ions in $CoCO_3$ (Refs. 13 and 14)] were exceptions. The distinction in the case of $YFeO_3$: $Fe^{+3}(c)$ is that here the orthogonality of the impurity is of an exchange nature, i.e., it is determined by the symmetry of the exchange field in the positions of the impurity.

Here we should also mention Ref. 15, where the spectra of $Fe^{+3}(b)$ and $Gd^{+3}(c)$ ions, present in amounts of the order of 1% in yttrium orthoaluminate $YAlO_3$, which is isomorphic to yttrium orthoferrite, were investigated. The gadolinium ion Gd^{+3} is analogous to the impurity ion $Fe^{+3}(c)$ in $YFeO_3$ (same position, ion in the s state), differing only by the magnitude of the spin (7/2 instead of 5/2) and by the absence of an interaction with the matrix. The spectrum of the Gd^{+3} ion in a magnetic field also consisted of seven closely and unequally spaced lines and was found to be very similar to the "impurity" spectrum which we observed. The "distance" between the extreme lines in the group in the case of Gd^{+3} in the direction of the c axis was ≈ 1.5 kOe. The larger splitting for the $Fe^{+3}(c)$ spectrum (the extreme lines were separated by a "distance" of about 30 kOe) can be explained by the presence of an interaction with the matrix and the larger crystallographic anisotropy for the case of the $3d$ ion.

We note, finally, that the investigation of the impurity mode can be utilized to check the quality of the single crystals grown, since impurities of this type are virtually impossible to detect by traditional methods of analysis.

SAMPLES AND EXPERIMENTAL PROCEDURE

The measurements were performed on yttrium orthoferrite single crystals, grown by zone melting with radiation heating[16] from blanks obtained by sintering yttrium oxide Y_2O_3 and iron oxide Fe_2O_3 at 1400 °C. The oxides were mixed in the ratio 1.00:1.00 (per formula unit) with an accuracy of 10^{-3}%. The total mass fraction of magnetic impurities in the starting components, according to the technical data supplied with the reagents, was less than 10^{-4} for Fe_2O_3 and 10^{-6} for Y_2O_3. Additional analysis of the samples for the presence of trace impurities was conducted at the Institute of Physical Chemistry of the Russian Academy of Sciences and the Institute of Experimental Optical Spectroscopy of the Russian Academy of Sciences (IEOS RAN), by methods of x-ray fluorescence analysis on VRA-30 setups (produced by the Carl Zeiss Company) and local x-ray spectral microanalysis on the Camscan C apparatus using a Link-10 000 analyzer (Institute of Physical Chemistry, Russian Academy of Sciences (IPC/RAN)). The spectral data were analyzed using service programs with Fe and Co standards. These analyses revealed the following: Impurities of rare earths, cobalt, and copper are not present, within an accuracy of 10^{-5}, and the mass fraction of manganese is less than $2\cdot 10^{-5}$, which corresponds to the certificate data. The presence of nickel impurity could not be established by means of x-ray fluorescence analysis because the diffraction angles of the K_α (Ni) line coincided with the second order of the K_α (Y) line. In order to reduce the number of defects and the content of Fe^{+2} and Fe^{+4} ions, the samples were annealed to 1400 °C in an oxygen medium (20 atm) for 8 h.

The samples were cut from the same boule as the sample investigated previously in Ref. 2. The samples to be used for the resonance measurements consisted of plates with the approximate dimensions $3\times 6\times 1$ mm, and they were oriented by the x-ray method perpendicular to the c and a axes. The sample to be used for the magnetization measurements was a parallelepiped with the dimensions $3.0\times 5.2\times 4.1$ mm and it was oriented with x-ray accuracy (3°) parallel to the principal crystallographic axes.

Magnetic resonance was investigated with the help of a transmission spectrometer[17] with a detector consisting of n-InSb cooled to 4.2 K. The intensity of the radiation passing through the sample was measured experimentally in the frequency range 75–400 GHz as a function of the applied magnetic field up to 140 kOe in the temperature interval 12–300 K. The radiation was directed along the magnetic field; the polarization of the radiation relative to the sample was not monitored. The end of the sample was glued in a holder and inserted into a beamguide so that the radiation propagated approximately along the normal to the surface of the sample. Further alignment of the sample was performed "according to the effect:" so as to achieve the maximum or minimum resonant field at a given frequency by means of small deviations of the sample in two mutually perpendicular planes. The final sample placement accuracy was equal to 2° along the c axis and less than 0.5° along the a axis.

