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Magnetic anisotropy quantitative estimation for the rhombohedral antiferromagnetic crystals containing *S*-state ions

V. V. Men'shikov, S. G. Ovchinnikov, V. V. Rudenko, A. N. Sudakov, V. I. Tugarinov, and A. M. Vorotynov*
L.V. Kirensky Institute of Physics SB RAS, 660036 Krasnoyarsk, Russia

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The method to investigate "single-ion" exchange anisotropy (as predicted by the pair model) is treated by exploration of several isostructural diamagnetic crystals containing magnetic impurities. The electron paramagnetic resonance (EPR) spectra were observed for ferric borate isostructural crystals $M\mathrm{BO}_3{:}\mathrm{Fe}^{3+}$ ($M=\mathrm{Ga},\mathrm{In},\mathrm{Lu},\mathrm{Sc}$). The experimental dependences of the spin-Hamiltonian axial parameters of the second-order D_S and fourth-order $(a\text{-}F)_{cS}$ versus total pair spin S are presented. The contributions arising from the distortion of the parent crystal lattice $M\mathrm{BO}_3$ under magnetic dilution are estimated. The microscopic derived expressions for the "single-ion" contribution to the anisotropy are also presented. The present experimental data enable estimation of the "single-ion" exchange contribution for FeBO_3, MnCO_3, and α-$\mathrm{Fe}_2\mathrm{O}_3$ crystals at $T=0$ K. The quantitative estimations for EPR are in satisfactory agreement among themselves and with the experimental data.

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I. INTRODUCTION

The method to examine the magnetic anisotropy of paramagnetic metal ions used in this paper has been long well known. It involves magnetic dilution of the diamagnetic host lattice with well-known parameters (parent lattice). The quantity of the magnetic impurity must be small enough for single-ion electron paramagnetic resonance (EPR) spectra to be observable. The magnitude and structure of the energy levels determined from these spectra are then used to describe the anisotropy parameters of the magnetically concentrated isostructural substance. However, in spite of the large number of papers using this method, the quantitative agreement between the experimental results and microscopic theories has not been good so far, in particular for magnetic dielectrics with *S*-state ions. For example, theoretical treatments of the basis of the single-ion model[1] for $\mathrm{Y}_3\mathrm{Fe}_5\mathrm{O}_{12}$,[2] EuO,[3] α-$\mathrm{Fe}_2\mathrm{O}_3$, FeBO_3, and MnCO_3,[4,5] taking into account the dipole-dipole interaction and spin-Hamiltonian parameters derived from experiments on isostructural diamagnetic materials with Fe^{3+}, Eu^{2+}, and Mn^{2+} magnetic impurities, reveal significant differences from the experimental results. Nevertheless, satisfactory agreement has been found for the temperature dependence of the effective anisotropy fields.[3–6]

One reason for such discrepancies may arise from use of the lattice parameters without accounting for the distortions of the host lattice by the impurity ions. Also, some questions arise concerning the validity of the application of the single-ion model, which is based not only on quantum-mechanical calculations, but also on mean-field theory.[7,8]

In Ref. 9 the first papers are mentioned, which have been tried to explain the existing theory and experimental results in the framework of pair model. The exploration of the copper ions pair interactions in $\mathrm{Cu(CH_3COO)_2H_2O}$ crystals (Ref. 9 and references therein) revealed the existence of an exchange anisotropy. However, the available computation data for the pair spin-Hamiltonian anisotropic exchange parameter[9] $D^{ex}=(1/8)J[(1/4)(g_z-2)^2-(g_\perp-2)^2]$ (used the experimental g values, isotropic exchange parameter J, and dipole-dipole interactions D_{dip}) were almost twice differed from the experimental ones.

Later experimental investigations[10] were performed for the compound-containing *S*-state ions. The study[10] deals with Fe-Y garnets with Ga and reveals the effect of the exchange field on the spin-Hamiltonian parameters. The model,[11] unlike that presented in Ref. 12, adopts the pair-exchange interaction dependent on the admixing of exited-ion states (at that different spin values were examined in the ground and exited states). The theoretical treatment[11] has been carried out by using the perturbation theory method. The crystal field was used as the zeroth-order approximation in this case, and the isotropic spin-orbit coupling and isotropic exchange interaction were considered as perturbation terms. Under this condition the magnetic anisotropy arises in the third order of perturbation theory, and the matrix elements depend linearly and to the second degree on the exchange and spin-orbit coupling energy, respectively.

