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The generalized method of quantitative description of the uniaxial anisotropy in weak ferromagnet rhombohedral calcite type structure crystals with S-state ions

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ABSTRACT

The method for investigation of the uniaxial and hexagonal anisotropies in weakly ferromagnetic rhombohedral FeBO_3 crystals with the Fe^{2+} magnetic impurity with the use of the single-ion and pair approximation has been developed. In the framework of this method, a quantitative discrepancy between theoretical and experimental data on a uniaxial field has been eliminated. The energy contributions to the hexagonal anisotropy that are caused by the Dzyaloshinsky–Moriya interaction, the crystal field of Fe^{3+} ions and the temperature dependence of this anisotropy were analytically treated. The experimental temperature dependence of the hexagonal anisotropy of FeBO_3 crystals is explained. It is shown that the compensation point and the typical temperature dependence of the hexagonal anisotropy result from the competition of the contributions of Fe^{3+} and Fe^{2+} ions. It is shown that respective considerable contributions to the anisotropy of Fe^{3+} and Fe^{2+} ions are made by the cubic symmetry and the uniaxial symmetry of the exchange “single-ion” type. The anisotropy constants for FeBO_3 crystal was obtained by using the described results. It was shown, that for the calcite type structure crystals (iron borate and manganese carbonate) with S-state ions, the single ion and pair models (which previously raised doubts in their validity and accuracy) describe the experimental data good enough.

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1. Introduction

The FeBO_3 and MnCO_3 compounds are rhombohedral antiferromagnets ($T_N=348$ and 32.5 K, respectively). The Fe^{3+} and Mn^{2+} ions have five 3d electrons in the S-state with the spin $s=5/2$. To solve the problem on the magnetic anisotropy of magnets with a S-ion [1], it is convenient to investigate FeBO_3 and MnCO_3 crystals due to simplicity of their magnetic structure and narrowness of antiferromagnetic and the electron paramagnetic resonance (EPR) lines. There also exists a series of isostructural diamagnetic crystals, which allow accurate quantitative estimation of the spin-Hamiltonian constants corresponding to the single-ion [2] and “single-ion” exchange terms [1] using the electron paramagnetic resonance (EPR).

Several decades ago, methodical study of the magnetic anisotropy stopped at the single-ion model and there was no progress in its studies for a long time. The significant discrepancies between the experimental data and calculations based on this model raised doubt on its validity. Only with the appearance of

theoretical publication [3] which describes the calculations based on the two-ions model (work also for a long time has not been noticed by the experimenters), the investigations (consider both models) were resumed with the application of the EPR method [1,2]. These investigations revealed that there are quantitative discrepancies about $1.5\text{--}4.5 \times 10^7$ erg/mol for some rhombohedral crystals (hematite, iron borate). However, anisotropy calculation for MnCO_3 gives good agreement with experimental data (see Table 1). For FeBO_3 crystals such agreement looks problematic evidently due to the presence of the impurities. So, some questions arise as follows. (1) At what level the agreement between the experiment and calculation will be reached for the iron borate at the impurity problem solution and is the generalization with MnCO_3 possible and as a consequence: (2) to what extend the single ion and two-ions models (see below) are applicable for the quantitative description of the magnetic anisotropy, (3) so far as these models are based on the molecular field theory, how accurate is it for the description of the experimental data of these compounds, (4) Since the results of the calculation includes the contribution of the dipole interaction, so how adequate the dipole interaction describes the anisotropy of the magnets.

The final answer to these questions provides the investigations performed on the basis of the developed quantitative method.

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Table 1

Contributions to the uniaxial anisotropy constant at $T=0$ K. $\omega_{A_{\text{dip}}}$ —dipole (calculation) [4], $\omega_{A_{\text{fmc}}}$ —single-ion and $\omega_{A_{\text{mc}}}^{\text{ex}}$ —“single-ion” exchange from EPR data [1,2]. $a_{A_T} = \omega_{A_{\text{fmc}}} + \omega_{A_{\text{mc}}}^{\text{ex}} + \omega_{A_{\text{dip}}}$ and $a(\text{Fe}^{3+})$, $a(\text{MnCO}_3)$ —theoretical and experimental values of the uniaxial anisotropy constant, respectively. $a(\text{MnCO}_3)$ value is obtained from the fitting theoretical curve with AFMR data, [34] manganese carbonate and from FeBO_3 [19] (corrected by the residue of the Fe^{2+} impurity ions contribution).

10^7 (erg/mol)	$\omega_{A_{\text{fmc}}}$	$\omega_{A_{\text{mc}}}^{\text{ex}}$	$\omega_{A_{\text{dip}}}$	a_{A_T}	$a(\text{Fe}^{3+})$, $a(\text{MnCO}_3)$
FeBO_3	11.79	−14.70	10.25	7.34	6.16
MnCO_3 [35]	0.25	−2.91	10.70	8.04	8.43

The method includes (1) Simulations of the anisotropy constants for the pure crystals, (2) simulations of the influence of the impurities on the magnetic anisotropy, (3) simulation of the contribution of the dipole interactions to the uniaxial anisotropy of the FeBO_3 and MnCO_3 crystals [4], (4) estimation of the single ion contribution to the anisotropy by using of the EPR method for the series of the isostructural diamagnetic crystals [2], and (5) estimation of the “single-ion” exchange contribution to the uniaxial anisotropy by using of the EPR pair spectra for the series of the isostructural diamagnetic crystals with the magnetic impurities [1].

Let us point out that the estimation of the pair spin-Hamiltonian constants in [1] has been made roughly, so in Chapter 56 we gave a refined experimental data of the paper [1] and adequate theoretical treatment (Chapter 45) for FeBO_3 and MnCO_3 .