The wavelength of the submillimeter radiation was measured to within 0.2% using a Fabry–Perot inteferometer with gridded mirrors. The magnetic field was calibrated according to the EPR signal from the DFPG; the field was measured with an accuracy of 1%. The temperature was measured with a copper–copper-iron thermocouple with an accuracy of better than 0.1 K. The temperature of the sample was maintained constant to within 0.1 K.

In contrast to the conditions of the experiment performed in Ref. 2, in the present case measures were taken to increase the sensitivity of the apparatus and to decrease interference effects which distort the shape of the lines. Since the prepared samples did not completely cover the cross section of the beamguide (7×3.5 mm), some of the radiation could reach the detector, bypassing the sample. For this reason, a thin copper plate, covering virtually completely the cross section of the beamguide and having a 2×4 mm opening at the center, was soldered in the holder beneath the sample. A radiation concentrator, consisting of a teflon "reducer" from the 7×3.5 mm cross section to the 2×4 mm cross section, tightly wound with aluminum foil was inserted into the beamguide in front of the sample in order to reduce the losses. These measures made it possible to reduce to 4% the fraction of the radiation bypassing the sample. In addition, dampers, made of rubber with a large amount of soot and absorbing submillimeter radiation, were inserted into the beamguide in order to reduce the effect of the standing waves arising in the guide.

The spontaneous magnetization was measured with an absolute accuracy of 2% and a relative accuracy of 0.5% on a Model 155 vibrating-coil magnetometer made by Princeton Applied Research. The sample was inserted into a magnetic field of up to 12 kOe using the standard method; the orientation was set with an accuracy of better than 2°. The temperature in the interval 20–700 K was measured with copper-constantan and chromel-alumel thermocouples to within 0.5 K; the temperature in the interval 2.6–20 K was measured with a carbon thermometer to within 0.3 K.

EXPERIMENTAL RESULTS

As was already reported in Ref. 2, the investigation of the sample with *c*-orientation revealed a descending mode, whose resonance frequency decreased linearly with increasing magnetic field. On plots of the field dependences of the intensity of the radiation passing through the sample this mode looked like a wide resonance line ($\Delta H \approx 8$ kOe at 12 K). As the temperature increased this line gradually broadened and became virtually unobservable at 70 K.

After the changes described above were made in the construction of the apparatus, the measurements were repeated on the same sample of $YFeO_3$. Examples of tracings of the impurity lines are presented in Fig. 1a. Five resonance absorption lines, whose intensity depends on the temperature, can be clearly seen. At low temperatures the first line, corresponding to the transition

$$|-5/2\rangle \leftrightarrow |-3/2\rangle,$$

is strongest (we recall that an increase in the external field corresponds to a decrease in the effective field on the impurity ion). As the temperature increases the intensities of the impurity lines tend to equalize. At high temperatures the line intensities should form the ratio 5:8:9:8:5, but we were not able to check this relation, since as the temperature increases the line widths increase and the lines coalesce and become unobservable. As one can see, the position of the lines was virtually independent of the temperature. The frequencies of the impurity lines, analyzed by the least-squares method, as a function of the external field (Fig. 2) were found to be linear, to within the limits of accuracy of the experiment (1%), and were described by the formulas

$$\nu_i(c) = \nu_{i0} - kH, \tag{1}$$

where $i = 1,\dots,5$ are the frequencies of the impurity lines in the absence of a field:

$$\nu_{10}=263. \quad \nu_{20}=266. \quad \nu_{30}=274, \quad \nu_{40}=286. \quad \nu_{50}=301 \text{ ГГц},$$
$$k=1.50 \text{ GHz/kOe}.$$

As one can see from Figs. 1a and 2, the lines are unequally spaced, and the unequal spacing remains throughout the entire range of frequencies. We note that similar unequal line spacing was observed, for example, in Refs. 9–12 on the impurity ion Mn^{+2} (substitution impurity). To complete the picture, the field dependence of the quasiferromagnetic mode of AFMR is also presented in Fig. 2.