The important result of the study described in Ref. 11 is the derivation of the "single-ion" exchange anisotropy. The appearance of such anisotropy may be explained[11] from the physical point of view by the following reasoning. The admixture of exited states to the ground state results in changing the spin and orbital moment values of the individual cation. As a result, there is a modification of the spherical configuration of the electron "cloud" of the *S*-state ion and, as a consequence, to the dependence of the ion energy on the spin orientation. Such a mechanism gives rise to the "single-ion" exchange anisotropy, which operator form coincides with the ordinary single-ion anisotropy one.[11,13] The studies[4,5] present the model based on the Kramers-Anderson superexchange mechanism.[8] This model leads to anisotropic exchange and "single-ion" anisotropy appearance governed by the crystal field.

For a series of magnetically concentrated crystals FeBO_3, MnCO_3, and α-$\mathrm{Fe}_2\mathrm{O}_3$,[4,5] a linear dependence has been found for $\Delta H_A = H_A - (H_{Adip} + H_{Acf})$ vs H_E at $T=0$ K. Here H_A is the experimental uniaxial anisotropy field, H_{Adip} is the calculated dipole anisotropy field, H_{Acf} is the single-ion anisotropy field determined from EPR data for the single ions in isostructural diamagnetic materials, and H_E is the experimentally measured exchange field. Let us note that $H_A(T)$ is satisfactorily described by both the single-ion and dipole anisotropy for these crystals.[4,5,14] These facts witness the existence of the "single-ion" exchange anisotropy contributions.[4,5]

The above-mentioned papers allow an advance in understanding of the anisotropy nature of the magnetically ordered crystals containing S-state ions. However, a number of aspects are still not understood such as the following.

(i) How much is the single-ion anisotropy theory valid for magnetically concentrated crystals?

(ii) Are there more reliable methods for estimation of the "single-ion" anisotropy contributions for such crystals?

(iii) What are the main sources of anisotropy for the hematite, ferric borate, and manganese carbonate crystals?

In this paper we present the results of an experimental EPR pair spectra investigation of $M\text{BO}_3\text{:Fe}^{3+}$ single crystals. The results have been used for quantitative estimations of the "single-ion" anisotropy of the exchange nature in FeBO_3, MnCO_3, and $\alpha\text{-Fe}_2\text{O}_3$.

The spin Hamiltonian (SH) for $M\text{BO}_3\text{:Fe}^{3+}$ (M $=\text{Ga},\text{In},\text{Lu},\text{Sc}$) is given by[11,15–21]

$$\mathcal{H} = g\beta H(s_{z1} + s_{z2}) + J\boldsymbol{s}_1\boldsymbol{s}_2 + D_{dip}[3s_{z1}s_{z2} - (\boldsymbol{s}_1\boldsymbol{s}_2)] + (D_c/3) \times[O_{21}^0 + O_{22}^0] - (1/180)(a-F)_c[O_{41}^0 + O_{42}^0], \qquad (1)$$

where g is the g factor, β the Bohr magneton, H an external magnetic field ($\boldsymbol{H}\parallel C_3$), $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$ the spin operator for Fe^{3+} ions at sites 1 and 2, s_{z1} and s_{z2} the projection of $\boldsymbol{s}_1$ and $\boldsymbol{s}_2$ onto the C_3 axis; J the exchange constant, D_{dip} $=(g^2\beta^2/2r_{12}{}^3)(1-3\cos^2\theta_{12})$ the dipole-dipole interaction parameter for the pair, r_{12} the distance between paired ions; θ_{12} the angle between the C_3 axis and $\boldsymbol{r}_{12}$, and D_c and $(a\text{-}F)_c$ the parameters of the equivalent spin operators O_{2i}^0 and O_{4i}^0, respectively ($i=1,2$).

It is assumed that the Heisenberg exchange interaction $J\boldsymbol{s}_1\cdot\boldsymbol{s}_2$ is much stronger than the other terms of Eq. (1) whereas the Zeeman energy exceeds that due to the anisotropic terms. Here omitted terms do not give the contribution in the first order of the perturbation theory.

