MAGNETISM
AND FERROELECTRICITY

Temperature Dependence of the Uniaxial Magnetic Anisotropy of Rhombohedral Antiferromagnetic Crystals with Ions in the S state

S. G. Ovchinnikov, V. V. Rudenko*, and V. I. Tugarinov

Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences,
Akademgorodok 50, Krasnoyarsk, 660036 Russia

* e-mail: rvv@iph.krasn.ru

Received February 18, 2009; in final form, May 12, 2009

Abstract—The contributions of the anisotropic exchange to the first- and second-order uniaxial anisotropy constants have been calculated for hematite at $T = 0$ K and arbitrary temperatures. The results of the calculations and the most significant mechanisms are taken into account in interpreting the temperature dependence of the anisotropy in rhombohedral antiferromagnetic crystals. The first-order anisotropy constant for hematite is described by the dipole interaction, contributions of the "single-ion" nature, and relatively small contributions of the anisotropic exchange. The second-order constant for hematite includes the "single-ion" contribution and the contribution of the anisotropic exchange. For $FeBO_3$ and $MnCO_3$ crystals, the main contributions to the first-order anisotropy constant come from the dipole and single-ion mechanisms.

A theoretical study by Nikiforov et al. [1], who calculated the anisotropy within the two-ion model, has long escaped notice by experimenters. This partially explains why the progress in the study of the anisotropy from the methodological viewpoint was absent for several decades. Only much later, there appeared works that included experimental investigations [2–4] and were devoted to a new mechanism of the "single-ion" exchange anisotropy following from the study performed in [1]. For example, in a number of magnetically concentrated crystals [3, 4], the quantitative evaluations of the anisotropy with due regard for the "single-ion" exchange mechanism solved the problem of achieving agreement with experimental data. However, in order to interpret the temperature dependence of the anisotropy, particularly in hematite, the anisotropic exchange should be taken into account [5] in addition to the "single-ion" exchange contribution and the contributions of other mechanisms. Unlike the research reported in [5], the present study has resulted in the analytical expressions obtained for the anisotropy fields. The relationships have also been established between the spin-Hamiltonian constants and the effective anisotropy fields. Filling the gap in the literature, the anisotropy exchange contribution to the second-order anisotropy constant has been calculated for the hematite.

There are two pairs of most closely spaced ions in the unit cell of the hematite (with the axis coinciding with the C_3 direction), which determine the effective crystal field with a high accuracy. This is supported by the electron paramagnetic resonance (EPR) measurements performed with Fe^{3+} and Cr^{3+} pairs in the isostructural corundum crystal [6, 7].

For a pair of iron ions in the hematite that interact with the nearest neighbors, the Hamiltonian, which describes the uniaxial exchange anisotropy in the coordinate system xyz and is located on one of the ions, can be written in the form [1, 5]

$$\mathcal{H} = \sum_j g\beta \mathbf{H}_j^{\text{eff}} \mathbf{s}_j + A_E s_{z1} s_{z2} + B_E O_{21}^0 O_{22}^0 + C_E O_{31}^0 O_{12}^0. \quad (1)$$

Here, the first term represents the isotropic exchange energy within the molecular field approximation and the other terms describe the anisotropic exchange energy written in terms of spin and equivalent spin operators. It is assumed that the isotropic exchange energy is much greater than the energy of anisotropic terms in the Hamiltonian.

Let us find the energy of a pair of ions with an accuracy of up to the first order of the perturbation theory. The isotropic part of the Hamiltonian is reduced to a diagonal form by rotating the coordinate system through the angles θ_j and φ_j, which determine the

exchange field direction. Then, Hamiltonian (1) takes the form

$$\mathcal{H} = \sum_j g\beta H_j^{\text{eff}} s_{zj} + A_E \cos\theta_1 \cos\theta_2 s_{z1} s_{z2}$$

$$+ (B_E/4)(3\cos^2\theta_1 - 1)(3\cos^2\theta_2 - 1)O_{21}^0 O_{22}^0$$

$$+ (C_E/12)(25\cos^3\theta_1 - 13\cos\theta_1)\cos\theta_2 O_{31}^0 O_{12}^0.$$

Here, the off-diagonal terms are omitted.

