Uniaxial and basal plane anisotropy caused by Cr^{2+} impurity ions in $CrBO_3$ crystals

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ABSTRACT

In this study, the uniaxial and basal anisotropy governed by Cr^{2+} impurity ions was treated based on the Cr^{2+}– BO_3^{3-} ion vacancy model using single ion approximation. The anomalous behavior of the basal anisotropy at low temperatures was predicted.

1. Introduction

$CrBO_3$ single crystals (calcite type structure) were synthesized using the gas-transport technique for the first time in 1964 [1]. Chromium borate is an antiferromagnet with a Neel temperature T_N of 15 K [2]. $CrBO_3$ crystals have a trigonal unit cell with R-$3c$ symmetry. The crystal structure of $CrBO_3$ is shown in Fig. 1.

The Cr ions are located in octahedra formed by oxygen ions bound to boron ions via strong covalent bonds. The C_3 axis of the crystal is the c axis in Fig. 1. The $CrBO_3$ compound has been poorly investigated. In particular, Bither et al. [2] showed that the magnetic properties of the $CrBO_3$ crystal can be described based on a simple model of a collinear two-sublattice antiferromagnet with magnetic moments along a third-order axis C_3. However, based on static magnetic measurements, Balaev et al. [3] suggested that it is more probable that the antiferromagnetism vector of $CrBO_3$ lies in a plane close to the basal plane. Moreover, Balaev et al. found [3] that the magnetization produced along mutually perpendicular crystallographic directions in the basal plane might imply that neither of these two directions is the easiest magnetization axis, and thus some anisotropy exists in the basal plane of the crystal.

In order to estimate the effects of various microscopic sources of this magnetic anisotropy, we performed theoretical calculations and compared them with data obtained from a series of different experiments. We propose a uniaxial and basal plane anisotropy model based on the Cr^{2+}– BO_3^{3-} ion vacancy using single ion approximation.

2. Phenomenological description of the magnetic anisotropy in $CrBO_3$ crystals

The Cr^{3+} ion has a spin $s = 3/2$ and the terms of fourth order in the free energy responsible for the single-ion and "single-ion" exchange anisotropy are absent for a pure $CrBO_3$ crystal. The expansion of the free energy in the polar coordinate system associated with the crystal axes ($z||c_3$, $y||c_2$) has the form [4,5]:

$$\Phi = (1/2)B\mathbf{m}^2 - m_\perp h_\perp, \qquad (1)$$

where B is the exchange constant, $\mathbf{m} = (\mathbf{M}_1 + \mathbf{M}_2)/M$, $M = 2|\mathbf{M}_1| = 2|\mathbf{M}_2| = Ng\mu_B sB_{3/2}(x)$, N is the Avogadro constant, g is a spectroscopic splitting factor, μ_B is the Bohr magneton, and $B_{3/2}(x)$ is the Brillouin function for the spin 3/2. The external magnetic field $H_\perp = h_\perp/M$ lies in the basal plane of the $CrBO_3$ crystal. From the minimization of (1), it follows that [5]:

$$m_\perp = \sqrt{m_x^2 + m_y^2} = \sqrt{(h_x^2 + h_y^2)/B^2} = \sqrt{2}\, m_y = \sqrt{2}\, h_y/B$$

Calculating the dipole field contribution to the uniaxial anisotropy gives the value: $H_{dip}(Cr^{3+}) = (a_{dip}/M) = 2.11$ kOe [6].

The single-ion anisotropy value based on a number of isostructural diamagnetic crystals MBO_3 (M = In, Sc, Lu) with a Cr^{3+} admixture was estimated using the electron paramagnetic resonance (EPR) method by Vorotynov et al. and large negative values were obtained [7]. These values are significantly higher than the absolute values of the dipole contributions. The contribution of the "single-ion" exchange value can be neglected due to the low Néel temperature. Thus, according to these estimates, the sublattice magnetic moments of the Cr^{3+} ions must lie along the triad axis of the $CrBO_3$ crystal, which is in agreement with the results obtained by Bither et al. [2]. The source of the basal plane anisotropy (as observed by Balaev et al. [3]) is investigated in the present study based on the Cr^{2+}– BO_3^{3-} ion vacancy model [8].

The oxygen and boron ions form strong covalent bounds, and thus they can exist in a solution-melt at the crystal growth temperatures as a whole BO_3^{3-} ion. The ions are spatially extended and it is difficult for them to be incorporated into a growing crystal. Thus, vacancies of these groups as well as Cr^{2+} impurities occur as a result (see Fig. 2).