In accordance with Refs. 15 and 22–24, the SH for two exchange-coupled ions can be presented in terms of the total spin $\boldsymbol{S}=\boldsymbol{s}_1+\boldsymbol{s}_2$ if the exchange interaction is much stronger than the effects of the other terms in the SH. So the SH (1) may be reduced in the case of the strong isotropic exchange interaction, which leads to six states with total spin $\boldsymbol{S}$.[15,16,23] The energy levels for each state and may be written[23] as

$$E_S = (J/2)[S(S+1) - s_1(s_1+1) - s_2(s_2+1)],$$

where the possible values of the total spin $S=s_1+s_2$, $s_1+s_2-1,\ldots,s_1-s_2$; $s_1=s_2=5/2$. In this case[15,16,18,23] we may write down the SH for the each possible value of the total spin:

$$\mathcal{H} = g\beta H S_z + (D_S/3)O_2^0(S_z) - (1/180)(a-F)_{cS}\gamma_S O_4^0(S_z). \qquad (2)$$

Here the total spin moment quantization axis coincides with the direction of the external magnetic field parallel to the C_3 axis, so that the matrix elements of the $B_4{}^3O_4{}^3$ type do not contribute to the energy states in the first order of the perturbation theory; $D_S=3\alpha_S D_{dip}+\beta_S D_{cS}$; $\alpha_S=(1/2)[S(S+1)+4s_1(s_1+1)]/(2S-1)(2S+3)$, $\beta_S=[3S(S+1)-3-4s_1(s_1+1)]/(2S-1)(2S+3)$, and γ_S are nonlinear functions of S mentioned in Refs. 15 and 16, respectively. In accordance with Refs. 15 and 16, α_S, β_S, and γ_S are the coefficients attached to D_{dip}, D_{cS}, and $(a\text{-}F)_{cS}$, respectively. The pseudodipole parameter attached to the α_S is neglected here due to its small value [as one can see from our experimental data (see below)].

Let us introduce the notion of the multiplet exchange field arising due to pair interactions, with absolute value

$$|\boldsymbol{H}^{ex}| = (1/g\beta)[\partial E_S/|\partial \boldsymbol{S}|] = (J/g\beta)\sqrt{S(S+1)}. \qquad (3)$$

As long as the energy of every multiplet depends on the S value,[15] so the SH constant D_{cS} may be than written as

$$D_{cS} = D_{cf} + D_{c0} + A\sqrt{S(S+1)}. \qquad (4)$$

The first term represents the zero-field-splitting (ZFS) contribution D_{cf}. The second one arises from the parent lattice distortion caused by the "stranger pair," and the third term describes "single-ion" anisotropic exchange.[11] Since the third term in Eq. (4) is governed by the anisotropic exchange interaction, it must include the isotropic exchange part in common case.[9,25] So, under the consideration of the pair interactions in the diamagnetic crystals with Fe^{3+} impurities, the third term in Eq. (4) is linearly dependent on the isotropic exchange field—i.e., on the total spin value S as $\sqrt{S(S+1)}$. Such a type of dependence is observed experimentally the compounds for explored here and, for example, for MgO:Mn^{2+}, CaO:Mn^{2+} (Ref. 23), and $(\text{CH}_3)_4\text{NCdCl}_3\text{:Mn}^{2+}$ (Ref. 22) with well-interpreted pair spectra.

In a similar manner, we assume the dependence on S for the SH parameter $(a\text{-}F)_{cS}$ to have the form

$$(a-F)_{cS} = (a-F)_{cf} + (a-F)_{c0} + BS(S+1). \qquad (5)$$

All terms in Eq. (5) have the same physical meaning respectively as in Eq. (4).

II. EXPERIMENTAL RESULTS AND DISCUSSION

The crystals $M\text{BO}_3\text{:Fe}^{3+}$ were grown from the system $M_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-B}_2\text{O}_3\text{-(70 PbO-30 PbF}_2\text{ wt \%)}$ by the flux method. The compound Fe_2O_3 was added as an impurity, with volume about 5–10 wt %. A similar growth technology for $M\text{BO}_3$ ($M=\text{Ga},\text{In},\text{Lu},\text{Sc}$) crystals is described elsewhere.[26,27]

The EPR spectrometer RE-1308 operating at the Q band was used to record the Fe^{3+} pair spectra in $M\text{BO}_3$ (M $=\text{Ga},\text{In},\text{Lu},\text{Sc}$) at room temperature. The external magnetic field coincided with the C_3 axis for $M\text{BO}_3\text{:Fe}^{3+}$ and was