Physically, the occurrence of the pair model (with accounting “single-ion” exchange anisotropy only) can be explained as follows. An admixture of excited states to the ground state and the covalence effect change the values of the spin and orbital moments of a cation. This results in modification of the spherical configuration of an electron cloud of an ion in the S -state and, as a consequence, in the occurrence of the dependence of the ion energy on the spin orientation. Such a mechanism gives rise to the “single-ion” exchange anisotropy whose operator form (written in terms of the total spin $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$) coincides with an ordinary single-ion anisotropy one. The mechanism of the “single-ion” exchange anisotropy is also described in [5].

For a complete and accurate solution to the problem it is theoretically necessary to investigate the following questions in these crystals.

The temperature dependence of the hexagonal anisotropy of iron borate and hematite crystals available in the literature [6–9] remains understudied. There is also some quantitative disagreement between the theoretical and experimental data on the uniaxial anisotropy of FeBO_3 crystals [1]. The existence of a compensation point of the hexagonal anisotropy FeBO_3 , different anisotropy values for different samples, and the significant growth in the low-temperature region indicate the presence of impurities [6–8]. Hence, we should clarify the effect of the host and impurity magnetic subsystems on uniaxial and hexagonal anisotropy of FeBO_3 . We need to derive the single ion and pair spin-Hamiltonian constants dependencies on the lattice constants for the diamagnetic analogs in order to determine of the uniaxial anisotropy constants in magnetically concentrated crystals. However, not a complete set of the experimental values of the constants of spin-Hamiltonians for the diamagnetic analogs does not allow performing a generalization for the hexagonal anisotropy for FeBO_3 and MnCO_3 crystals. Note, that large numbers of the fitting parameters force us in order to improve the accuracy to use simultaneously two experimental curves (uniaxial and hexagonal) during the fitting procedure. Moreover, the values of the these parameters determined from the EPR data were used as the starting values of the fitting procedure.

1.1. Magnetic anisotropy of pure FeBO_3 crystals. Phenomenological description

The thermodynamic potential [10,11] for the FeBO_3 crystal can be written as

$$\Phi = (1/2)Bm^2 + (1/2)acos^2\theta - dsin\theta(m_y\cos\varphi - m_x\sin\varphi) + q\sin^3\theta\cos\theta\cos 3\varphi + e\sin^6\theta\cos 6\varphi + tm_z\sin^3\theta\sin 3\varphi \quad (1)$$

where the first, second, and third terms are the exchange interaction, uniaxial anisotropy, and Dzyaloshinsky interaction, respectively [12,13]. The last three terms correspond to the hexagonal anisotropy in the basal plane of the crystal. Below, we omit the six-order invariant at constant e in this equation, since for $3d$ ions this invariant is zero [6]. The last term in (1) can be neglected due to smallness of m_z . In Eq. (1), $m = (M_1 + M_2)/M$ is the ferromagnetic vector; M_1 and M_2 are the sublattice magnetizations of a Fe^{3+} ion, $M = 2|M_1| = 2|M_2|$; and θ and φ are the polar and azimuth angles of the antiferromagnetic vector $l = (M_1 - M_2)/M$.

Minimization of Φ yields the effective hexagonal anisotropy

$$\omega_q(\text{Fe}^{3+})\cos 6\varphi = -\frac{q^2}{4[a + (d^2/B)]}\cos 6\varphi.$$

2. Hexagonal anisotropy of pure FeBO_3 single crystals. Microscopic consideration

To determine the value of $\omega_q(\text{Fe}^{3+})\cos 6\varphi$, one should know the temperature dependence and, at least, some contributions of different mechanisms to the hexagonal anisotropy that were determined by independent methods. The effect of the cubic crystal field (single-ion contribution) on the basal anisotropy of FeBO_3 caused by Fe^{3+} ions was considered in [7]. There are no experimental data on the “single-ion” exchange anisotropy of the cubic symmetry in the literature. However, as is known, the contribution of the uniaxial “single-ion” exchange anisotropy can exceed the single-ion anisotropy [1].

In addition, the considerable contribution of Fe^{3+} ions to the basal anisotropy that is determined by the crystal field and the Dzyaloshinsky–Moriya interaction with unknown temperature dependence can exist.

Fig. 1 shows a subimage of the two positions of Fe^{3+} ions in the iron borate unit cell. In the calculation, it is convenient to use the $x'y'z'$ coordinate system ($X \rightarrow x', Y \rightarrow -y', Z \rightarrow z'$) with the origin at position 1 of a Fe^{3+} ion. Positions 1 and 2 are nonequivalent. This is related to different orientations of the BO_3^{3-} groups in the plane normal to the C_3 axis of the crystal. The BO_3^{3-} groups are shown by dark and light triangles.

Mutually perpendicular cubic axes ξ_j , η_j , and ζ_j are shown by arrows. The solid and dotted arrows are directed upwards and downwards the figure plane, respectively. The angles between the projections of the ξ_1 , η_1 , ζ_1 and ξ_2 , η_2 , ζ_2 axes onto the (111) plane and the crystal axis are $\alpha_1 = -\alpha$ and $\alpha_2 = \alpha$, respectively; $j = 1$ and 2 correspond to positions 1 and 2. The axial components of the crystal field for the both complexes are parallel to the C_3 -axis of the crystal. This orientation of the axes in the crystals with the calcite structure was confirmed by the EPR data [2].