In $YFeO_3$ a spin-reorientational transition (turning of the antiferromagnetism vector from the *a* axis to the *c* axis) occurs when a field is applied along the *a* axis. This transition is accompanied by softening of the frequency of the quasiferromagnetic AFMR mode[18] and above the transition field ($H_{tr} = 71.5$ kOe) the AFMR frequency is observed to increase once again. The frequencies of the impurity lines along the *a* axis also decrease with increasing field, but not as rapidly as the frequency of the quasiferromagnetic mode for $H < H_{tr}$. For this reason, when the field is oriented exactly along the *a* axis the AFMR lines intersect with the lines of the impurity modes. This interaction is of a quite complicated character, which depends on the number of the impurity line and on the temperature. At low temperatures the inter-

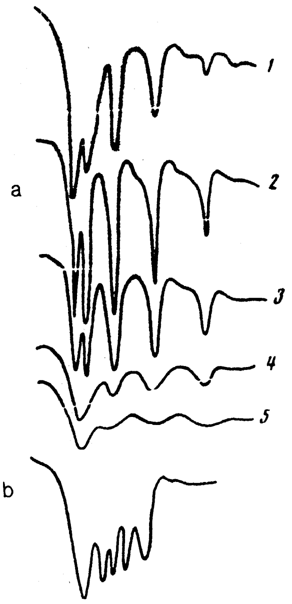

FIG. 1. Examples of tracings of impurity absorption lines: a) field directed along the *c* axis, $f = 158$ GHz, $T = 15$ (*1*), 30 (*2*), 40 (*3*), 58 (*4*), and 69 K (*5*); b) field directed along the *a* axis, $f = 143$ GHz, $T = 15$ K.

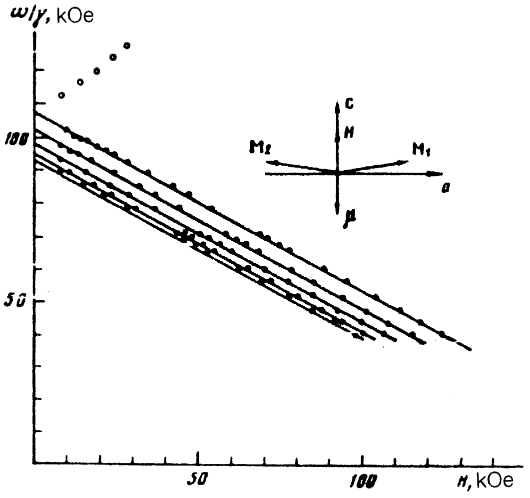

FIG. 2. Field dependences of the frequencies of impurity lines (**H**||**c**). The dots represent the experimental data and the solid lines represent the calculations. The open circles show the field dependence of the low-frequency AFMR mode. Inset: The configuration of the magnetic field of the matrix sublattices (M_1 and M_2) and of the magnetic moment of the impurity (μ) relative to the crystallographic axes.

section of the AFMR mode with the impurity modes is accompanied by significant "repulsion" of the modes, and this results in strong distortions of their field dependence.

Digressing from the effects of mode interaction, we present the field dependence of the frequencies of the impurity lines and the quasiferromagnetic AFMR mode with the field inclined by a small angle ($\approx 6°$) away from the a axis in the ac plane (Fig. 3). Since the minimum AFMR frequency (near $H_{\rm tr}$) is extremely sensitive to the precise orientation, even a small deviation away from the a axis results in a strong increase in the frequency and decrease in the interaction of the impurity modes and the AFMR mode. In weak fields ($H < H_{\rm tr}$) we could not resolve all five lines, and we observed only two impurity lines experimentally, one of which (the first one) was quite narrow and strong, while the other was approximately two times wider and three times weaker. In fields exceeding $H_{\rm th}$, five lines were observed. An example of the tracing of these lines is given in Fig. 1b. As one can see from Fig. 3, in strong fields, when the antiferromagnetism vector is virtually perpendicular to the external field, the frequencies of the impurity modes decrease almost linearly, just as along the c axis. Just as in the direction of the c axis, the lines are unequally spaced, though the unequal spacing is of a somewhat different character.

As we have already mentioned, measurements of the spontaneous magnetization along the c axis were also performed. In performing these measurements, we had in mind the fact that the orthogonality of the impurity will allow it to be detected by purely magnetic methods. Figure 4 shows the temperature dependence $\sigma(T)$, obtained by extrapolating the curves $\sigma_c(H)$ to $H = 0$ (the hysteresis loop is almost square and the coercive force at low temperatures is equal to 0.5 kOe). Our data on σ_c at 4.2 K are virtually identical to the data of Ref. 19 and are 10% higher than those of Ref. 20, $T_N = 643$ K.