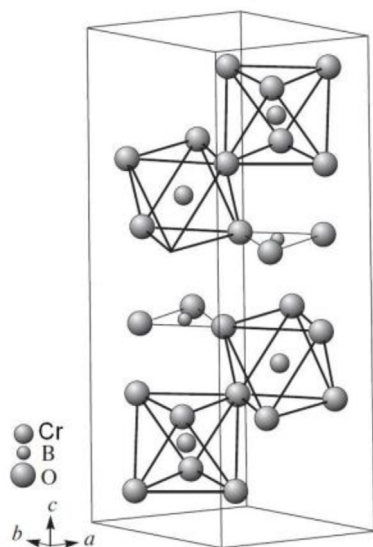Some of the vacancies were apparently compensated for by Pb^2 the

Fig. 1. Crystal structure of CrBO3. Not all of the atoms are shown for simplicity.
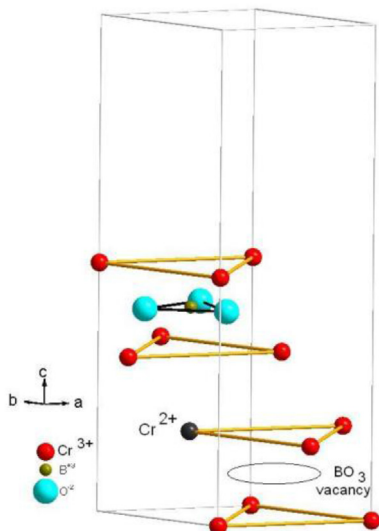

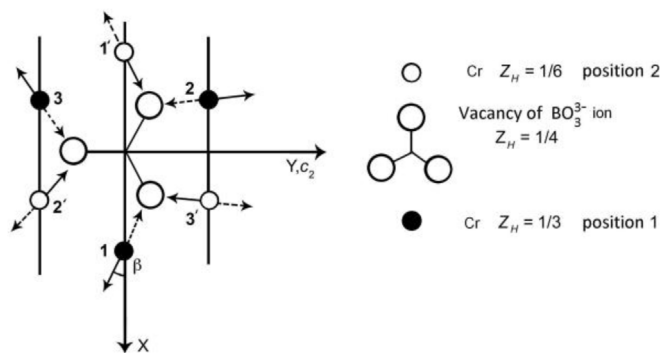Fig. 2. Cr^{2+}– BO_3^{3-} ion vacancy model. Not all of the atoms are shown.

Fig. 3. Crystal field orientations of Cr^{2+} positions due to BO_3^{3-} ion vacancies (complex 1). Z_H is the coordinate along the c_3 axis.

Fig. 4. Crystal field orientations of Cr^{2+} positions due to BO_3^{3-} ion vacancies (complex 2). Z_H is the coordinate along the c_3 axis.

observed upon rotation of the external field in the basal plane (in the experiment) or when the effective basal anisotropy becomes equal to the potential barrier under the action of temperature.

Figs. 3 and 4 show the distributions of the crystal field axes based on the BO_3 vacancies on the Cr^{2+} ions. The dashed and solid arrows denote the negative and positive components on the Z axis, respectively. The Z axis is perpendicular to the plane in the figure. The Z_H coordinates of the borate groups and chromium ions are presented along the third-order axis in the hexagonal setting. The X axis lies in the crystal symmetry plane.

In our experiment, the electrons moved around the vacancies in complexes 1 and 2 when an applied magnetic field with a certain value rotated in the basal crystal plane (see Figs. 3 and 4). Both the basal plane (hexagonal) and uniaxial anisotropies were observed at certain values for the external magnetic field rotating in the basal plane as well as the temperature and crystal complex parameters.

After further considering the Cr^{2+} impurity anisotropy, we neglected the terms of the fourth power of the angular variables. In addition, we assumed that the Cr^{2+}–Cr^{3+}–Cr^{2+} exchange interaction in $CrBO_3$ is induced by the external magnetic field in the basal plane of the crystal. The anisotropy energy related to a single Cr^{2+} ion for two nonequivalent positions can be written in the form:

$$
\begin{aligned}
E_\alpha = {}& (1/2)(B_{11} + B_{22}) + [B_{33} - (1/2)(B_{11} + B_{22})]\cos^2\theta_i' \\
& + (1/2)(B_{11} - B_{22})\cos 2(\phi_i' + \alpha \pm \beta)\sin^2\theta_i' \\
& + B_{12}\sin 2(\phi_i' + \alpha \pm \beta)\sin^2\theta_i' + B_{13}\cos(\phi_i' + \alpha \pm \beta)\sin 2\theta_i' \\
& + B_{23}\sin(\phi_i' + \alpha \pm \beta)\sin 2\theta_i',
\end{aligned}
\tag{2}
$$

