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MAGNETISM

Weak Ferromagnetism along the Triad Axis of $FeBO_3$ Crystals

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Abstract—Weak ferromagnetic moment along the triad axis of $FeBO_3$ crystals has been calculated on the basis of the single-ion model taking into account the cubic invariant of the crystal field in the spin Hamiltonian.

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Although iron borate crystals have been synthesized and investigated quite thoroughly for a long time, they continue to arouse the interest of researchers, as they are convenient objects for constructing various magnetic models. These crystals have a simple (calcite) lattice structure, are characterized by a high Néel temperature and narrow antiferromagnetic resonance lines, and have a series of isostructural diamagnetic analogs. Dmitrienko et al. [1] were, in 2014, the first to determine the magnitude and sign of the vector components in the Dzyaloshinskii–Moriya interaction (in iron borate crystals). Pulsed excitation of interacting magnetic moments in $FeBO_3$ by linearly polarized light was observed quite recently in [2]. In addition, the uniaxial magnetic anisotropy in magnetically concentrated crystals with ions in the S state was described quantitatively by the electron paramagnetic resonance (EPR) technique using isostructural diamagnetic analogs with trivalent iron impurity [3].

However, in spite of the simple crystal lattice (whose elements were studied in [3, 4]; see also Fig. 1), the magnetic system exhibits a complex behavior [5, 6] during rotation of the antiferromagnetism vector $\mathbf{l} = (\mathbf{M}_1 - \mathbf{M}_2)/M$ in the (111) plane of the crystal, where $M = 2|\mathbf{M}_1| = 2|\mathbf{M}_2|$, $\mathbf{M}_1$ and $\mathbf{M}_2$ being sublattice magnetizations. In particular, such complex behavior is exhibited by ferromagnetism vector $\mathbf{m} = (\mathbf{M}_1 + \mathbf{M}_2)/M$ when we take into account the penultimate term in the expression for free energy derived by Dzyaloshinskii [5]:

$$\Phi = (1/2)B\mathbf{m}^2 + (1/2)a\cos^2\theta + (1/2)c\cos^4\theta + d\sin\theta(m_y\cos\varphi - m_x\sin\varphi) + q\sin^3\theta\cos\theta\cos3\varphi + tm_2\sin^3\theta\sin3\varphi + e\sin^6\theta\cos6\varphi. \quad (1)$$

The first term in this equation characterizes the isotropic exchange energy of the crystal, the second and third terms describe the axial anisotropy, the fourth term takes into account the Dzyaloshinskii interaction that leads to the emergence of weak ferromagnetism in the (111) basal plane, the last three terms describe the anisotropy energy in the (111) plane, and θ and φ are the polar and azimuthal angles of vector $\mathbf{l}$, measured from the triad axis (z axis) and from the crystal symmetry plane (x axis), respectively (Fig. 1). Weak ferromagnetism of crystals was studied in detail by Turov (in particular, in [6]).

Since $FeBO_3$ is used quite frequently as a model crystal, information about the mechanisms responsible for the emergence of anisotropic interactions in it is sometimes found to be quite useful. One of the anisotropy parameters considered in this work is weak paramagnetic moment m_z along the triad axis of the crystal. The search for the factors responsible for the emergence of m_z is also an interesting problem.

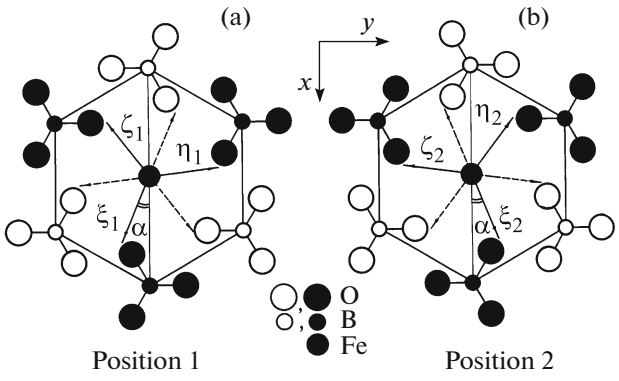

Fig. 1. Cubic crystal field axes for two inequivalent positions of Fe^{3+} in the $FeBO_3$ lattice. Dark and light circles show the BO_3 groups lying above and below the plane of the figure, respectively.