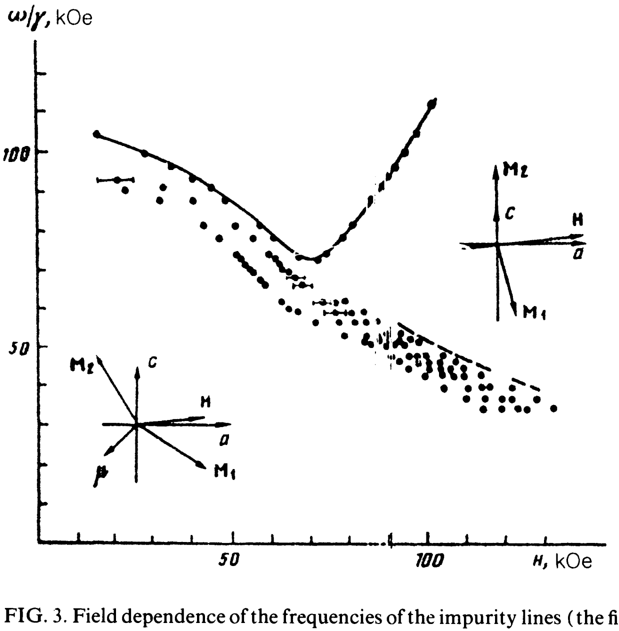

FIG. 3. Field dependence of the frequencies of the impurity lines (the field H makes a small angle with the a axis). The solid line shows the field dependence of the low-frequency AFMR mode. Insets: The configuration of the external field, the magnetic moments of the sublattices of the matrix, and the impurity in weak and strong fields.

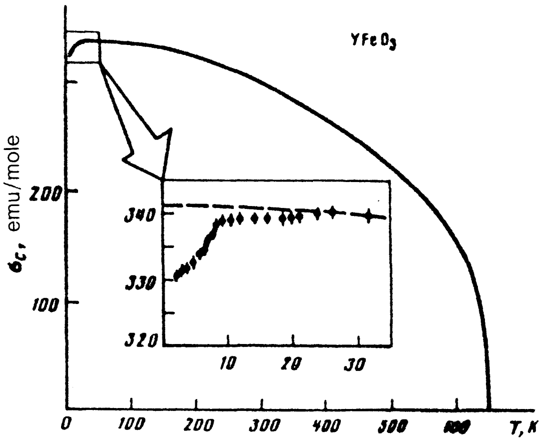

FIG. 4. Temperature dependence of the spontaneous magnetization. Inset: The anomaly at low temperatures (enlarged scale).

Indeed, an anomaly was found at low temperatures. The anomaly is shown in the inset on an enlarged scale. As one can see, the decrease in magnetization, as compared with extrapolation of the curve $\sigma_c(T)$ to 0 K from high temperatures (dashed line), is equal to 10.5 G·cm^3/mole (3.2%). The concentration of the $\mathrm{Fe}^{+3}(c)$ impurity ions can be obtained by assuming that this difference is determined by these ions magnetized up to saturation. The result is $3.5\cdot 10^{-4}$ per formula unit. We note that this result is an estimate, since in obtaining it we neglected the possible distortions arising in the matrix when the impurity is introduced. Taking these distortions into account could increase the concentration by 30–40%.

DISCUSSION

We first analyze qualitatively the experimental data obtained. It is natural to associate the five observed lines to electronic transitions within the multiplet $^6S_{5/2}$ of the $\mathrm{Fe}^{+3}(c)$ ion. Indeed, the hyperfine interaction should be excluded in this case, since only 2.2% of the iron ions can have nonzero nuclear spin, and this spin is equal to 1/2; no other impurities with concentration exceeding 10^{-5} were found. The fact that the frequency of the impurity modes decreases linearly with increasing field indicates that the magnetic moments of the impurity are oriented opositely to the external field and therefore oppositely to the weak-ferromagnetic moment: This is also supported by the magnetization data. In other words, the matrix-impurity system behaves in a magnetic field as a single entity. The crystallographic cell of orthoferrite contains a single regular position (for the positively charged ion), the symmetry of whose exchange field with the matrix corresponds to these requirements—this is the c position, which is usually occupied by the rare-earth element or yttrium.

