

Uniaxial Magnetic Anisotropy of Rhombohedral CoCO_3 Crystals at $T = 0$ K

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Abstract—A method for calculating the contribution of exchange interaction to uniaxial anisotropy with the use of g' factors has been worked out using CoCO_3 crystals as an example. The calculated contribution of dipole–dipole interactions to the anisotropy of CoCO_3 is 0.93 cm^{-1} . The sum of the contributions to the anisotropy constant of CoCO_3 with the inclusion of the dipole–dipole interactions is 36.1 cm^{-1} .

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1. INTRODUCTION

Rhombohedral antiferromagnetic crystals $M\text{CO}_3$ ($M = \text{Mn, Fe, Ni, Co}$) with the calcite structure have been intensively studied by Borovik-Romanov and colleagues since 1956 in order to clarify the character and specific features of weak ferromagnetism [1]. The phenomenological theory of this phenomenon was developed by Dzyaloshinskii in 1957 [2] and its microscopic nature was elucidated by Moriya in 1960 [3]. It was shown taking into account the symmetry properties [2] that the existence of weak ferromagnetism is the natural phenomenon for rhombohedral crystals. More specifically, weak ferromagnetism takes place when the minimum of the thermodynamic potential

$$\Phi = (1/2)B\mathbf{m}^2 + (1/2)a \cos^2 \theta - d \sin \theta (m_y \cos \varphi - m_x \sin \varphi) \quad (1)$$

corresponds to the state in which the antiferromagnetic and ferromagnetic vectors $\mathbf{l} = (\mathbf{M}_1 - \mathbf{M}_2)/M$ and $\mathbf{m} = (\mathbf{M}_1 + \mathbf{M}_2)/M$ lie in the basal plane (111). Here, \mathbf{M}_1 and \mathbf{M}_2 are the sublattice magnetizations, $M = 2|\mathbf{M}_1| = 2|\mathbf{M}_2|$, θ and φ are the polar and azimuthal angles of the vector \mathbf{l} in the xyz reference frame (the z axis is parallel to C_3). The first, second, and third terms in Eq. (1) correspond to the exchange energy, uniaxial anisotropy, and Dzyaloshinskii–Moriya interaction, respectively.

CoCO_3 crystals have the Néel temperature $T_N = 18.1 \text{ K}$ [4], the coordination number $Z = 6$, the orbital momentum $L = 3$ of the free Co^{2+} ion, and the spin $S = 3/2$. The magnetic structure was determined from the measurements of neutron scattering [5] and corrected in [6]. The measurements [5, 6] revealed the presence of weak ferromagnetism and the magnetic

structure [6] in agreement with the thermodynamic theory [2].

The available experimental data on the uniaxial anisotropy constant are controversial: $a = 0.1$ [4], 3.4 [7], and 24.9 cm^{-1} , which corresponds to the g factor of 3.3 [8, 9]. There are also considerable differences in values of the g factors measured using antiferromagnetic resonance (AFMR) [9, 10] in CoCO_3 and electron paramagnetic resonance (EPR) in its diamagnetic analogues with an impurity of Co^{2+} ions [11]. According to the calculations [12] of the g factors, the results of AFMR and EPR should be nearly the same. The anisotropy and g factor are sensitive to the impurity with an orbital momentum. Thus, a small amount of such an impurity will change these parameters. However, the exchange integral and T_N remain practically unchanged at a small concentration of the impurity. However, in [13] the data for the g_{xy} factor (which is 4.55) found from the measurement of a weak ferromagnetic moment correspond to the EPR measurements on individual Co^{2+} ions in diamagnetic analogues of CoCO_3 [11, 12]. Therefore, the initial experimental parameters can be referred to the nominally pure CoCO_3 crystal.

This work is aimed at working out the method for calculating the contribution of exchange interaction to the uniaxial anisotropy of cobalt ions in the axial crystal field and its verification by the example of nominally pure CoCO_3 .

The calculation is based on the following concepts:

(1) The initial data were the experimental results [13]: the g factor in the basal plane $g_{xy} = 4.55$; the effective exchange parameter J in the (111) plane for the pair of CoCO_3 ions, which was determined in [13]

from the equation $4kT_N = 3J'_{xy}$. Here, k is the Boltzmann constant. The other “microscopic” parameters were found from the Abragam and Pryce equations [12] (see Section 2 below).