The phenomenological expression for the weak ferromagnetic moment along the triad axis follows from the minimization of free energy (1) in m_z:

$$m_z = (-t/B)\sin^3\theta\sin 3\varphi. \quad (2)$$

The spin Hamiltonian taking into account two inequivalent positions of Fe^{3+} ions has the form [3, 4]

$$\mathcal{H} = g\beta\mathbf{H}_j^{\text{eff}}\mathbf{s}_j + (1/3)D_{\text{cf}}O_{2j}^0 + (F_{\text{cf}}/180)O_{4j}^0 \quad (3)$$
$$-(a_{\text{cf}}/180)[O_{4j}^0 - 20\sqrt{2}(O_{4j}^3\cos 3\alpha_{\text{cf}\,j} - \tilde{O}_{4j}^3\sin 3\alpha_{\text{cf}\,j})].$$

In this equation, the first exchange interaction term is written in the molecular field approximation; **s** is the ion spin operator; O_n^m are the equivalent spin operators that are given together with their matrix elements, for example, in [7, 8]; and $\alpha_{\text{cf}\,j}$ is the angle through which the projections of the axes of the cubic crystal field onto the (111) plane are deflected from the crystal symmetry plane in the jth position (see Fig. 1). A more detailed description of Fig. 1 can be found in [3, 4]. The second, third, and fourth terms (with constant a_{cf} in the Hamiltonian) describe the axial and cubic symmetry interactions, respectively.

The exchange term in (3) can be written in the zeroth approximation in perturbation theory assuming that the quantization axis is determined by angles θ_j and φ_j measured from the triad axis and from the symmetry plane, respectively. The Hamiltonian can be presented in the form [8]

$$\mathcal{H} = g\beta H_j^{\text{eff}}s_{zj} + \sum_{m=0}^{2}a_{2j}^m O_{2j}^m + \sum_{m=0}^{4}a_{4j}^m O_{4j}^m + \sum_{m=1}^{4}\tilde{a}_{4j}^m\tilde{O}_{4j}^m.$$

Here, for simplicity we have omitted the symbols marking the appurtenance of expressions to a coordinate system turned through an angle. To take into account the weak ferromagnetic moment along the triad axis (in the first approximation of perturbation theory), we shall be interested in the term containing a_{cf}:

$$a_{4j}^0O_{4j}^0 = (1/72)\{a_{\text{cf}}\sqrt{2}\sin^3\theta_i\cos\theta_j\cos 3(\varphi_j + \alpha_{\text{cf}\,j}) \quad (4)$$
$$-[(a-F)_{\text{cf}}/20](35\cos^4\theta_j - 30\cos^2\theta_j + 3)\}O_{4j}^0.$$

The energy levels obtained from this equation have the form [4]

$$W_{jm_j} = g\beta H_j^{\text{eff}}m_j + c_4^0(m_j)a_{4j}^0,$$
$$c(m_j) = [35m_j^4 - 30m_j^2s(s+1) + 25m_j^2 \quad (5)$$
$$-6s(s+1) + 3s^2(s+1)^2].$$

The anisotropic energy (5) for magnetic quantum number $m_1 = -5/2$ ($T = 0$ K) per mole of the substance can be written in the form

$$\sum_j W_{jm_1=-5/2} = (N/18)a_{\text{cf}}\sqrt{2s}(s-1/2)(s-1)$$
$$\times(s-3/2)[\sin^3\theta_1\cos\theta_1\cos 3(\varphi+\alpha_{\text{cf}}) \quad (6)$$
$$+\sin^3\theta_2\cos\theta_2\cos 3(\varphi+\pi-\alpha_{\text{cf}})].$$

Here, the azimuthal angles are used for the antiferromagnetism vector, and N is the Avogadro number. Expanding the cosine functions in (6) including azimuthal angles, adding the expressions within brackets containing $\cos\theta_1$ and $\cos\theta_2$, setting $\sin^3\theta_1 = \sin^3\theta_2 = \sin^3\theta$, and considering that $\cos\theta_1 + \cos\theta_2 = 2m_z$ (0) by definition, we obtain

$$\sum_j W_{jm_1=-5/2} = -(N/9)a_{\text{cf}m_z}(0)\sqrt{2s}(s-1/2)$$
$$\times(s-1)(s-3/2)\sin 3\alpha_{\text{cf}}\sin^3\theta\sin 3\varphi. \quad (7)$$