Let us calculate the energy. In the rotated coordinate system (located on the ion 1), setting the magnetic quantum number $m = m_1 = -m_2$, we introduce the angles for the antiferromagnetic vector: $\theta_1 = \theta$, $\theta_2 = \pi - \theta$, $\varphi_1 = \varphi$, and $\varphi_2 = \varphi + \pi$. We assume that the direction of spins 1 and 2 coincides with the corresponding exchange field direction. Then, the lower level (at a temperature of 0 K) including the energies in the zeroth and first approximations will take the form

$$(W^0 + W')_{m = -5/2} = -\sum_j g\beta \left| H_j^{\text{eff}} \right| s + A_E s^2 \cos^2\theta$$

$$+ B_E s^2 (s - 1/2)^2 (9\cos^4\theta - 6\cos^2\theta + 1)$$

$$+ (C_E/12)s^2(2s^2 - 3s + 1)(25\cos^4\theta - 13\cos^2\theta).$$

By multiplying the obtained expression by (N) (where N is the Avogadro number) and comparing with the thermodynamic potential

$$\Phi = (a/2)\cos^2\theta + (c/2)\cos^4\theta, \qquad (2)$$

we write the anisotropy constants as

$$a(0) = (N)[2A_E s^2 - 12B_E s^2 (s - 1/2)^2$$

$$- (13C_E/3)s^2(s - 1/2)(s - 1)],$$

$$c(0) = (N)[18B_E s^2 (s - 1/2)^2$$

$$+ (25C_E/3)s^2(s - 1/2)(s - 1)].$$

As can be seen from the expressions for the anisotropy constants, the terms at B_E and C_E are zero for $s = 1/2$ and $s \leq 1$, respectively.

Let us calculate the temperature dependence of the anisotropy constants. To do this, we write the free energy per mole of a substance as

$$F = -(NkT)\ln \sum_{m_1 m_2} \exp(-g\beta H_j^{\text{eff}} m_j / kT)$$

$$\times \exp\{(A_E/kT)m_1 m_2 \cos^2\theta - (B_E/4kT)$$

$$\times [3m_1^2 - s(s+1)][3m_2^2 - s(s+1)](3\cos^2\theta - 1)^2$$

$$+ (C_E/12kT)[5m_1^3 - (3s(s+1) - 1)m_1]m_2$$

$$\times (25\cos^3\theta - 13\cos\theta)\cos\theta\}.$$

Now, expanding the free energy in a series in powers of a small parameter (the ratio of the anisotropy constants to kT), summarizing over m_1 and m_2, and then comparing with Eq. (2), we obtain the following expressions for the uniaxial anisotropy constants as a function of temperature:

$$a = (N)[(A_E/2)(z_4/z_0)^2 - 12B_E(z_1/z_0)^2$$

$$- (13C_E/4)(z_3 z_4/z_0^2)],$$

$$c = N[18B_E(z_1/z_0)^2 + (25C_E/4)(z_3 z_4/z_0^2)].$$

We write the expressions for the anisotropy fields H_A and H_c as the temperature dependences of the effective field constants of the second and fourth orders on the Fe^{3+} ion in the hematite. In so doing, one more dipole expression and two more expressions of the "single-ion" nature are taken into account [1, 4, 8]; that is,

$$H_A = (A'_{\text{dip}} + A'_E)(z_4/5z_0) + B'_E(z_1^2/5z_0 z_4)$$

$$+ C'_E(z_3/5z_0) + D'_c(-z_1/z_4) + E'_c(-5z_2/z_4),$$

$$H_c = -(3/2)B'_E(z_1^2/5z_0 z_4) - (25/13)C'_E(z_3/5z_0)$$

$$- (7/6)E'_c(-5z_2/z_4).$$

Here, the coefficients are the values of the anisotropy fields at $T = 0$ K, and A'_{dip} is the directly calculated dipole field in the magnetically concentrated crystal: when fitting, it is assumed to be a fixed parameter. This is because the adequacy of the dipole calculations has been proved, for example, for MnF_2 crystals, when the quantitative calculations [9] and the calculations of the temperature dependence within the spin-wave theory [10] are compared with the experiment. Here, $A'_E = (5/2)(A_E/g\beta)$ is the anisotropic exchange field (the second term in Hamiltonian (1)); $B'_E = -60(B_E/g\beta)$ is the anisotropic exchange field (the third term in Hamiltonian (1)); $C'_E = -(65/4)(C_E/g\beta)$ is the anisotropic exchange field (the last term in Hamiltonian (1)); D'_c is the total "single-ion" anisotropy field determined by the second-order invariants [4, 8] (which includes the contributions of "single-ion" and "single-ion" exchange mechanisms); E'_c is the "single-ion" field corresponding to the fourth-order invariants [4, 8], which was not included in [5];