(2) Anisotropy of the exchange interaction was considered according to the Oguchi method [14] with the inclusion of the g' factors (see Section 2 below). A pair of ions coupled by the exchange interaction in the molecular field of the neighbors was considered. In addition, in contrast to [14], the Dzyaloshinskii–Moriya interaction was included and the energy of the molecular field had the off-diagonal form. The calculation was performed for the lowest doublet level with the effective spin $s = 1/2$.

(3) The contribution of the dipole–dipole interactions was calculated according to the method [15] with the inclusion of the inequivalence of the g factors along the $C_3(g_z)$ axis in the basal plane.

2. HAMILTONIAN OF THE Co^{2+} ION IN AN AXIAL CRYSTAL FIELD

The Co^{2+} ion has the electronic configuration $3d^7$ and appears in the state 4F . The cubic crystal field splits the 4F term into the orbital singlet and two low-lying orbital triplets. The lowest triplet can be characterized by the effective orbital momentum $\mathbf{L} = -\alpha\mathbf{l}'$ with $l' = 1$ [12]. The joint action of the trigonal crystal field and spin–orbit interaction splits the orbital and spin levels ($S = 3/2$) of the lowest triplet into six doublets with an energy spacing between the doublets of several hundred inverse centimeters [12, 13]. The Hamiltonian that leads to the above results has the form

$$\hat{H} = \Delta(1 - l'_z{}^2) - \alpha\lambda l'_z S_z - \alpha'\lambda(l'_x S_x + l'_y S_y),$$

where the first term describes the levels which split in the trigonal crystal field, and the second and third terms describe the spin–orbit interaction. Inequality of α and α' reflects anisotropy of the spin–orbit interaction caused by the impurity of excited states [13], is the effective spin–orbit interaction constant, which is $(-)$ 180 cm^{-1} for a free ion, the z axis of the reference frame is parallel to the C_3 axis of the crystal.

Since the operator $l'_z + S_z$ commutes with the Hamiltonian, the energy levels can be described by the eigenvalues $m_j = \pm 1/2, \pm 3/2, \pm 5/2$. The characteristic equation for the magnetic quantum number $m_j = \pm 1/2$ can be obtained with the use of the corresponding wave functions $|l'_z, S_z\rangle$ [12, 13]. The solution of the equation can be found by introducing the parameter x defined by the relation $E = (1/2)\alpha\lambda(x + 3)$. In this case, $E(m_j = \pm 1/2)$ corresponds to three doublet energy levels. The states $m_j = \pm 1/2$ of the lower doublet can be represented in the form [12, 13] $|\pm 1/2\rangle = a|\mp 1,$

Table 1. Parameters a , b , and c for $p = 1.0$ in CoCO_3 [13]

p	α	Δ, cm^{-1}	a	b	c
1.0	1.2	−230	−0.59	0.69	−0.40

$\pm 3/2\rangle + b|0, \pm 1/2\rangle + c|\pm 1, \mp 1/2\rangle$. The normalization condition $a^2 + b^2 + c^2 = 1$, the value $g_{xy} = 4.55$, the relations $a : b : c = \frac{\sqrt{6}}{x} : -\frac{\alpha}{\alpha'} : \frac{\sqrt{8}}{x+2}$, the expression $\Delta = -\lambda \frac{\alpha^2}{\alpha'} \left(\frac{3}{x} + \frac{4}{x+2} \right) + \frac{\lambda\alpha}{2}(x+3)$, and Eqs. (2) for the g factors allow finding the quantities $g_z, \Delta, x, \alpha, a, b$, and c (the parameter $p = (\alpha/\alpha')^2$ is set to 0.6 to 2 [13]). The expressions for the g factors have the form [12]

$$g_z = 2 + \left[4(\alpha + 2) \left(\frac{3}{x^2} - \frac{4}{(x+2)^2} \right) \right] / \left(p + \frac{6}{x^2} + \frac{8}{(x+2)^2} \right), \quad (2)$$

$$g_{xy} = 4 \left(p + \frac{2\alpha}{x+2} + \frac{12}{x(x+2)} \right) / \left(p + \frac{6}{x^2} + \frac{8}{(x+2)^2} \right).$$

The lower doublet state can be described by the effective spin $s = 1/2$. Thus, the relation between the real spin $S = 3/2$ and the effective spin $s = 1/2$ can be written in the form $S_{xy} = \eta_{xy} S_{xy}, S_z = \eta_z S_z$ [16, 17]. According to [17], $J'\eta_{xy}^2 = 4(ac\sqrt{3} + b^2)^2 J' = J'_{xy}, J'\eta_z^2 = (3a^2 + b^2 - c^2)J' = J'_z, d_{xy} = d'\eta_{xy}^2$ for the ground state of the pair of ions in CoCO_3 . Here, J' is the isotropic exchange constant for the pair of ions. The quantities $g'_{xy} = \eta_{xy}^2$ and $g'_z = \eta_z^2$ (the g' factors), in particular, reflect the effect of the orbital momentum on the parameter J' . The values of a, b and c for α, p and Δ are given in [13] and in Table 1, J'_z is the effective exchange parameter along the C_3 axis.