Equating this relation to the phenomenological expression for energy with constant t in Eq. (1) ($T = 0$ K), we obtain the expression for $t(0)$ and then for m_z (0):

$$t(0) = -N(\sqrt{2}/9)s(s-1/2)(s-1)(s-3/2)a_{\text{cf}}\sin 3\alpha_{\text{cf}},$$
$$m_z(0) = [N\sqrt{2}/9B(0)]s(s-1/2)(s-1)(s-3/2) \quad (8)$$
$$\times a_{\text{cf}}\sin 3\alpha_{\text{cf}}\sin^3\theta\sin 3\varphi.$$

For the weak ferromagnetic moment per mole of the substance being measured in this case, we obtain

$$\sigma_z^0 = m_z(0)M(0)$$
$$= [N\sqrt{2}a_{\text{cf}}g\beta S/3H_E(0)]\sin 3\alpha_{\text{cf}}\sin^3\theta\sin 3\varphi. \quad (9)$$

In expression (8), constants $B(0)$ and a_{cf} are written in energy units in (9) while a_{cf} and $H_E(0)$ have the dimensions of field (oersteds). Here, $H(0) = B(0)/M(0)$ is the effective exchange field, g is the spectral splitting factor, and β is the Bohr magneton.

The single-ion contribution to the weak ferromagnetic moment along the triad axis at arbitrary temperatures can be determined by expanding the free energy of the crystal

$$F = -(NkT/2)\sum_j \ln Z_j$$

into a power series in the ratio of anisotropy constant to kT, where

$$Z_j = \sum_{m_j}\exp(-W_{jm}/kT)$$

is the sum of states of the jth ion.

We expand the exponential function in the expression for the crystal free energy into a power series in $(c_4^0(m_j)a_{4j}^0)/kT$. Confining the expansion to linear terms only, we obtain

$$F = -\frac{NkT}{2}\sum_j \ln \times \sum_{m_j} \exp\left(-\frac{g\beta H_j^{\text{eff}} m_j}{kT}\right)\left(1 - \frac{c_4^0(m_j)a_{4j}^0}{kT}\right).$$

Introducing the notation $Y_j = \exp(-g\beta|H_j^{\text{eff}}|)/kT$, summing over m_j (for strong exchange interaction $H_1^{\text{eff}} = -H_2^{\text{eff}} = |H_j^{\text{eff}}|$, $m_1 = -m_2 = m$), we can write the expression for F in the form

$$\begin{aligned} F =& -(NkT/2)\sum_j \ln\{(Y_j^{1/2} + Y_j^{-1/2})[1-(120\alpha_{4j}^0)/kT] \\ &+ (Y_j^{3/2} + Y_j^{-3/2})[1 + (180a_{4j}^0)] \\ &+ (Y_j^{5/2} + Y_j^{-5/2})[1 - (60a_{4j}^0)/kT]\} \\ =& -(NkT/2)\sum_j \ln[z_{0j} + (60a_{4j}^0)/kT]a_{2j}] \\ =& -(NkT/2)\sum_j \{\ln z_{0j} + \ln[1 + (60a_{4j}^0/kT)(z_{2j}/z_{0j})]\}, \end{aligned}$$

where

$$z_{0j} = (Y_j^5 + Y_j^4 + Y_j^3 + Y_j^2 + Y_j + 1)/Y_j^{5/2},$$
$$z_{2j} = (-Y_j^5 + 3Y_j^4 - 2Y_j^3 - 2Y_j^2 + 3Y_j - 1)/Y_j^{5/2}.$$

Expanding function $\ln[1 + (60a_{4j}^0/kT)(z_{2j}/z_{0j})$ into a series in small parameter $(60a_{4j}^0 z_{2j})/(kTz_{0j})$ and confining the expansion to the first-order terms, we obtain the following expression accurate to within the constants:

$$F = -\frac{N}{2}\sum_j \left(60a_{4j}^0 \frac{z_{2j}}{z_{0j}}\right). \quad (10)$$