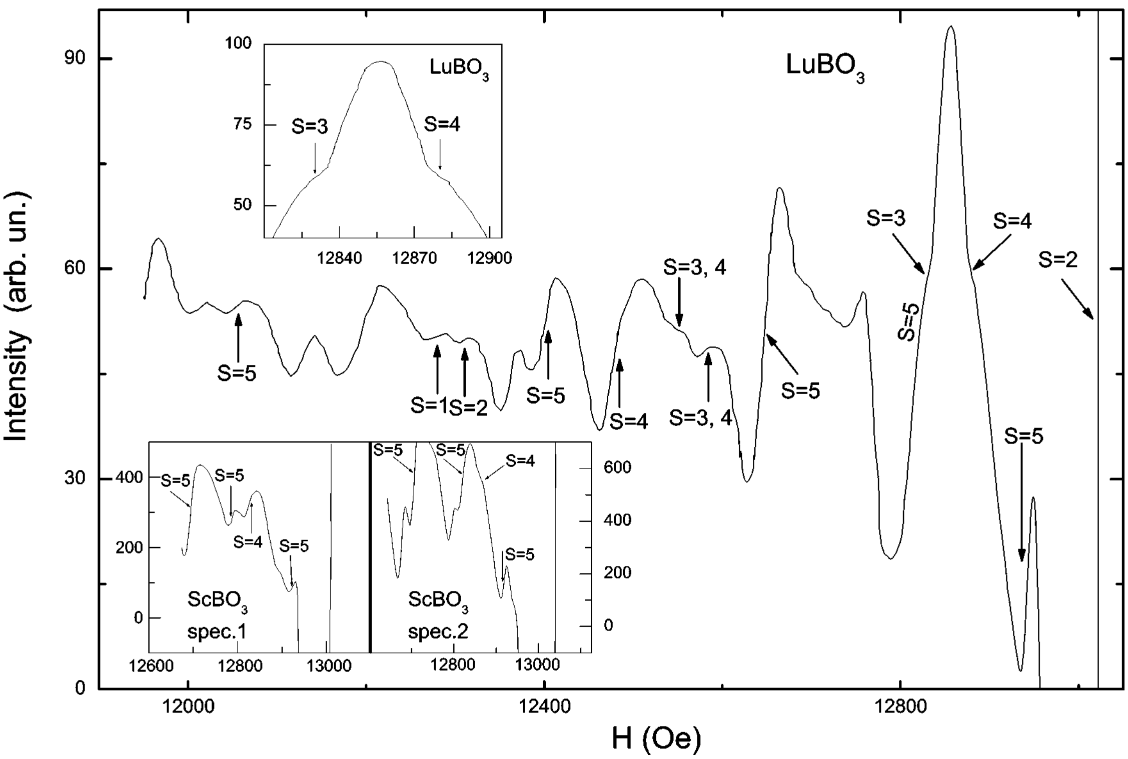

FIG. 1. EPR spectrum of the antiferromagnetic Fe^{3+} pair in $LuBO_3$ crystals at the *Q* band and room temperature.

measured with an accuracy not less than 10 Oe.

The fine structure of the Fe^{3+} pair EPR spectra has not been discussed in the literature earlier.

The records of the low-field part of the EPR spectra for $MBO_3{:}Fe^{3+}$ (from two to five samples with approximately the same weight for each composition have been used) reveal the following.

(i) For $GaBO_3{:}Fe^{3+}$, approximately 25 pair lines were obtained with the central single-ion fine-structure linewidth (corresponds to the $1/2 \leftrightarrow -1/2$ transition) more than 100 Oe.

(ii) For $LuBO_3{:}Fe^{3+}$ approximately 23–30 pair lines were obtained with the minimal central fine-structure linewidth of about 28 Oe.

(iii) For $ScBO_3{:}Fe^{3+}$ approximately 35–50 pair lines were obtained with the central fine-structure linewidth varying from 31 to 32 Oe.

(iv) For $InBO_3{:}Fe^{3+}$ approximately 16–28 pair lines were obtained with the central fine-structure linewidth less than for $GaBO_3{:}Fe^{3+}$ but greater than for $ScBO_3{:}Fe^{3+}$.

The conclusion we made from these results are that (a) the observed resonance lines belong to at least three types of pairs (possibly not for all samples) and (b) some lines may be absent or have a low intensity for some reasons. The inset in Fig. 1 has been made to confirm the last conclusion. Samples 1 and 2 ($ScBO_3{:}Fe^{3+}$) with weights 0.65 and 0.70 mg, respectively, and equal central single-ion fine-structure resonance linewidth reveal pair spectra with corresponding pair resonance line intensities markedly different from each other.