where B_{ij} are the components of the symmetrical second rank tensor in energy units per ion, θ_i' and ϕ_i' are the polar and azimuthal angles for the i-sublattice magnetic moments, respectively, and β is the angle between the crystal electric field axes of divalent chromium ions and the crystal symmetry planes in the Cr^{2+}– BO_3^{3-} ion vacancy model (see Figs. 3 and 4). We set the angles for the antiferromagnetism vector $\mathbf{l} = (\mathbf{M}_1 - \mathbf{M}_2)/M$ ($\mathbf{M}_1$ and $\mathbf{M}_2$ are the chromium magnetic moments for the open and closed circles sites in Figs. 3 and 4, respectively) as $\theta_1' = \theta'$, $\theta_2' = \pi - \theta'$, $\phi_1' = \phi'$, $\phi_2' = \phi' + \pi$, and α with values of 0, −120, −240°.

The relative concentrations c_n^0 and constants describing the distribution of Cr^{2+} impurities in $CrBO_3$ over n "directions" at equilibrium conditions can be derived by solving the kinetic equations [8]. In the present study, the n "direction" corresponds to α. The impurity anisotropy of the antiferromagnetism vector energy per mole of $CrBO_3$ up to a quadratic term in the expansion can be represented in the form [8]:

$$
E = Nc_0 \sum_n^3 c_n^0 E_n \cong (Nc_0/3)\left[\sum_n E_n - (1/kT) \sum_n E_n^2 \right],
\tag{3}
$$

where N is the Avogadro number, c_n^0 is the relative concentration of the impurity ions in the n "direction," c_0 is the impurity concentration, k is

oxide and fluoride were used as solvents during $CrBO_3$ crystal growth [9]. The relative concentration of the BO_3 vacancies is $<\ <1$. The vacancy is surrounded by the six nearest chromium ions, one of which is Cr^{2+} (Figs. 2–4). The electron motion around the BO_3 vacancy is
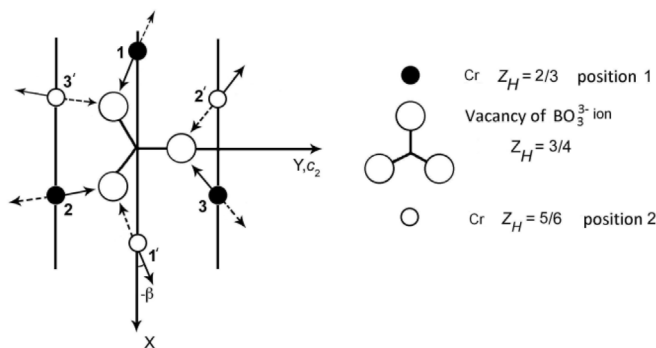
the Boltzmann constant, and T is the temperature. It is assumed that the sign of the constant for the uniaxial impurity anisotropy a' is positive. Calculating (3) by considering (2) written in terms of the antiferromagnetism vector yields the following expressions (per mole $CrBO_3$):

$$E = Nc_0(1/2)a' \cos^2 \theta' - Nc_0 D' \sin^3 \theta' \cos \theta' \cos(3\phi' - \psi)$$

$$Nc_0(a'/2)\cos^2 \theta' = Nc_0[B_{33} - (1/2)(B_{11} + B_{22})]\cos^2 \theta',$$
$$Nc_0 D' = (Nc_0 \cos \beta \cos 2 \beta / kT)[2B_{12}B_{23} - (B_{11} - B_{22})B_{13}],$$
$$\text{tg}\psi = \frac{(B_{11} - B_{22})B_{23} + B_{12}B_{13}}{(B_{11} - B_{22})B_{13} - B_{12}B_{23}}.$$

where ψ, θ', and ϕ' are the phase, polar, and azimuthal angles respectively, for the antiferromagnetism vector of the Cr^{2+} impurities in $CrBO_3$ (ψ is equal to 90° based on considerations of symmetry; see below).