It has already been mentioned that a microscopic theory of impurity ions of this type ("quadrupole" impurity) was proposed in Refs. 5–7. One of the main consequences of this theory is that the spectrum of the impurity should be described by a Hamiltonian of the form

$$\hat{\mathcal{H}}=A(\hat{S}_z^2-{}^1/_3S(S+1)). \qquad (2)$$

Here $\hat{S}_z$ is the spin operator of the impurity, the z axis is oriented along the antiferromagnetism vector of the matrix, and the constant A is of the order of J^2/J_{12}, where J is the exchange interaction integral between the impurity and its nearest neighbors in one of the sublattices, and J_{12} is the exchange interaction integral between the sublattices of the matrix. We call attention to the fact that J is the uncompensated exchange interaction of the impurity with one of the sublattices of the matrix and is significantly greater in absolute magnitude than the compensated effective matrix-impurity interaction. It is easy to estimate the constant A in the case of $\mathrm{YFeO_3}$: The compensated interaction is of the order of 10 cm^{-1} (the frequency of the impurity mode with $H=0$) and is largely determined by the presence of the weak-ferromagnetic interaction in the matrix (see below). Therefore, the uncompensated interaction is of the order of

$$J=10(nS\sin\alpha)^{-1}\approx 50\ \mathrm{cm}^{-1},$$

where $n=8$ is the number of nearest neighbors, $S=5/2$, and α is the canting angle of the sublattices. The exchange interaction between the sublattices of the matrix vs $J_{12}\approx 100$ cm^{-1}, and hence $A\approx 25$ cm^{-1}. Such a large splitting would indicate that in the submillimeter range we could observe, in the best case, a single line, corresponding to the transition $|-1/2\rangle\leftrightarrow|+1/2\rangle$, and not five lines.

As a result of this, we were not able to utilize the results of Refs. 5–7, and in order to describe the experimental data we used a phenomenological Hamiltonian, written in the molecular-field approximation (the external field is oriented along the c axis, which is also the quantization axis):

$$\mathscr{H}_{0c}=g\mu_B(H_{0c}-k_cH)\hat{S}_z+D_c\hat{S}_z^2+a_{3c}\hat{S}_z^3+a_{4c}\hat{S}_z^4. \tag{3}$$

Here $g=2$ and μ_B is the Bohr magneton. In deriving the Hamiltonian (3) we proceeded as follows. All invariants, admitting symmetry and consisting of products of the components M_z, L_x and S_z (Ref. 4) up to fourth order in S_z were written out. ($\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2=\mathbf{M}_0+\chi_\perp\mathbf{H}$, $\mathbf{L}=\mathbf{M}_1-\mathbf{M}_2=\mathbf{L}_0$, and $\mathbf{M}_1$ and $\mathbf{M}_2$ are the magnetizations of the sublattices of the matrix.) Next, we dropped the terms which give a nonlinear field dependence $\nu_i(\mathbf{H})$ and change the spacing of the lines, and we added similar terms; in addition, we treated M_0 and L_0 as parameters. Thus the constants in the Hamiltonian (3) implicitly depend on the parameters of the matrix. Assuming *a priori* the existence of an exchange interaction between the matrix and the impurity, we dropped the effective g factor and introduced a coefficient k_c depending on this interaction, and we set $g=2.00$. In other words, the coefficient k_c reflects the fact that the external field not only interacts directly with the impurity spin, but it also changes the weak-ferromagnetic moment of the matrix, and this changes the effective field acting on the impurity.

Analysis of the experimental dependences with the help of the Hamiltonian (3) gave the following values of the constants:

$$\begin{gathered}H_{0c}=98\ \mathrm{kOe}\pm0.3\%,\\ k_c=0.536\pm0.7\%,\\ D_c=0{,}176\ \mathrm{cm}^{-1}\pm5\%,\\ a_3=0.017\ \mathrm{cm}^{-1}\pm20\%,\\ a_4\approx0.\end{gathered} \tag{4}$$

The sign of the constant D_c was chosen from the temperature dependence of the line intensities. We call attention here to the agreement between the set of constants (4) obtained here and the data of Refs. 9 and 11, where a cubic anisotropy also had to be introduced in order to describe the unequal spacing of the impurity lines of the Mn^{+2} ion and where the biquadratic anisotropy was found to be negligibly small. The theoretical dependences corresponding to the parameter set (4) are presented in Fig. 2. As one can see, the agreement with experimental data is good.