3. ANISOTROPY OF EXCHANGE INTERACTION IN CoCO_3 CRYSTALS

We consider the exchange interaction of a pair of Co^{2+} ions in the environment of the nearest neighbors. There are five such neighbors for each ion in the pair and we determine their influence from the molecular field [14]. The initial Hamiltonian ($S = 3/2$) of the isotropic exchange interaction of the pair in the molecular field (in an arbitrary reference frame) has the form

$$\hat{H}^{\text{ex}} + JS_1 S_2 + \sum_{i,j=1}^5 J[S_1 \langle S_i \rangle + S_2 \langle S_j \rangle]. \quad (3)$$

Table 2. Hamiltonian (5) represented in the space of the corresponding wave functions

	Ψ_1	Ψ_2	Ψ_3	Ψ_4
Ψ_1	$(J/4)$ $\times [(g'_{xy} - g'_z)(g'^2_{xy}/g'^2)$ $\times \sin^2\theta + g'_z]$	$(J/2\sqrt{2})$ $\times [(g'_{xy} - g'_z)(g'_{xy}g'_z/g'^2)$ $\times \sin\theta \cos\theta]$	$-(id'/2\sqrt{2})(g'^2_{xy}/g')\sin\theta$	0
Ψ_2	$(J/2\sqrt{2})$ $\times [(g'_{xy} - g'_z)(g'_{xy}g'_z/g'^2)$ $\times \sin\theta \cos\theta]$	$(J/4)$ $\times [-2(g'_{xy} - g'_z)(g'^2_{xy}/g'^2)$ $\times \sin^2\theta + 2g'_{xy} - g'_z]$	$-5Jg'$	$-(J/2\sqrt{2})$ $\times [(g'_{xy} - g'_z)(g'_{xy}g'_z/g'^2)$ $\times \sin\theta \cos\theta]$
Ψ_3	$(id'/2\sqrt{2})(g'^2_{xy}/g')\sin\theta$	$-5Jg'$	$-(J/4)(2g'_{xy} + g'_z)$	$-(id'/2\sqrt{2})(g'^2_{xy}/g')\sin\theta$
Ψ_4	0	$(J/2\sqrt{2})$ $\times [(g'_{xy} - g'_z)(g'_{xy}g'_z/g'^2)$ $\times \sin\theta \cos\theta]$	$(id'/2\sqrt{2})(g'^2_{xy}/g')\sin\theta$	$(J/4)$ $\times [(g'_{xy} - g'_z)(g'^2_{xy}/g'^2)$ $\times \sin^2\theta + g'_z]$

Taking into account the anisotropic exchange and the Dzyaloshinskii–Moriya interaction, the effective Hamiltonian for the lower doublet ($m_j = \pm 1/2$) in the reference frame xyz can be written as

$$\begin{aligned} \hat{H} = & [J'_{xy}(s_{x1}s_{x2} + s_{y1}s_{y2}) + J'_z s_{z1}s_{z2}] \\ & + d_{xy}(s_{x1}s_{y2} - s_{x2}s_{y1}) - 5\{J'_{xy}[\langle s \rangle_x(s_{x1} - s_{x2}) \\ & + \langle s \rangle_y(s_{y1} - s_{y2})] + J'_z[\langle s \rangle_z(s_{z1} - s_{z2})]\}. \end{aligned} \quad (4)$$

Here, the first term in square brackets corresponds to the anisotropy of the exchange interaction energy of the pair and the second term is the Dzyaloshinskii–Moriya interaction and the molecular field, $\langle s \rangle$ is the temperature-average spin operator projected to the corresponding axes of the reference frame xyz . The exchange term written in the molecular-field approximation can be transformed to $(-5J'g'_z\langle s \rangle_z(s_{z1} - s_{z2}))$ by rotating the reference frame xyz to the angle β such that $\sin\beta = (g'_{xy}/g')\sin\theta$, $\cos\beta = (g'_z/g')\cos\theta$ [18], where θ is the angle between the z axis and the molecular field. At $T = 0$, Hamiltonian (4) can be written in the form