The spin-Hamiltonian (SH) can be written as

$$\hat{H} = \sum_j \left\{ g\beta H_j^{\text{eff}} s_j + \frac{D_{\text{cf}}}{3} O_{2j}^0 + \frac{F_{\text{cf}}}{180} O_{4j}^0 - \frac{a_{\text{cf}}}{180} [O_{4j}^0 - 20\sqrt{2}(O_{4j}^3 \cos 3\alpha_j - \tilde{O}_{4j}^3 \sin 3\alpha_j)] \right\} + d_M(s_{x_1}s_{y_2} - s_{y_1}s_{x_2}) \quad (2)$$

where $g\beta H_j^{\text{eff}} s_j$ is the isotropic exchange in the molecular field approximation, g is the Lande factor, β is the Bohr magneton, s_j is

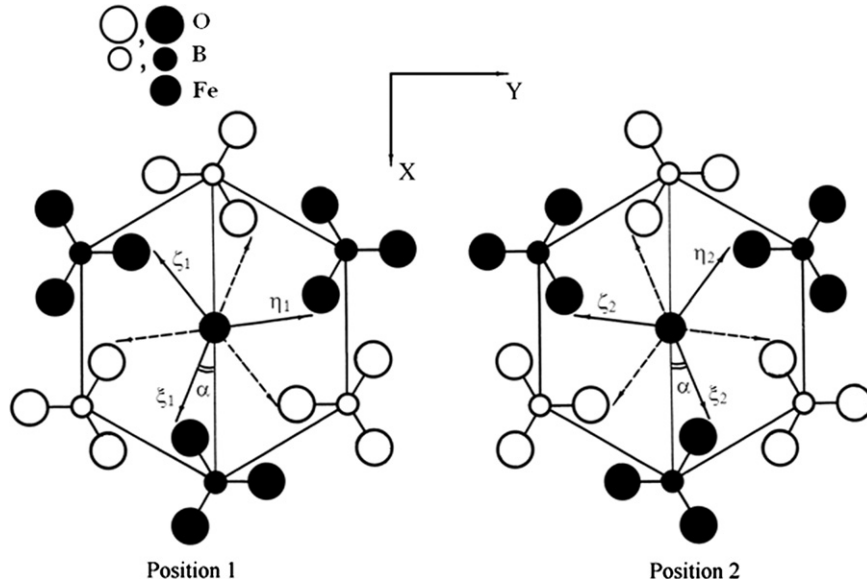


Fig. 1. Distribution of axes of the cubic crystal field for two nonequivalent positions of Fe³⁺ ions in the FeBO₃ lattice.

the ion spin in the positions $j=1$ and 2 , the second and third terms in parenthesis correspond to the single-ion uniaxial energy, the fourth term corresponds to the cubic crystal field, d_M is the Dzyaloshinsky–Moriya constant. For simplicity, we omitted indexes of the coordinate system.

The isotropic exchange term can be transformed to the diagonal form by rotation of the initial $x_j y_j z_j$ coordinate system by angles θ_j and φ_j . In the $x_1 y_1 z_1$ coordinate system, the orientation of the quantization axis for energy (2) is determined by angles θ_1 and φ_1 and s_{z_1} is directed along the z_1 -axis.

After this transformation, we retain expression (3), since the calculation of the matrix elements indicates that only Hamiltonian (3) makes a nonzero contribution to the hexagonal anisotropy:

$$\hat{H} = \sum (g\beta H_j^{eff} s_{zj} + \tilde{a}_{4j}^1 \tilde{O}_{4j}^1) + d_M (s_{z_1} s_{z_2} \sin\theta_1 - s_{y_1} s_{z_2} \sin\theta_2) \cos(\varphi_2 - \varphi_1) \quad (3)$$

where \tilde{O}_{4j}^1 is the equivalent spin operator for ion j and $\tilde{a}_{4j}^1 = -(a_{cf} \sqrt{2}/12) \sin^2 \theta_j \cos\theta_j \sin 3(\varphi_j + \alpha_j)$. Denotation of the constants in Eq. (3), operator forms, and matrix elements were given, for example, in [14–16].

To calculate the free energy, the effective fields affecting the first ($j=1$) and second ($j=2$) sublattices can be introduced:

$$d_M n \langle s_{z_2} \rangle \cos(\varphi_2 - \varphi_1) = -d_M n \langle s_{z_2} \rangle \cos 2\gamma = g\beta H_{DM_1}, d_M n \langle s_{z_1} \rangle \cos 2\gamma = g\beta H_{DM_2}$$

Here, angle γ characterizes nonparallelity of the exchange fields affecting ions 1 and 2, n is the number of the neighbours. Below, we assume $\cos 2\gamma \approx 1$.

Within the second-order perturbation theory [17], the energy levels in the $x_1 y_1 z_1$ coordinate system are

$$W''_{\pm 1/2} = +(-) \sum_j \frac{60 H_{DM_j} \sin\theta_j \tilde{a}_{4j}^1}{|H_j^{eff}|},$$

$$W''_{\pm 3/2} = -(+) \sum_j \frac{90 H_{DM_j} \sin\theta_j \tilde{a}_{4j}^1}{|H_j^{eff}|},$$

$$W''_{\pm 5/2} = +(-) \sum_j \frac{30 H_{DM_j} \sin\theta_j \tilde{a}_{4j}^1}{|H_j^{eff}|}.$$

Here the sign in and without brackets corresponds to $j=2$ and $j=1$ respectively.

Now, we write the free energy per mole, taking into account the isotropic exchange term and the energy in the second-order perturbation theory:

$$F = -\left(\frac{NkT}{2}\right) \sum_j \ln Z_j = -\left(\frac{NkT}{2}\right) \sum_j \left[\ln \sum_m \exp\left(-\frac{g\beta |H_j^{eff}| m}{kT}\right) \exp\left(-\frac{W''_m}{kT}\right) \right]$$

$$= +(-) \left(\frac{N}{2}\right) \sum_j \left(\frac{30 a_{cf} \sqrt{2} H_{DM_j}}{12 |H_j^{eff}|} \right) \sin^3 \theta_j \cos \theta_j \sin 3(\varphi_j + \alpha_j) \left(\frac{Z_{2j}}{Z_{0j}} \right).$$

Here, the temperature averaging was performed; m is the magnetic quantum number; Z_j is the partition function for the j th ion, $\alpha_1 = -\alpha$, $\alpha_2 = \alpha$ (angle α is assumed to be positive as it was done for CaCO₃+Mn²⁺ crystals in [18]), and N is Avogadro's number.