It is known (for example, Ref. 4) that in orthoferrites the antisymmetric and anisotropic contributions of the exchange interaction with the matrix can predominate at the positions of the rare-earth ion because the isotropic exchange interaction is almost completely compensated. If the coefficients H_{0c} and k_c are known, the contributions due to the symmetric and antisymmetric exchange interactions can be separated. Indeed, the exchange field at the c position can be represented in the general form as[4]

$$\mathbf{H}_M{}^{\pm}=\hat{\lambda}_c{}^{\pm}\mathbf{M}+\hat{\lambda}_a{}^{\pm}\mathbf{L},$$

$$\hat{\lambda}_c^{\pm}=\begin{pmatrix}\lambda_1 & \pm\lambda_5 & 0\\ \pm\lambda_4 & \lambda_2 & 0\\ 0 & 0 & \lambda_3\end{pmatrix},\quad \hat{\lambda}_a^{\pm}=\begin{pmatrix}0 & 0 & \lambda_6\\ 0 & 0 & \pm\lambda_7\\ \lambda_8 & \pm\lambda_9 & 0\end{pmatrix}. \tag{5}$$

Here the $\pm$ signs reflect the existence of two nonequivalent c positions, differing from one another by the orientation of the crystallographic environment, and λ_i are exchange constants. For a field oriented along the c axis, we have

$$H_{Mz}{}^{\pm}=\lambda_3M_z+\lambda_8L_x. \tag{6}$$

As one can easily see from Eq. (5), the coefficients λ_3 and λ_8 correspond, respectively, to the symmetric and antisymmetric exchange interaction. Substituting into Eq. (6) the explicit expressions for M_z and L_x and comparing with Eq. (3), we obtain

$$\begin{gathered}\lambda_3M_0=65\ \mathrm{kOe},\\ \lambda_8L_0=33\ \mathrm{kOe}.\end{gathered} \tag{7}$$

For a field oriented along the a axis, the Hamiltonian (3) with the index c replaced by a and the x axis relabeled as the z axis (neglecting the small deviation of the field from the a axis), can once again be used, to a first approximation, for strong fields. Analysis of the data gave the following values of the constants:

$$\begin{gathered}H_{0a}=98\ \mathrm{kOe}\pm3\%,\\ k_a=0{,}521\pm5\%,\\ D_a=0{,}05\ \mathrm{cm}^{-1}\pm40\%,\\ a_{3a}=-0{,}005\ \mathrm{cm}^{-1}\pm40\%,\\ a_{4a}=0{,}004\ \mathrm{cm}^{-1}\pm75\%.\end{gathered} \tag{8}$$

The significantly lower accuracy of the constants along the a axis (especially the anisotropy constants) is explained by the fact that the lines were observed in a much smaller range of frequencies than along the c axis and also by the fact that the spacing between the lines was smaller.

As one can see, to the accuracy of the experiment, the values of the parameters H_{0a} and k_a are equal to the corresponding values along the c axis. Calculations analogous to

Eqs. (6)–(7) give the following values for the symmetric and antisymmetric interaction parameters for the *a* axis (in the present case, we neglected the constants λ_4 and λ_9):

$$\begin{gathered}\lambda_1 M_0=65 \text{ kOe},\\ -\lambda_6 L_0=33 \text{ kOe},\end{gathered}\tag{9}$$

whence we obtain

$$\begin{gathered}\lambda_1=\lambda_3=5800,\\ \lambda_8=-\lambda_6=32.\end{gathered}\tag{9a}$$

Thus the matrix-impurity exchange interaction in the *ac* plane is isotropic. As a result of the compensation of this interaction, the antisymmetric exchange interaction makes a significant contribution.

Having the experimentally determined sets of parameters (4) and (8), we return once again to the question of the origin of the term in Eq. (3) quadratic in S_z. This term could arise due to both the characteristic anisotropy of the impurity ion and the interaction with the matrix. It can be shown that in the latter case such a contribution appears even in the approximation of interaction of only nearest neighbors. Indeed, consider a cluster consisting of an impurity ion and eight matrix ions surrounding it. We write the Hamiltonian of the cluster, depending on the spin operator of the impurity, in the following form:

$$\begin{aligned}\hat{\mathscr{H}}_{\text{cl}}=&-8JS_1\hat{S}_z\sin(\alpha+\beta)-8J_{12}S_1^2\\ &\times\{{}^3/_2\cos(2\beta+2\alpha)+3\cos(\beta+2\alpha)\}\\ &-8d_1S_1^2\{3\cos(\beta+\alpha)\sin(\beta+\alpha)\\ &+3[\cos(\beta+\alpha)\sin\alpha+\sin(\alpha+\beta)\cos\alpha]\}\\ &-8\mu_B gHS_1\cdot\sin(\alpha+\beta)+{}^1/_2a\hat{S}_z^2+\mu_B gH\hat{S}_z.\end{aligned}\tag{10}$$