The equilibrium base plane anisotropy governed by the Cr^{2+} ions can be derived from the minimization of the free energy [10,11], including the expressions for the base and uniaxial anisotropy, as well as the exchange invariant written in terms of the Cr^{2+} and Cr^{3+} antiferromagnetism vectors. Analogous to previous studies [10,11] (according to the identical symmetry of the $CrBO_3$ and $FeBO_3$ crystals), the energy of the impurity equilibrium base plane anisotropy has the form:

$$\omega_q \sin^6 \theta \cos 6 \phi = -Nc_0(D'^2/4a')\sin^6 \theta \cos(6\phi - 2\psi) \text{ for } \psi = 90^0.$$

We note that Cr^{2+} ion is rarely detected by EPR method [12], e.g., the axial constant value is $|D| = 2.24$ cm^{-1} in $CrSO_4 \cdot 5H_2O$ (the spin-Hamiltonian term $D[s_z^2 - (1/3)s(s + 1)]$ with a small rhombic symmetry and g-value close to 2).

3. Microscopic description of the uniaxial and basal hexagonal anisotropy governed by Cr^{2+} impurity ions in $CrBO_3$ crystals

The single-ion spin-Hamiltonian for the impurity Cr^{2+} ion for the lowest symmetry case is [8,10,11]:

$$H = g\mu_B \mathbf{H}_i^{eff} s_i' + A_2^0 O_{2i}^0 + A_2^1 O_{2i}^1 + A_2^2 O_{2i}^2 + \widetilde{A}_2^1 \widetilde{O}_{2i}^1 + \widetilde{A}_2^2 \widetilde{O}_{2i}^2,$$

where $i = 1$ and 2 correspond to the first and second Cr^{2+} ion positions in the lattice, respectively, the first term describes the isotropic exchange energy in the mean-field approximation, H_i^{eff} denotes the exchange field Cr^{3+} ions produced on Cr^{2+} sites, s_i' denotes the spin of Cr^{2+} ions, the spin operators O_j^l and $\widetilde{O}_j^l$ and their matrix elements were defined by Altshuler and Kozyrev [13], and $A_2^0, A_2^1, A_2^2, \widetilde{A}_2^1, \widetilde{A}_2^2$ are the spin-Hamiltonian constants. Solving the eigenvalues for this Hamiltonian yields an expression for the energy levels obtained in the first order of perturbation theory:

$$E_{i\alpha m_i} = g\mu_B H_i^{eff} m_i +$$
$$\begin{bmatrix} \frac{A_2^0}{2}(3\cos^2 \theta_i' - 1) + \frac{A_2^1}{4}\sin 2\theta_i' \cos(\phi_i' + \alpha \pm \beta) + \\ \frac{\widetilde{A}_2^1}{4}\sin 2\theta_i' \sin(\phi_i' + \alpha \pm \beta) + \\ + \frac{A_2^2}{2}\sin^2 \theta_i' \cos 2(\phi_i' + \alpha \pm \beta) \\ + \frac{\widetilde{A}_2^2}{2}\sin^2 \theta_i' \sin 2(\phi_i' + \alpha \pm \beta) \end{bmatrix} \times (3m_i^2 - 6),$$

(4)

where m_i is the magnetic quantum number for the i-th Cr^{2+} ion, the n "direction" takes the values of 0, $-120, -240°$ according to the symmetry of the BO_3^{3-} ion vacancy, and the angle β is denoted in Figs. 3 and 4. We write the free energy in the form:

$$F = -(Nc_0 kT/2) \sum_i \ln Z_i, \quad Z_i = \sum_{im_i} \exp(-E_{im_i}/kT),$$

(5)

where m_i is the magnetic quantum number for the i-th ion. The procedure used for calculating the free energy is given in detail by Ovchinnikov et al. [14]. Comparing expressions (2) and (4) subject to (5)

implies a connection between the microscopic and phenomenological energy anisotropy constants per ion:

$$(a'/2) = B_{33} - (1/2)(B_{11} + B_{22}) = 9A_2^0(z_7/z_6),$$
$$(B_{11} - B_{22}) = 6A_2^2(z_7/z_6),$$
$$B_{12} = 3\widetilde{A}_2^2(z_7/z_6),$$
$$B_{13} = (3/2)A_2^1(z_7/z_6),$$
$$B_{23} = (3/2)\widetilde{A}_2^1(z_7/z_6),$$

$$(z_7/z_6) = \frac{Y^4 - (1/2)Y^3 - Y^2 - (1/2)Y + 1}{Y^4 + Y^3 + Y^2 + Y + 1},$$
$$Y = \exp[-g\mu_B H^{eff}/kT], \quad H^{eff}(0) = 1.91 \cdot 10^5 \text{ Oe [3]};$$