Next, we introduce the angles for the antiferromagnetic vector: $\varphi_1 = \varphi$, $\varphi_2 = \varphi + \pi$, $(\cos\theta_1 - \cos\theta_2) = (2M_{z_1}/M) - (2M_{z_2}/M) = (2L_z/M) = 2\cos\theta$. We also make the following denotations: $H_{DM_1} = H_{DM_2} = H_{DM}$, $|H_j^{eff}| = H^{eff}$, $z_{0j} = z_0$, $z_{2j} = z_2$, $z_0 = (Y^5 + Y^4 + Y^3 + Y^2 + Y + 1)/Y^{5/2}$, $z_2 = (-Y^5 + 3Y^4 - 2Y^3 - 2Y^2 + 3Y - 1)/Y^{5/2}$, $Y = \exp(-2x/5)$, $x = (g\beta H^{eff}/kT) = (15/7)(T_N/T) B_{5/2}(x)$, $B_{5/2}(x)$ (the Brillouin function), and $\sin\theta_j = \sin\theta$.

The ratio between the Dzyaloshinsky–Moriya field and the isotropic exchange field can be presented in the form of a trigonometric function of angle γ . This ratio $\text{tg}2\gamma = H_{DM}/H^{eff} \approx \sin 2\gamma$ is determined by minimization of the total energy of the Dzyaloshinsky–Moriya interaction and the isotropic exchange [12]. The expression for the hexagonal anisotropy caused by the cubic crystal electric field and the Dzyaloshinsky–Moriya interaction acquires the form

$$q_D = -N\sqrt{2} a_{cfmc} \sin 3\alpha_{mc} \sin 2\gamma r(Y),$$

where $r(Y) = 5z_2/2z_0$. The equation for the hexagonal anisotropy can be written as

$$\omega_{qcfD}(\text{Fe}^{3+}) \cos 6\varphi = -\frac{(5/2)Ng\beta a_{cfmc}^2 \left[\left(\frac{1}{3}\right) \cos 3\alpha_{mc} + \sin 3\alpha_{mc} \sin 2\gamma \right]^2 r^2(Y)}{2 \left[H_A(0) + (H_D^2(0)/H_E(0)) \right] B_{5/2}^2(x)} \cos 6\varphi \quad (4)$$

In (4), the first term in brackets corresponds to the interaction between the spin and the crystal field. The second term in brackets reflects the effect of the crystal field and the

Dzyaloshinsky–Moriya interaction. Here, in $H_A(0)$ (uniaxial anisotropy field) only the dipole interaction is included, so as the single ion and “single-ion” exchange terms almost compensate each other [1]. The field values $H_A(0) = [a(0)/M(0)] = 3.13$ kOe (anisotropy field), $H_E(0) = [B(0)/M(0)] = 2H^{eff}(0) = 6020$ kOe (exchange field), and $H_D(0) = [d(0)/M(0)] = 100$ kOe (Dzyaloshinsky field) were reported in [19]. The values $a_{cfmc} = 130$ Oe and $\alpha_{mc} = 24^\circ$ were reported in [2] (index $\ll mc \gg$ corresponds to magnetically concentrated crystals).

The occurrence of the hexagonal anisotropy is related to the deviation of the sublattice moments from the basal (111) plane [6,7]. The Dzyaloshinsky–Moriya interaction and the cubic crystal field contribute to the hexagonal anisotropy in the following way. The Dzyaloshinsky–Moriya interaction causes sublattice angularity in the (111) plane of the crystal and the cubic crystal field rotates the magnetic moments out of the (111) plane (Fig. 1). The experimental curve of the $\omega_q(\text{Fe}^{3+})$ extrapolated to 0 K yields the value $(-3.1 \cdot 10^2 \text{ erg/mol})$ [7]. Taking into account the crystal field only, we obtain the value is $\omega_{qcf}(\text{Fe}^{3+}) = -3.3 \times 10^3 \text{ erg/mol}$ at $T=0$ K. The value of $\omega_{qcfD}(\text{Fe}^{3+})$ calculated in the second order of the perturbation theory with regard to the crystal field (Eq. (4)) is $\omega_{qcfD}(\text{Fe}^{3+}) = -5.6 \times 10^3 \text{ erg/mol}$ at $T=0$ K. The deviation from the experimental data can be caused by the fact that the covalence effects and admixture of upper states (in particular, those implemented in the “single-ion” exchange interaction) were not taken into account [3,5]. If we take these effects into account, the calculated absolute values of $\omega_{qcf}(\text{Fe}^{3+})$ and $\omega_{qcfD}(\text{Fe}^{3+})$ should be lower.

Thus, according to Eq. (4), the most significant contributions to the hexagonal anisotropy have the same temperature dependence. Therefore, this dependence, together with the EPR data on isostructural diamagnetic crystals with the Fe^{3+} impurity [1,2], can be used to determine the single-ion and “single-ion” exchange contributions of the cubic symmetry.