A specially designated computer program was used. At definite orientation of the external magnetic field, the resonance fields for every given S will depend on the g value and SH constants D_S and $(a-F)_{cS}$. The corresponding equations for the resonance fields for $S=3,4,5$ were solved by a least-squares method. All possible combinations of the equations were solved for every S and corresponding magnetic quantum numbers. For the case when the pair resonance lines coincide with the single-ion fine-structure ones, the resonance field for these pair lines was assumed a number of values in the range of the fine-structure linewidth with equal probabilities. The following factors were taking into account for choosing of the optimal equation solving: the minimal χ^2 value, coincidences of the theoretical and experimental line intensities, and the monotonous dependence of the SH constants on S. After the optimal choice had been made for every S (3, 4, 5), the values of D_S and $(a-F)_{cS}$ were extracted analytically by utilizing the fitting parameters. Then we were able to compute the resonance fields for $S=1,2$ using the obtained D_S and $(a-F)_{cS}$ values. If the calculated lines were observed in the recorded spectra, then the interpretation was considered as complete.

In order to check the obtained values, two compounds were chosen: $LuBO_3{:}Fe^{3+}$ and $GaBO_3{:}Fe^{3+}$, for which SH parameters may be calculated by another independent method. The first compound must have a weak exchange interaction, due to the symmetry and lattice parameters (see Fig. 6) [at $(c_H/a_H) \approx 3.3$ the exchange field is approximately equal to zero]. So, in Eq. (4), the A parameter for $LuBO_3{:}Fe^{3+}$ was assumed equal to zero. The parameter D_{dip} may be calculated, and the value of the ZFS parameter D_{cf} is mentioned in Ref. 17, so the value of D_{c0} may be estimated from our data to be about $D_{c0}=-660$ Oe. From the other side, D_{c0} value is mentioned in Ref. 28 as $D_{c0}=\Delta D_{cf}/$

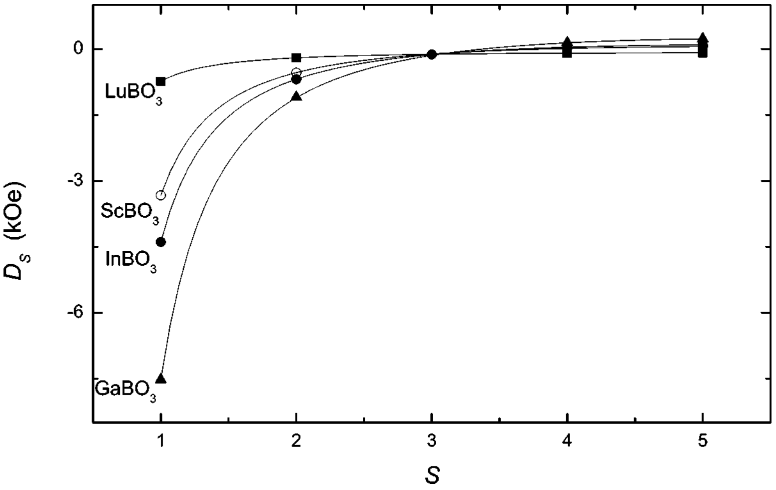

FIG. 2. The uniaxial second-order spin-Hamiltonian parameter D_S for the Fe^{3+} pair in MBO$_3$ vs S dependence.

$\Delta(c_H/a_H)]\times 0.169=-2600\times 0.169$ Oe$=-440$ Oe. The factor 0.169 is the difference between the lattice parameters c_H/a_H for LuBO$_3$ and FeBO$_3$.

The $GaBO_3:Fe^{3+}$ compound has approximately the same lattice constants as for FeBO$_3$ and therefore should have close values for the pair and single-ion interactions therein. So, in Eq. (4), for $GaBO_3:Fe^{3+}$ the A value, calculated from our data, is equal to $A=-102$ Oe (Fig. 4). The A value, obtained from independent data, was estimated as $A=-84$ Oe.[4,5,29–31]

An example of the interpreted spectrum for the antiferromagnetic pair in LuBO$_3$ crystal is shown in Fig. 1. One can see that the pair line for $S=2$ coincides with the central fine-structure line. It is noticeable that some pairs of lines for $S=3,4$ coincide too.

Partial coincidence of the pair lines with each other or single-ion lines turns out to be a typical feature for all explored crystals. Note that such coincidence and relatively low intensity of some lines is typical for the pair Mn^{2+} spectrum—for example, Refs. 22, 23, 32, and 33.