Here $\hat{S}_z$ is the spin operator of the impurity; S_1 is the spin of the matrix; J and J_{12} are, as previously, the impurity-matrix and matrix-matrix exchange interaction integrals; d_1 is the Dzyaloshinskiĭ interaction constant; a is the anisotropy constant of the impurity ion; α is the canting angle of the sublattices due to the external field and the Dzyaloshinskiĭ interaction:

$$\sin\alpha=\frac{g\mu_B(H+H_D)}{12J_{12}S_1},\quad H_D=\frac{6d_1S_1}{g\mu_B},\tag{11}$$

where β is the addition canting of the sublattices caused by the presence of the impurity spin. Assuming that the angles α and β are small and minimizing (10) with respect to β, we obtain the equilibrium value of β_0:

$$\beta_0\approx-\frac{J\langle S_z\rangle}{9J_{12}S_1}.\tag{12}$$

Substituting the expressions (11) and (12) into Eq. (10) and dropping the terms which do not depend on S_z, we have

$$\begin{aligned}\hat{\mathscr{H}}_{\text{cl}}=&-\frac{2J}{3J_{12}}g\mu_B H_D\hat{S}_z\\ &+g\mu_B H\left(1-\frac{2J}{3J_{12}}\right)\hat{S}_z-\left(\frac{4J^2}{9J_{12}}-\frac{1}{2}a\right)\hat{S}_z^2.\end{aligned}\tag{13}$$

Comparing Eqs. (3) and (10), we obtain

$$1-{}^2/_3J/J_{12}=k_c,\quad J/J_{12}=0{,}7.\tag{14}$$

Knowing the ratio J/J_{12}, we obtain the following more accurate value of the contribution to the quadratic anisotropy:

$$-{}^4/_9J^2/J_{12}=-10{,}5\ \text{cm}^{-1}.\tag{15}$$

As follows from the forgoing analysis, the physical meaning of the contribution to the anisotropy (15) is that the presence of this impurity results in additional tilting of the matrix spins surrounding the impurity. This tilting should lead to an increase in the magnetization of the matrix along the *c* axis equal to about 30% of the magnetization of the impurity (at 0 K). Unfortunately, the existence of the additional tilting of the matrix spins cannot be checked experimentally, since the impurity concentration cannot be determined by an independent method.

Comparing Eq. (15) with Eq. (4), we see that this contribution is almost two orders of magnitude larger in absolute magnitude then the experimentally observed contribution and has the opposite sign. It is extremely unlikely that the contribution (15) of the characteristic anisotropy, of the impurity ion can be compensated. There are two reasons for this: First, it is difficult to expect for an *S* ion such large values of the anisotropy constant and, second, the reorientation of the impurity spin from the *a* axis to the *c* axis does not change much the splitting of the spectrum. Analysis of the disturbance introduced in the coordination spheres beyond the nearest neighbor sphere (up to the fifth coordination sphere) by the impurity spin showed that such a disturbance decays very quickly, and taking it into account only increases the absolute value of the contribution (15). The contribution (15) can in principle be compensated by taking into account higher order terms in the impurity-matrix and matrix-matrix interaction, but in so doing it must be assumed that these terms (non-Heisenberg interaction) compensate virtually exactly the exchange interaction of the Heisenberg type. At the present time we do not understand the reasons for this large discrepancy between the results of the microscopic theory and experiment.

We note here also the following feature of the spectra, which has not yet been interpreted reliably. An additional line, weaker than the impurity lines which we discussed above, was observed along the *a* axis (the field dependence of this line is shown by the dashed curve in Fig. 3). An analogous additional line was observed in Ref. 11, where it was associated to a pair resonance (transitions within a multiplet with $S=5$ of a pair of impurity spins coupled by a weak interaction). It is possible that the additional line arises due to transitions which are intensified by the interaction with the AFMR mode. However, it is necessary to take into account the fact that the concentration of such pairs in $YFeO_3$ is still very low (10^{-7}). Another possibility is the existence of two nonequivalent *c* positions. In this case, two spectra, somewhat, shifted from and superposed on one another, can be observed; this is manifested effectively in the appearance of "extra" lines and distortion of the line shapes. This situation can arise, for example, in the presence of a weak component of the magnetic field along the *b* axis. Note that in this case the parameters given in Eq. (8) will change somewhat, but remaining within the given limits of the error.