3. Hexagonal and uniaxial extrinsic anisotropy of FeBO_3 crystals. Phenomenological consideration

The thermodynamic potential for a Fe^{2+} ion in the FeBO_3 crystal (the impurity magnetic system is in thermodynamic equilibrium) can be written as [8]

$$\Phi' = A[\sin \theta \sin \theta' \cos \varphi \cos \varphi' + \sin \theta \sin \theta' \sin \varphi \sin \varphi' + \cos \theta \cos \theta'] + (1/2)a' \cos^2 \theta' - D \sin^3 \theta' \cos \theta' \cos (3\varphi' - \psi) \quad (5)$$

where A is the Fe^{2+} – Fe^{3+} isotropic exchange interaction constant; θ' and φ' are the polar and azimuth angles of the impurity antiferromagnetic vector $l' = M_{10} - M_{20}/M_0$; $M_0 = 2|M_{10}| = 2|M_{20}|$ and M_{10} and M_{20} are the sublattice magnetizations. The second and third terms in Eq. (5) are the uniaxial and hexagonal anisotropies, respectively; D is the hexagonal anisotropy constant of the impurity, and ψ is the phase angle.

Minimization of the sum $\Phi + \Phi'$ yields the equation for the total effective hexagonal anisotropy

$$\omega_q = \omega_q(\text{Fe}^{3+}) \cos 6\varphi + \omega_q(\text{Fe}^{2+}) \cos(6\varphi' - 2\psi) = \omega_q(\text{Fe}^{3+}) \cos 6\varphi - \frac{D^2}{4a'} \cos(6\varphi - 2\psi) \quad (6)$$

Since the hexagonal anisotropy field changes its sign above the compensation point, in Eq. (6) $\psi = 90^\circ$. The tangent of this angle, however, is temperature-independent, which follows partially from our microscopic treatment. Thus, the equation $\omega_q(\text{Fe}^{2+}) \cos(6\varphi - 2\psi) = \omega_q'(\text{Fe}^{2+}) \cos 6\varphi$ is valid over the entire temperature range (under the strong exchange interaction between Fe^{3+} and Fe^{2+} , we have $\theta' = \theta$, $\varphi' = \varphi$). Here, the trivalent

and bivalent iron spins are assumed to be parallel to each other and to the exchange field.

According to Eq. (6), the hexagonal and uniaxial anisotropies are interrelated. Therefore, simultaneous fitting of the theoretical curves of the hexagonal and uniaxial anisotropies to the experimental data can yield more accurate values of parameters (1) and (5) of the thermodynamic potential. In addition, this fitting allows one to eliminate the quantitative disagreement reported in [1] and to explain the temperature dependences of the anisotropy.

However, the description of the hexagonal anisotropy of the FeBO_3 crystals (for example, hematite [9]) is more complex and can be considered within the following model.

The model represents a vacancy of BO_3^{3-} around which an electron can move. The vacancy is surrounded by six nearest iron ions, one of which is a Fe^{2+} ion. An electron can jump in the basal plane of the crystal from one Fe^{2+} ion to another when the effective energy of the hexagonal anisotropy becomes equal to the potential barrier. This process is illustrated in Fig. 2. Here, the Z_H coordinates correspond to the atomic positions in the hexagonal unit cell representation.

The boron ions in BO_3^{3-} groups are energetically strongly coupled with oxygen ions and may exist as a whole in the solution-melt at the crystal growing temperatures [8]. Due to their spatial extent, it is difficult for them to build into the crystal structure that leads to the vacancies of these groups. As a consequence, a small deficiency of the negative charge will result in the appearance of the Fe^{2+} ions.

Solving the kinetic equations in this model, we arrive at expression (5) of the thermodynamic potential for the impurity equilibrium state.

4. Extrinsic anisotropy of FeBO_3 crystals. Microscopic consideration

In accordance with the study [20], a Fe^{2+} ion, depending on whether the potential of the axial electric field along the trigonal axis is minimum or maximum, can be in the singlet or doublet ground state in terms used in [21]. The calculation of the coefficient $(1/2)B_2^0 = (1/2)\sum_i(q_i/R_i^5)(3z_i^2 - R_i^2)$ in the expression for the potential [21] yields the positive value $(1.99 \times 10^{13} \text{ CGS/cm}^3)$ [22]. Here, q_i is the ion charge and R_i is the distance between the origin of coordinates and the i th ion (i is the index of summation of the crystal ions; the origin of coordinates is positioned at a Fe^{2+} ion). Therefore, the potential will be minimum and, according to [23,24]; the lower energy levels of the Fe^{2+} ion spin-triplet can be described by the Hamiltonian with the effective spin $s = 1$.

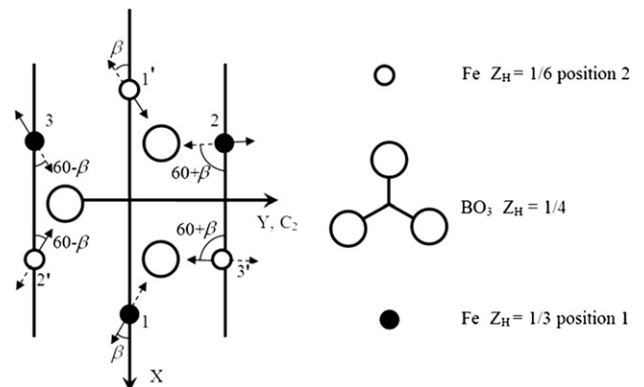


Fig. 2. Distribution of axes of the crystal field on iron ions for a subimage of the FeBO_3 lattice with a vacancy in the center ($Z_H = 1/4$).

The Hamiltonian for the Fe^{2+} impurity in the single-ion approximation for the case of the lowest symmetry is [15]

$$\hat{H} = g\beta H_j^{\text{eff}} s_j + A_2^0 O_{2j}^0 + A_2^1 O_{2j}^1 + A_2^2 O_{2j}^2 + \tilde{A}_2^1 \tilde{O}_{2j}^1 + \tilde{A}_2^2 \tilde{O}_{2j}^2 \quad (7)$$

where $j = 1$ and 2 correspond to the first and second positions (Fig. 2). The first term in (7) characterizes the isotropic exchange interaction in the molecular field approximation; H_j^{eff} is the exchange field induced by Fe^{3+} ions in the Fe^{2+} site; s_j is the spin of the Fe^{2+} ions in the positions $j = 1, 2$. Operators O_k^l and \tilde{O}_k^l were given, for example, in [15].