where $g = 1.98$ [7], μ_B is the Bohr magneton, $H^{eff} = H^{eff}(0)B_{3/2}(x)$, and $B_{3/2}(x)$ is the Brillouin function for the sublattice magnetic moment with $s = 3/2$. The final expression for the energy of the uniaxial and base plane anisotropy governed by the Cr^{2+} ions per mole takes the form:

$$Nc_0(a'/2)\cos^2 \theta' = 9Nc_0 A_2^0(z_7/z_6)\cos^2 \theta',$$
$$\omega'_q(Cr^{2+})\sin^6 \theta' \cos 6\phi' = (Nc_0 D'^2/4a')\sin^6 \theta' \cos 6\phi'$$
$$= [Nc_0 A_{imp}/(kT)^2](z_7/z_6)\sin^6 \theta' \cos 6\phi',$$

and the effective constants A_2^0 and A_{imp} are expressed in energy units, and they have first and third degree dimensions, respectively. Fig. 5 presents the normalized temperature dependency of the uniaxial anisotropy governed by Cr^{2+} impurities. Fig. 6 shows the normalized temperature dependency of the energy of the basal plane hexagonal anisotropy.

The intensive growth of the base plane anisotropy can be seen at low temperatures: $\omega'_q(Cr^{2+})\sin^6 \theta \cos 6 \phi$.

4. Conclusion

In this study, calculations performed based on the $Cr^{2+} - BO_3^{3-}$ ion vacancy model confirmed the existence of base plane anisotropy [3] in the uniaxial antiferromagnet $CrBO_3$ governed by Cr^{2+} impurities. As observed by Balaev et al. [3], the features with an external magnetic field growing from $5.5 \cdot 10^4$ up to $6.5 \cdot 10^4$ Oe may be explained by the proposed model and they develop more clearly at temperatures below 2 K (see Fig. 6).
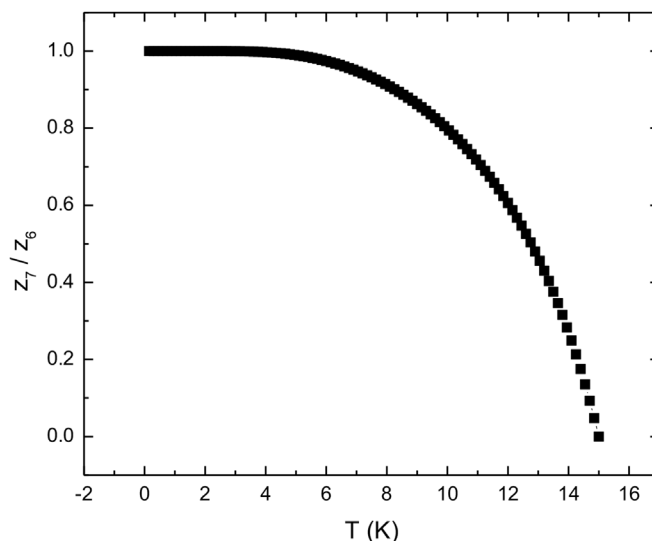

Fig. 5. Normalized temperature dependency of the uniaxial anisotropy governed by Cr^{2+} impurities in the $CrBO_3$ crystal.
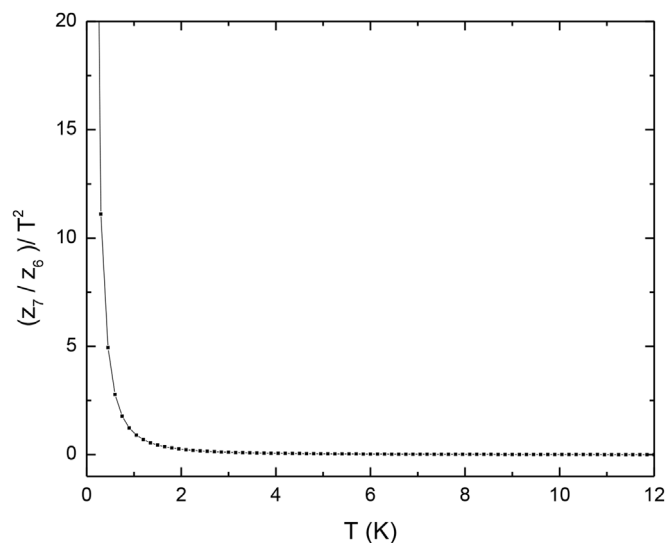
Fig. 6. Normalized temperature dependency of the energy of the base plane anisotropy governed by Cr^{2+} impurities in the $CrBO_3$ crystal.

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