The experimental results for SH constant D_S and $(a-f)_{cs}$ in $MBO_3:Fe^{3+}$ single crystals are presented as a plot in Figs. 2 and 3, respectively. Some fitting parameters, obtained from our experimental data—namely, D_{c0}, D_{dip}, $(a-F)_{c0}$, and calculated $D_{dip\ calc}$—are presented in Table I for the $MBO_3:Fe^{3+}$ compound.

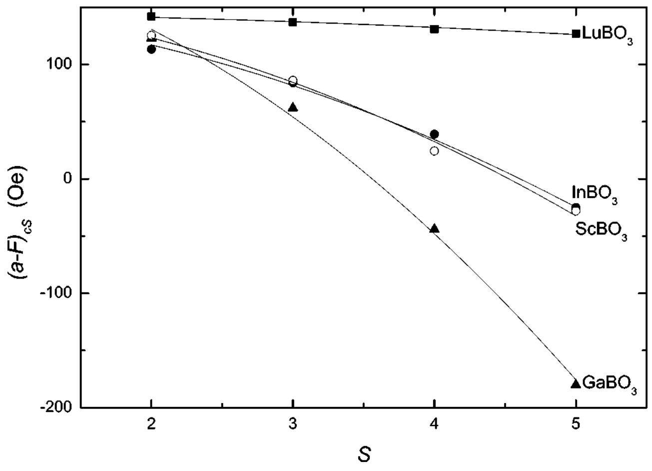

FIG. 3. The uniaxial fourth-order spin-Hamiltonian parameter $(a-F)_{cS}$ for the Fe^{3+} pair in MBO$_3$ vs S dependence.

Figure 4 presents the linear dependence of the parameter A versus the hexagonal lattice ratio c_H/a_H of MBO$_3$ crystals. The arrows indicate A values corresponding to FeBO$_3$ and MnCO$_3$ compounds.

The dependence of the parameter B on the hexagonal lattice ratio c_H/a_H of MBO$_3$ compounds is presented in Fig. 5. From Figs. 2–5, one can see that the pair exchange field for $LuBO_3:Fe^{3+}$ is about zero, in contradiction with other compounds. It is in agreement with Refs. 4 and 5.

To establish the correlation between presentation exchange-coupled pairs in "magnetically concentrated" and diamagnetic crystals, we performed the next computations. Let us write down the exchange energy for the ith ion in magnetically concentrated crystal at $T=0$ K as $E(T=0\text{ K})=-nJS_iS_j$, where n is the nearest-neighbor number. Assuming $n=n_0=1$ and

$$E(T=0,n_0)=E_{S\ mc}, \tag{6}$$

we define the pair effective spin value S_{n0} for paramagnetic impurity in diamagnetic substance. It will corresponds to the ith ion ground-state energy $E(T=0)$ in "magnetically concentrated" crystal at a given n. [For Eq. (6) and below the lower index "mc" (magnetically concentrated) indicates the coincidence of the unit cell parameters of the magnetically concentrated and diamagnetic compounds.] Solution of Eq. (6) for

TABLE I. Experimentally determined $(D_{c0}, D_{dip}, (a-F)_{c0})$ and calculated $(D_{dip\ calc})$ spin-Hamiltonian parameters for $MBO_3:Fe^{3+}$ compound.

$MBO_3:Fe^{3+}$	$D_{dip\ calc}$ (Oe)	D_{dip} (Oe)	D_{c0} (Oe)	$(a-F)_{c0}$ (Oe)
$GaBO_3:Fe^{3+}$	−70.3	−71.0	116.0	−6
$InBO_3:Fe^{3+}$	−65.1	−70.0	−124.0	24.0
$ScBO_3:Fe^{3+}$	−68.5	−68.0	−321.0	28.0
$LuBO_3:Fe^{3+}$	−65.8	−78.0	−593.0	29.5
FeBO$_3$	−71.0	—	0	0