$$\begin{aligned} \hat{H} = & J' \{ [-(g'_{xy} - g'_z)(g'^2_{xy}/g'^2)\sin^2\theta + g'_{xy}]s_{x1}s_{x2} \\ & + g'_{xy}s_{y1}s_{y2} + [(g'_{xy} - g'_z)(g'^2_{xy}/g'^2)\sin^2\theta + g'_z]s_{z1}s_{z2} \\ & + (g'_{xy} - g'_z)(g'_{xy}g'_z/g')(s_{x1}s_{z2} + s_{z1}s_{x2})\sin\theta \cos\theta \\ & - (5/2)g'(s_{z1} - s_{z2}) \} \\ & - d'(s_{z1}s_{y2} - s_{y1}s_{z2})(g'^2_{xy}/g'^2)\sin\theta \cos 2\gamma. \end{aligned} \quad (5)$$

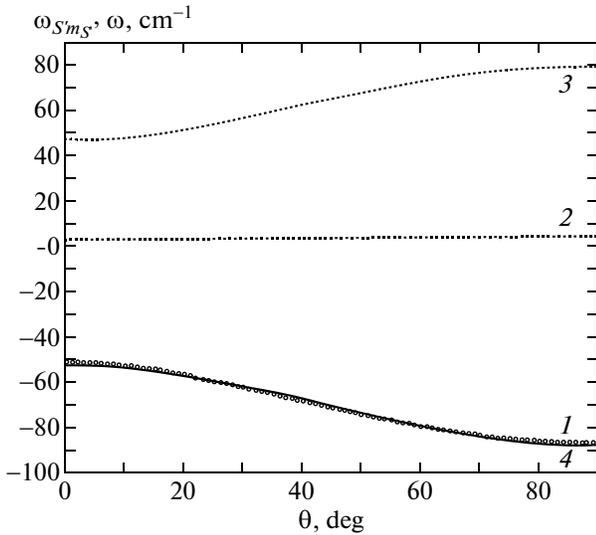
As is seen, under the assumption $g'_{xy} = g'_z = 1$, Eq. (5) corresponds to the Oguchi Hamiltonian [14] neglecting the Dzyaloshinskii–Moriya interaction. In

Eq. (5), the signs belonging to the other reference frame are omitted, $g' = \sqrt{q'^2_{xy}\sin^2\theta + g'^2_z\cos^2\theta}$, γ is the angle describing the deviation of the sublattice magnetic moment from the antiferromagnetic axis owing to the Dzyaloshinskii–Moriya interaction [19]. Hamiltonian (5) written in the space of the wave functions $\psi_1 = \alpha_i\alpha_j$, $\psi_2 = (1/\sqrt{2})(\alpha_i\beta_j + \beta_i\alpha_j)$, $\psi_3 = (1/\sqrt{2})(\alpha_i\beta_j - \beta_i\alpha_j)$, $\psi_4 = \beta_i\beta_j$ (where α_i , α_j and β_i , β_j are the wave functions of the spin 1/2 directed up and down, respectively, in the lattice sites i and j) is presented in Table 2. At this choice of the wave functions [13, 20], the energy levels of the pair are characterized by the spin $S' = 0$ and 1 (the diagonal components of pair Hamiltonian agree with [13, 20] under the condition $g'_{xy} = g'_z = 1$).

With the use of the above Hamiltonian, the characteristic equation can be written in the following form

$$\begin{aligned} & (A - \omega)[A - \omega(B - \omega)(C - \omega) \\ & - (1/4)(B - \omega)d^2(g'^4_{xy}/g'^2)\sin^2\theta \\ & - (1/4)(C - \omega)J'^2(g'_{xy}g'_z/g'^2)(g'_{xy} - g'_z)^2\sin^2\theta \cos^2\theta \\ & - 25(A - \omega)g'^2J'^2] \\ & + (1/16)d^2J'^2(g'^4_{xy}/g'^2)(g'_{xy}g'_z/g'^2)^2(g'_{xy} - g'_z)^2 \\ & \times \sin^4\theta \cos^2\theta = 0. \end{aligned} \quad (6)$$

Here, $A = (1/4)J'[(g'_{xy} - g'_z)(g'^2_{xy}/g'^2)\sin^2\theta + g'_z]$, $C = -(1/4)J'(2g'_{xy} + g'_z)$, $B = (1/4)J'[-2(g'_{xy} - g'_z)(g'^2_{xy}/g'^2)\sin^2\theta + 2g'_{xy} - g'_z]$.