It is believed that the impurity concentration of bivalent iron is very low and the complexes shown in Fig. 2 do not interact.

The solution of Hamiltonian (Eq. (7) Fig. 2) yields Eq. (8) for the energy levels obtained within the first-order perturbation theory. In this equation, σ describes the anisotropy energy in the 0° , -120° , and -240° directions in the (111) basal plane of the crystal; β is the angle that determines the projection of the principal axes of the spin-Hamiltonian onto the (111) plane of the crystal.

$$E_{\sigma j} = g\beta H_j^{\text{eff}} m_j + \left[\frac{A_2^0}{2} (3\cos^2 \theta_j - 1) + \frac{A_2^1}{4} \sin 2\theta_j' \cos(\varphi_j' + \sigma \pm \beta) + \frac{A_2^2}{4} \sin 2\theta_j' \sin(\varphi_j' + \sigma \pm \beta) + \frac{A_2^0}{2} \sin^2 \theta_j' \cos 2(\varphi_j' + \sigma \pm \beta) + \frac{A_2^2}{2} \sin^2 \theta_j' \sin 2(\varphi_j' + \sigma \pm \beta) \right] (3m_j^2 - 2) \quad (8)$$

We write the free energy [25] in the form

$$F = -\frac{Nc_0 kT}{2} \sum_{\sigma} c_{\sigma} \ln Z_{\sigma}; \quad Z_{\sigma} = \sum_{m_j} \exp\left(-\frac{E_{\sigma j}}{kT}\right)$$

Here, m_j is the magnetic quantum number, c_0 is the concentration of Fe^{2+} ions in the crystal, k is the Boltzmann constant, and c_{σ} is the degeneracy factor.

Now, we expand the anisotropic part of this expression and introduce the angles of the vector of antiferromagnetism. In calculation of the anisotropy, we take into account only the first term of the expansion. For the easy plane anisotropy, $c_{\sigma} = 1/3$; for the uniaxial one, there is no dependence of the anisotropy on σ and therefore $c_{\sigma} = 1$.

The uniaxial extrinsic anisotropy constant can be written as

$$a'(\text{Fe}^{2+}) = 3Nc_0 A_2^0 \left(\frac{z_1'}{z_0'}\right).$$

The hexagonal effective anisotropy has the form

$$a'_q(\text{Fe}^{2+}) = \frac{Nc_0 B_{\text{imp}} z_1'}{(kT)^2 z_0'} \quad (9)$$

Here, B_{imp} is the constant value that includes the constants of Hamiltonian (8).

$$z_0' = (Y'^2 + Y' + 1)/Y',$$

$$z_1' = (1 - Y')^2/Y',$$

where $Y'(x')$ and $x'[B_{5/2}(x')]$ dependences have the same form as in Section 2.

5. Spin Hamiltonian (SH) for two exchange-coupled ions. Anisotropy constants

In accordance with [26,27–29], the SH for two exchange-coupled ions (here $\text{Fe}^{3+}-\text{Fe}^{3+}$) can be presented in terms of the total spin $S = s_1 + s_2$ if the exchange interaction is much stronger than effects of the other terms in the SH, that leads to the six states with total spin S [26,28,30]. The energy levels for each state

and may be written [28] 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 $S = s_1 + s_2, s_1 + s_2 - 1, \dots, s_1 - s_2; s_1 = s_2 = 5/2$. In this case [26,28,30] we may write down the SH for the each possible value of the total spin

$$\widehat{\mathcal{H}} = g\beta H S_z + (D_S/3)O(S_z) - (1/180)(a-F)_{cS} \gamma_S O(S_z) \quad (10)$$

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 $B_4^3 O_4^3$ type do not contribute to the energy states in the first order of the perturbation theory; $D_S = 3\alpha_S D_{\text{dip}} + \beta_S D_{cS}; \alpha_S = (1/2)[S(S+1) + 4s_1(s_1+1)]/(2S-1)(2S+3), \beta_S = [3S(S+1) - 3 - 4s_1(s_1+1)]/(2S-1)(2S+3)$, and γ_S are non-linear functions of S mentioned in [26,30]. In accordance with [26,30], α_S, β_S and γ_S are the coefficients attached to D_{dip}, D_{cS} and $(a-F)_{cS}$, 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

$$|H^{\text{ex}}| = (1/g\beta)[\partial E_S / \partial S] = |J/g\beta| \sqrt{S(S+1)} \quad (11)$$

As long as the energy of every multiplet depends on S value [26], so SH constant D_{cS} may be than written as

$$D_{cS} = D_{cf} + D_{c0} + A\sqrt{S(S+1)} \quad (12)$$

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 [3]. Since the third term in Eq. (12) is governed by the anisotropic exchange interaction it must include the isotropic exchange part in common case [31]. So, under the consideration of the pair interactions in the diamagnetic crystals with Fe^{3+} impurities, third term in Eq. (12) is linearly dependent on isotropic exchange field, i.e on total spin value S as $\sqrt{S(S+1)}$. Such type of dependence is observed experimentally for explored here compounds and, for example, for the $\text{MgO} + \text{Mn}^{2+}$, $\text{CaO} + \text{Mn}^{2+}$ [28], $(\text{CH}_3)_4\text{NCdCl}_3 + \text{Mn}^{2+}$ [27], MBO_3 ($M = \text{Ga, In, Sc, and Lu}$) + Fe^{3+} [1] with well interpreted pair spectra.