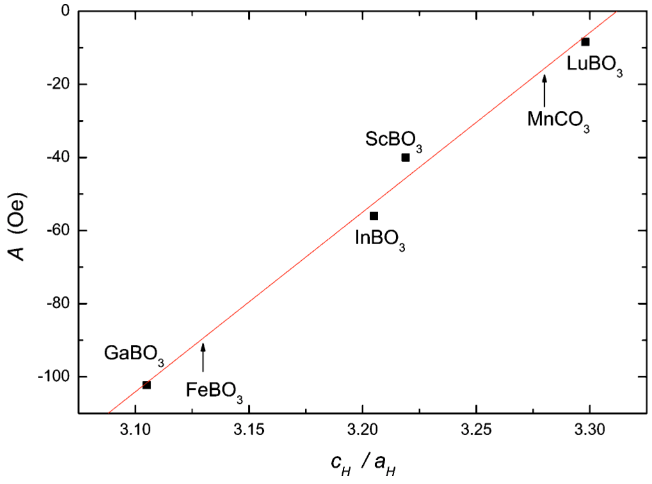

FIG. 4. Fitting parameter A for $M\mathrm{BO}_3:\mathrm{Fe}^{3+}$ vs hexagonal lattice ratio c_H/a_H. Arrows denote A for FeBO_3 and MnCO_3 crystals.

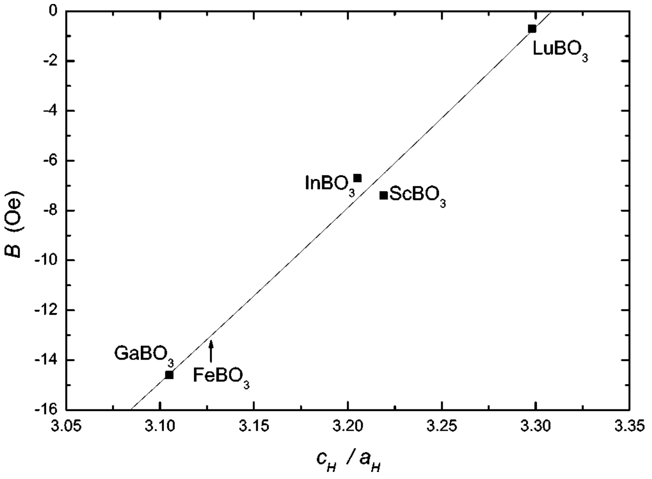

FIG. 5. Fitting parameter B for $M\mathrm{BO}_3:\mathrm{Fe}^{3+}$ vs hexagonal lattice ratio c_H/a_H. Arrows denote B for FeBO_3 crystal.

$s_i=s_j=5/2$ is $S_{n0}=1.8$. Then, taking a sum over all neighbors of the ith ion in the left part of Eq. (6), one can find the exchange energy for the ith ion in a magnetically concentrated crystal at $T=0$ K to be

$$E(T=0) = nE_{S\ mc}(S_{n0}). \tag{7}$$

The right part of Eq. (7) represents the energy of n paramagnetic pairs in a diamagnetic crystal.

Taking into account Eqs. (4) and (5) and derived from Figs. 4 and 5 values of the A_{mc} and B_{mc} parameters, the values of the SH (2) parameters, responsible for the "single-ion" anisotropy of the ith ion in magnetically concentrated crystal, are equal to

$$D_{mc} = D_{cfmc} + 2.25nA_{mc}, \tag{8}$$

$$(a-F)_{mc} = (a-F)_{cfmc} + 5.04nB_{mc}. \tag{9}$$

The parameters D_{mc} and $(a\text{-}F)_{mc}$ involve not only the well-known single-ion terms D_{cfmc} and $(a\text{-}F)_{cfmc}$ but the exchange correction terms also. The single-ion expressions at $T=0$ K well known in the literature can be used to write down the effective anisotropy field with exchange correction terms for the rhombohedral antiferromagnetic crystals.[29] In accordance with Eqs. (8) and (9) and Ref. 29 "single-ion" contributions to the uniaxial anisotropy field (for second and fourth orders of magnitude, respectively) at $T=0$ K may be written as follows:

$$H_{Amc}(0) = 2(S_i - 1/2)\{D_{cfmc} + 2.25nA_{mc} + (1/6)(S_i-1)(S_i - 3/2)[(a-F)_{cfmc} + 5.04nB_{mc}]\}, \tag{10}$$

$$H_{cmc}(0) = -(7/18)(S_i - 1/2)(S_i - 1)(S_i - 3/2)[(a-F)_{cfmc} + 5.04nB_{mc}]. \tag{11}$$