CONCLUSIONS

Thus it can be concluded, on the basis of the data presented, that in $YFeO_3$ a small fraction of the trivalent iron ions may not be in their own positions (in "*c*" position instead of the "*b*" position). Such impurity ions were found to possess a number of interesting features: the fact itself that the impurity ion and a matrix ion differ only by their position in the crystallographic cell, the fact that the magnetic moments of the impurity are orthogonal to the matrix moments, and the frequencies of the impurity moments are close to the quasiferromagnetic mode of AFMR. It is not excluded that such substitutions also occur in other binary compounds, but they have not been found because of the difficulties of observing them. For this reason, we plan a further study of the properties of these impurity ions. In particular, we plan to elucidate the question of the limits of the impurity concentrations as well as the possibility of back substitution of rare-earth ions or yttrium in the *b* position. We note that in the latter case strongly anisotropic rare-earth ions can significantly change the properties of the matrix.

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[1] A. M. Balbashov, A. A. Volkov, G. V. Kozlov *et al.*, Fiz. Tverd. Tela **27**, 270 (1985) [Sov. Phys. Solid State **27**, 165 (1985)].

[2] A. M. Balbashov, A. G. Berezin, Yu. V. Babryshev *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **50**, 401 (1989) [JETP Lett. **50**, 434 (1989)].

[3] M. Marezio, J. P. Remeika, and P. D. Dernier, Acta Crystallogr. B **26**, 2008 (1970).

[4] K. P. Belov, A. K. Zvezdin, A. M. Kadomtseva, and R. Z. Levitin, *Orientational Transitions in Rare-Earth Magnets* [in Russian], Nauka, Moscow, 1979.

[5] M. A. Ivanov, Fiz. Tverd. Tela **14**, 562 (1972) [Sov. Phys. Solid State **14**, 467 (1972)].

[6] M. A. Ivanov and A. Ya. Fishman, Fiz. Tverd. Tela **15**, 2378 (1973) [Sov. Phys. Solid State **15**, 1583 (1973)].

[7] M. A. Ivanov and V. Ya. Mitrofanov, Phys. Status Solidi **61**, 403 (1974).

[8] M. Motokawa and M. Date, J. Phys. Soc. Jpn. **23**, 1216 (1967).

[9] G. Mischler, P. Carrara, and Y. M. D'Augibne, Phys. Rev. B **15**, 1568 (197).

[10] J. Tuchendler, J. Magarino, A. R. Fert, and D. Bertraud, Solid State Commun. **27**, 1123 (1978).

[11] J. Tuchendler, J. Magarino, D. Bertraud, and A. R. Fert, J. Phys. C **13**, 233 (1980).

[12] E. Bertz and U. Durr, Physica B **98**, 197 (1980).

[13] A. S. Borovik-Ramanov and V. F. Meshcheryakov, Pis'ma Zh. Eksp. Teor. Fiz. **8**, 425 (1968) [JETP Lett. **8**, 262 (1968)].

[14] B. S. Dumesh, V. M. Agorov, and V. F. Meshcheryakov, Zh. Eksp. Teor. Fiz. **61**, 320 (1971) [Sov. Phys. JETP **34**, 168 (1971)].

[15] R. L. White, G. F. Herrmann, J. W. Carson, and M. Mandel, Phys. Rev. **136**, 231 (1964).

[16] A. M. Balbashov, A. Ya. Chervonenkis, A. V. Antonov, and V. E. Bukhteuzov, Izv. Akad. Nauk SSR, Ser. Fiz. **35**, 1234 (1971).

[17] A. S. Prokhorov, E. G. Rudashevsky, and L. V. Velikov, IEEE Trans. **MTT-22**, 1064 (1974).

[18] A. M. Balbashov, A. G. Berezine, Yu. M. Gufan *et al.*, Zh. Eksp. Teor. Fiz. **93**, 302 (1987) [Sov. Phys. JETP **66**, 174 (1987)].

[19] G. Gorodetsky, S. Shtrikman, Y. Tenenbaum, and D. Treves, Phys. Rev. **181**, 823 (1969).

[20] I. S. Jacobs, H. G. Burne, and L. M. Levinson, J. Appl. Phys. **42**, 1638 (1971).

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