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

$$(a-F)_{cS} = (a-F)_{cf} + (a-F)_{c0} + BS(S+1) \quad (13)$$

All terms in Eq. (13) have the same physical meaning respectively as in Eq. (12).

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 i -th ion in magnetically concentrated crystal at $T=0$ K as $E(T=0 \text{ K}) = -nJ S_i S_j$, where n is the nearest neighbor number. Assuming $n = n_0 = 1$ and

$$E(T=0, n_0) = E_{S \text{ mc}} \quad (14)$$

we define the pair effective spin value S_{n0} for paramagnetic impurity in diamagnetic substance. It will correspond to the i th ion ground-state energy $E(T=0)$ in “magnetically concentrated”

crystal at a given n . Solution of Eq. (14) for $s_i = s_j = 5/2$ is $S_{n0} = 1.79$. Then, taking a sum over all neighbors of i th ion in the left part of Eq. (14), one can find the exchange energy for i th ion in a magnetically concentrated crystal at $T = 0$ K to be

$$E(T = 0) = n_0 E_{S_{n0}}(S_{n0}) \quad (15)$$

The right part of Eq. (15) represents the energy of n paramagnetic pairs in a diamagnetic crystal.

Taking into account (12) and (13) and values of A_{mc} , B_{mc} parameters, that are responsible for the “single-ion” anisotropy of i th ion in magnetically concentrated crystal (can be derived, for example from Fig. 5) are equal to

$$D_{mc} = D_{cfmc} + 2.26nA_{mc} \quad (16)$$

$$(a-F)_{mc} = (a-F)_{cfmc} + 5.00nB_{mc} \quad (17)$$

Parameters D_{mc} and $(a-F)_{mc}$ involve not only well known single-ion terms D_{cfmc} and $(a-F)_{cfmc}$ but the exchange correction terms also. The well-known in literature single-ion expressions at $T = 0$ K can be used to write down the effective anisotropy field with exchange correction terms for the rhombohedral antiferromagnetic crystals [32]. In accordance with Eqs. (16), (17) and [32], the “single-ion” exchange and single-ion contributions to the uniaxial anisotropy constant (for second order of magnitude) at $T = 0$ K may be written as follows

$$\omega_{Acfmc} + \omega_{A_{mc}}^{ex} = 2Ng\beta s(s-1/2)\{D_{cfmc} + 2.26nA_{mc} + (1/6)(s-1)(s-3/2)[(a-F)_{cfmc} + 5.0nB_{mc}]\} \quad (18)$$

6. Comparison between the calculation and the experiment

Theoretical curves of the hexagonal (ω_q) and uniaxial (ω_A) anisotropies governed by the contributions of Fe^{2+} and Fe^{3+} ions were fitted to the experimental data using the least-squares method. Six fitting parameters were used at this procedure, four of which were fixed and correspond to the calculated dipole contribution, experimental easy plane anisotropy value (-3.1×10^2 erg/mol) and two parameters that represent the sum of single ion and “single-ion” exchange contributions and were obtained from EPR data ($[\omega_{Acfmc}(s^2) + \omega_{A_{mc}}^{ex}(s^2)] = 2.352 \times 10^7$ erg/mol and $[\omega_{Acfmc}(s^4) + \omega_{A_{mc}}^{ex}(s^4)] = 5.60 \times 10^6$ erg/mol] at $T = 0$ K) (see Eq. (18)).

Fig. 3 presents temperature dependences of the hexagonal anisotropy $\omega_q = \omega_q(Fe^{3+}) + \omega'_q(Fe^{2+})$ of the $FeBO_3$ crystals. In the calculation of ω_q , expressions (4) and (9) were used.

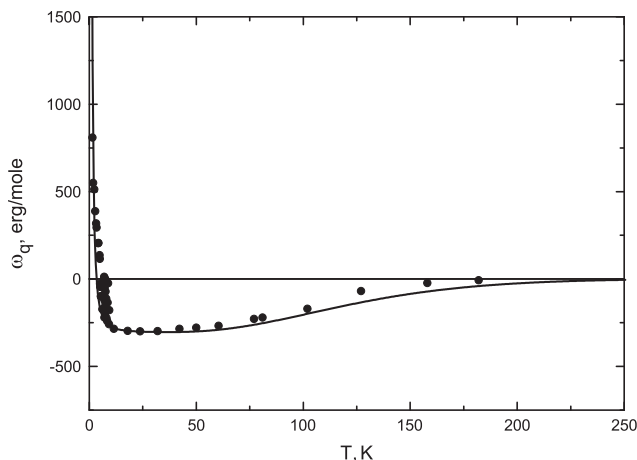


Fig. 3. Temperature dependence of the hexagonal anisotropy $\omega_q = \omega_q(Fe^{3+}) + \omega'_q(Fe^{2+})$ in $FeBO_3$ crystals. Points correspond to the experiment [6]; solid curve corresponds to the theory.

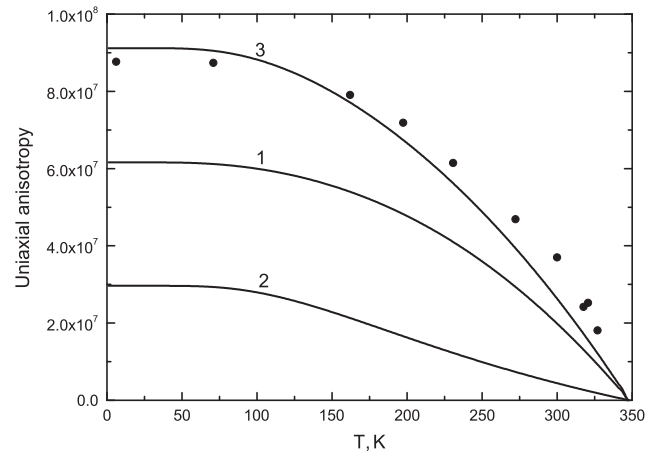


Fig. 4. Temperature dependence of the uniaxial anisotropy of Fe^{3+} ions [$a(Fe^{3+})$] (curve 1) and Fe^{2+} ions [$a'(Fe^{2+})$] (curve 2) in $FeBO_3$ crystals. Curve 3 corresponds to $\omega_A = a(Fe^{3+}) + a'(Fe^{2+})$. Solid curve shows the theoretical data; points show the experimental ones [19].