(1–3) Dependences of the energy levels of the Co^{2+} ion $\omega_{S'm_S}$ on the angle θ in CoCO_3 crystals according to calculations for (1) the lower energy level, $S' = 1, m_{S'} = -1$; (2) two energy levels, $S' = 0$ and $1, m_{S'} = 0$; and (3) the upper energy level, $S' = 1, m_{S'} = 1$. (4) Fitting function ω (solid curve).

In this work, we calculated the angular dependence of the energy levels of a Co^{2+} ion in a CoCO_3 crystal for the case of (see Table 1) $\Delta = -230 \text{ cm}^{-1}$, $p = 1.0$, $\alpha = 1.2$; $J = 5.12 \text{ cm}^{-1}$, $g'_{xy} = 3.24$, $g'_z = 1.90$, $d' = 1.63 \text{ cm}^{-1}$.

The Dzyaloshinskii constant d' was determined from the ratio of the experimental Dzyaloshinskii and exchange fields and the relation between d' and J [1, 9].

The results are presented in the figure. Curves 1 and 3 correspond to the lower and upper energy levels of a Co^{2+} ion in a CoCO_3 crystal ($S' = 1, m_{S'} = -1$ and $S' = 1, m_{S'} = 1$). The values of the spin S' and $m_{S'}$ can be found from the dependence of the energy levels on the angle θ . In particular, the curve 2 corresponds to two energy levels independent of the angle, which is the case for $S' = 0$ or 1 and $m_{S'} = 0$. The solid fitting curve (4) for the lowest energy level at $T = 0$ is described by the function $\omega = 2[(b/2) + (a_{\text{ex}}/2)\cos^2\theta] \text{ cm}^{-1}$ (its angular part corresponds to the magnetic anisotropy energy per one Co^{2+} ion in the CoCO_3 crystal). Here, $a_{\text{ex}} = 35.2 \text{ cm}^{-1}$ is the anisotropic exchange constant. The values of a_{ex} are nearly independent of p , α , and Δ , at least within the ranges of the parameters given in Table 2 and in [13].

The theoretical value $a_{\text{ex}} = 35.2 \text{ cm}^{-1}$ is the closest to the experiment [8] (24.9 cm^{-1}). However, the discrepancy between the calculation in [8] is approximately 5 cm^{-1} if one takes into account the experimental error [8]. It is worth mentioning that in [8] the

intensity of the peak caused by the single-magnon transition and partly responsible for the magnitude of the uniaxial anisotropy field in CoCO_3 is quite low. This remained unclear to Eremenko et al. [8]. They noted that the intensities of single-magnon light scattering and exciton lines were of the same order of magnitude for all previously studied antiferromagnetic compounds of the Co^{2+} ion, which was not observed in the experiment [8]. This fact inspires some doubts in the purity of the CoCO_3 samples used in [8]. An approximately 17% discrepancy between the experiment [8] and the calculation apparently can be explained by the effect of impurities.

4. DIPOLE CONTRIBUTION TO THE ANISOTROPY ENERGY

The detailed calculation of the contribution of the dipole–dipole interactions to the anisotropy energy of the crystals with the calcite structure was performed in [21] without inclusion of the inequivalence of the g factors. The expression for the anisotropy energy determined by the dipole–dipole interactions taking into account the non-equivalent values of the g factors ($g_{xy} = 4.55$ [13], $g_z = 3.21$) has the form

$$a_{\text{dip}} = [(g_z \beta S)^2 / (a_{\text{H}}^3 \times 10^{-24})] [1 + (1/2)(g_{xy}/g_z)^2] \times [a_{\text{H}}^3 S_{0,0,1/2}^z + 2a_{\text{H}}^3 S_{2/3,2/3,1/6}^z - a_{\text{H}}^3 S_{0,0,0}^z - 2a_{\text{H}}^3 S_{1/3,1/3,1/3}^z].$$

Here, $a_{\text{H}} = 4.641 \text{ \AA}$ and $c_{\text{H}} = 15.023 \text{ \AA}$ are hexagonal lattice constants in the basis plane and along the C_3 axis, respectively; $a_{\text{H}} S_{i_1, i_2, i_3}^z$ are the lattice sums given in [15], $a_{\text{H}}^3 \sum S_{i_1, i_2, i_3}^z = 5.01$. As a result, one has $a_{\text{dip}} = 0.92 \text{ cm}^{-1}$.

5. CONCLUSIONS

It was shown that the method of the performed calculation can be used to estimate the uniaxial magnetic anisotropy in compounds containing Co^{2+} ions in the axial crystal field. Comparison of the contributions to the uniaxial anisotropy constant found by the proposed method with the results of [8] indicates the presence of impurities in the samples of [8].

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