The dependence of the "single-ion" anisotropy field H^{ex}_{Amc} defined by the exchange correction terms (A_{mc}, B_{mc}) on hexagonal cell parameters c_H/a_H for FeBO_3, MnCO_3, and α-$\mathrm{Fe}_2\mathrm{O}_3$ at $T=0$ K is presented in Fig. 6 (open circles). The parameters A_{mc} and B_{mc} (used for MnCO_3 and α-$\mathrm{Fe}_2\mathrm{O}_3$) have been determined from the same dependence for the $M\mathrm{BO}_3:\mathrm{Fe}^{3+}$ system. The SH parameters for Fe^{3+} and Mn^{2+} single ions have been determined from the similar dependence for $M\mathrm{BO}_3$, $\mathrm{Al}_2\mathrm{O}_3$, and $M\mathrm{CO}_3$ $(M=\mathrm{Ca},\mathrm{Cd},\mathrm{Mg},\mathrm{Zn})$, respectively, and are presented in Ref. 4. The deviations of the theoretical values of the single-ion and dipole-dipole anisotropy ΔH_A (determined above) from the experimental ones are shown by the solid circles in Fig. 6. The experimental data for the exchange fields are denoted by the squares in Fig. 6. From this figure one can see (taking into consideration the "single-ion" exchange anisotropy besides of the rest of the usual terms) that the results in good agreement with the experimental data.

Thus, the dipole and "single-ion" mechanisms may be considered as the main ones responsible for the anisotropy in the considered crystals.

The estimation for the anisotropy field value $H_{cmc}(0)$ in a magnetically concentrated crystal of hematite gives 980 Oe, while the experimental value $H_c(0)=-60$ Oe.[14] The origin of such a discrepancy may be caused by neglect of the fourth-order terms of the anisotropic exchange, which are calculated in general form in Refs. 11 and 13. These terms may be significant for hematite (due to a large exchange field), in contrast to all the crystals explored in this papers.

III. CONCLUSIONS

Below, answers are given for the questions listed in the Introduction.

(i) The single-ion theory describes the experimental results with sufficient accuracy.

(ii) The methods presented here to explore "single-ion" exchange anisotropy are the only up-to-date ones allowing its quantity evaluation for magnetically concentrated crystals. These methods may be extended to magnetic dielectrics with S-state ions.

(iii) The dipole and "single-ion" mechanisms may be considered as the main ones responsible for the anisotropy in α-$\mathrm{Fe}_2\mathrm{O}_3$, FeBO_3, and MnCO_3.

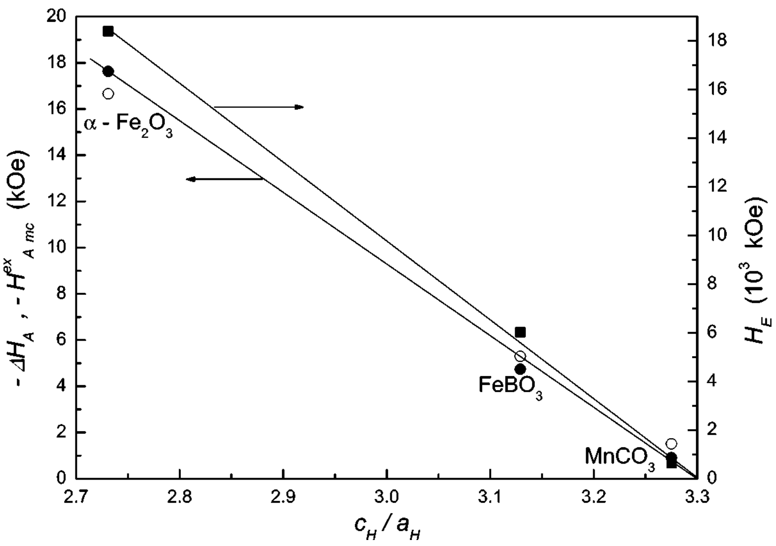

FIG. 6. Exchange fields (H_E) (squares) and deviations of the theoretically calculated contributions from single-ion and dipole-dipole interactions from the experimental data (ΔH_A) (solid circles) for $MnCO_3$, $FeBO_3$, and α-Fe_2O_3 vs hexagonal lattice ratio c_H/a_H $T=0$. Open circles: "single-ion" field contributions defined by the exchange corrections (H^{ex}_{Amc}).

To our mind, satisfactory accuracy has been reached for our EPR experimental results presented in this paper. However, in to evaluate the exchange corrections the exchange interaction was written in terms of the "mean-field approximation" for isolated pairs of ions. Such expressions to some extent take into account the correlation effects, in contrast with the "ordinary" mean-field approximation.

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*Electronic address: sasa@iph.krasn.ru

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