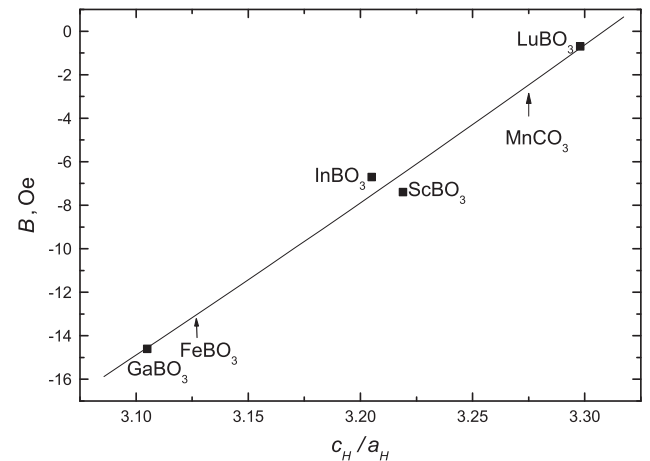


Fig. 5. Parameter B dependency (see Eq. (13)) that was derived from EPR pair spectra on hexagonal lattice ratio c_H/a_H for $MBO_3 + Fe^{3+}$ crystals [1]. The arrow indicates B value for $FeBO_3$ and $MnCO_3$ crystals.

Fig. 4 shows the temperature dependence of the uniaxial anisotropy constants for the Fe^{3+} and Fe^{2+} ions. Calculated curve 2 reflects the contribution of the Fe^{2+} ions to ω_A . Fitting of the curve that includes the single-ion, “single-ion” exchange, and dipole mechanisms of the anisotropy of Fe^{3+} ions (without the consideration of the Fe^{2+} contribution) in iron borate and manganese carbonate to the experimental data was described in [33].

Fig. 5 shows dependency of the parameter B (see Eq. (13)) that was derived from EPR pair spectra on hexagonal lattice ratio c_H/a_H for $MBO_3 + Fe^{3+}$ crystals. The arrow indicates B value for $FeBO_3$ and $MnCO_3$ crystals. Such definition of the B parameter turns out to be possible due to its monotonic experimental dependency on c_H/a_H [1] for $FeBO_3$, $MnCO_3$ and $\alpha-Fe_2O_3$ crystals.

7. Conclusions

The calculated uniaxial (ω_A) and hexagonal (ω_q) anisotropies are in satisfactory agreement with the experimental data. Similar to the case of Fe^{3+} ions [1], the anisotropy governed by Fe^{2+} ions contains two large contributions of the opposite sign: the

single-ion and “single-ion” exchange. The significant contributions of the single-ion and, as a consequence, “single-ion” exchange are confirmed by the large experimental axial constants of the Hamiltonian of Fe^{2+} ion spins [15] (for example, the uniaxial constant of $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O} + \text{Fe}^{2+}$ is $3A_2^0 = 20.2 \text{ cm}^{-1} \text{ ion}^{-1}$).

The following fitting parameters have been obtained:

$$c_0 A_2^0 = 9.87 \times 10^{-18} \text{ erg/ion}, c_0 B_{imp} = 1.125 \times 10^{-52} \text{ erg}^3/\text{ion}$$

The existence of the relatively large contribution of the “single-ion” exchange to the cubic symmetry is demonstrated by the temperature dependences and quantitative estimation of the basal anisotropy on the Fe^{3+} ion sites. Taking into account that there are three main mechanisms of the hexagonal anisotropy, the value $\omega_q(\text{Fe}^{3+}) \sim (-)(a_{c_{fmc}} + a_{ex})^2$ extrapolated from 77 K to 0 K is $-3.1 \times 10^2 \text{ erg/mol}$. Constant a_{ex} corresponds to the contribution of the “single-ion” exchange whose value is relatively large (Section 2). So far, the presence of the contribution of the cubic symmetry “single-ion” exchange to the anisotropy has not been discussed in the literature.

It has been shown that the contribution governed by the Dzyaloshinsky–Moriya interaction and the cubic crystal field must be taken into account in the analytical treatment of the hexagonal anisotropy.

Note that the analytical treatment of a Fe^{3+} ion in FeBO_3 can be applied to a Mn^{2+} ion in MnCO_3 . The computation technique used is suitable for carbonates with the orbital-singlet ground state.

We derived the theoretical expressions for the contribution of Fe^{2+} ions to the uniaxial and hexagonal extrinsic anisotropies of the FeBO_3 crystals in the single-ion approximation. The method for calculating the uniaxial anisotropy of the divalent iron impurity can be used for a series of rhombohedral (MnCO_3 , CoCO_3 , NiCO_3) + Fe^{2+} and FeCO_3 crystals also.

The validity and accuracy of the model accounting single-ion and “single-ion” exchange contributions for the quantitative description of the anisotropy of the iron borate and manganese carbonate is shown (see Table 1). It was also shown that the calculation of contributions of dipole interactions to the magnetic anisotropy gives good results. The developed method can be applicable to other compounds with S-state ions.

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