Setting $|H_j^{\text{eff}}| = H^{\text{eff}}$ and expanding a_{4j}^0 in expression (10), we consider the term with a_{cf} as usual. Carrying out similar operations with trigonometric functions in (10) as during the derivation of formula (7) from (6) and comparing with the penultimate term in expression (1), we obtain the single-ion contributions to macroscopic parameters at arbitrary temperatures:

$$\begin{aligned} t(T) &= (N\sqrt{2}/3)a_{\text{cf}} \sin 3\alpha_{\text{cf}} r(Y), \\ m_z(T) &= -(N\sqrt{2}/3B)a_{\text{cf}} \sin 3\alpha_{\text{cf}} \sin^3\theta \sin 3\varphi r(Y), \\ \sigma_z(T) &= m_z M \quad (11) \\ &= -[Ng\beta\sqrt{2}a_{\text{cf}}/3H_E(0)B_{5/2}(x)]r(Y)\sin 3\alpha_{\text{cf}}\sin^3\theta\sin 3\varphi. \end{aligned}$$

Parameters a_{cf} and $H_E(0)$ in the expression for $\sigma_z(T)$ in (11) have the dimensions of field (oersteds) and $r(Y) = (5/2)(z_2/z_0)$. The dependence $r(Y)$ was calculated in [9] by using Brillouin function $B(x)_{5/2}$. For $T = 0$ K, we have $r(Y) = -5/2$, and expressions (11) are transformed into relations (8), (9) for spin equal to 5/2.

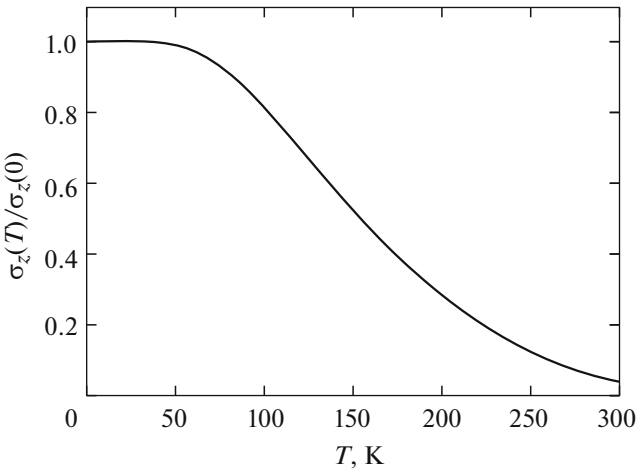

Fig. 2. Temperature dependence of the weak relative ferromagnetic moment $\sigma_z(T)/\sigma_z(0)$ along the triad axis of $FeBO_3$ crystals.

Figure 2 shows the relative temperature dependence of weak ferromagnetic moment along the triad axis $\sigma_z(T)/\sigma_z(0)$, calculated for $FeBO_3$. The experimental value of m_z obtained for $FeBO_3$ crystals in [10] is equal to 1.3×10^{-3} emu g^{-1}. The estimate was obtained for $T = 77$ K using the results from [11]. Theoretical estimate obtained by taking into account the contribution from Fe^{3+} ions at $T = 0$ K is found to be 2.4×10^{-3} emu g^{-1} for the following values of the constants: $a_{\text{cfmc}} = 130$ Oe, $\alpha_{\text{cfmc}} = 24°$ [3] (here, the subscript "mc" indicates the correspondence of parameters obtained in diamagnetic analogs to a magnetically concentrated crystal) and $H_E(0) = 6.02 \times 10^6$ Oe [12]. Theoretical and experimental results are found to be quite close, indicating that the mechanism under consideration is at least one of the main mechanisms.

Resultant expression (9) can also be used for obtaining a rough estimate for $\sigma_z(0)$ in $MnCO_3$ from the data obtained in [13, 14]: $a_{\text{cf}} = 2.2$, $H_E(0) = 6.4 \times 10^5$ Oe, and $\alpha_{\text{cf}} = 15.5°$. Using these values, we obtain $\sigma_z(0) \sim 2.9 \times 10^{-4}$ emu g^{-1}. No EPR results are available for theoretical estimates of weak ferromagnetic moment in hematite.

The mechanism of the effect of the cubic crystal field on exchange-coupled spin moments is similar to the one described in [4], the only difference being that the antiferromagnetism vector for a certain orientation in the basal plane "is bent" under the action of the cubic field, producing the moment along the triad axis.

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