$$z_0 = (Y^5 + Y^4 + Y^3 + Y^2 + Y + 1)Y^{5/2},$$
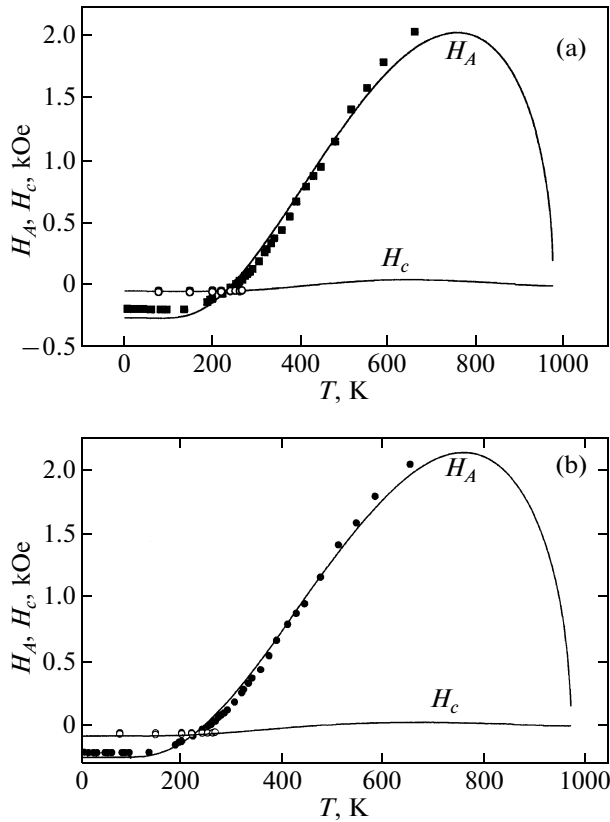
Fig. 1. Temperature dependences of the uniaxial anisotropy fields H_A and H_c for hematite: (a) the first version of fitting and (b) the second version of fitting. Points are the experimental data taken from [12, 13], and solid curves indicate the results of the calculations.

$$z_1 = (-5Y^5 + Y^4 + 4Y^3 + 4Y^2 + Y - 5)/Y^{5/2},$$

$$z_2 = (-Y^5 + 3Y^4 - 2Y^3 - 2Y^2 + 3Y - 1)/Y^{5/2},$$

$$z_3 = (-5Y^5 + 7Y^4 + 4Y^3 - 4Y^2 - 7Y + 5)/Y^{5/2},$$

$$z_4 = (-5Y^5 - 3Y^4 - Y^3 + Y^2 + 3Y + 5)/Y^{5/2},$$

$$Y = \exp(-2x/5);$$

$$x = (5g\beta H^{\text{eff}}/2kT) = (15/7)(T_N/T)B_{5/2}(x),$$

H^{eff} is the effective exchange field on the Fe^{3+} ion; and $B_{5/2}(x) = (z_4/5z_0)$ is the Brillouin function.

Obtained in the numerical form and normalized to unity at $T = 0$ K, the temperature dependences of the anisotropy fields (determining the values of H_A and H_c) agree with the corresponding curves described in [5].

Altogether, we have used five fitting functions. The temperature dependences of the functions, which describe the anisotropic exchange and the single-ion interaction by the second-order terms, are sufficiently similar in behavior. The temperature dependences of

the functions due to the fourth-order terms (at the constants B'_E, C'_E, and E'_c) are also similar in their behavior. Therefore, the factors such as the experimental error, the use of the Brillouin functions instead of the magnetization, the lack of precise data on the Néel temperature (we used $T_N = 972$ K [11]), and a great number of fitting parameters can lead to erroneous results. In order to demonstrate that using a great number of functions can yield a mistake, we fitted the value of H_A with five independent parameters. Having done this, we obtained the solution $A'_E = -13.00$, $D'_C = 10.77$, $C'_E = -43.99$, $E'_C = 13.55$, and $B'_E = 22.42$ kOe with the absolute minimum value of the root-mean-square deviation $\sigma_A = 0.0001$ kOe. Now, if we use these data to determine the value of H_c, we find it to be 35.16 kOe, while its experimental value is 0.06 kOe [12]. Therefore, we tried to obtain a matched solution for the effective fields of the first- and second-order anisotropy constants from the temperature dependence for the hematite using the minimum number of fitting parameters. Moreover, we took into account the electron paramagnetic resonance data, which allowed the quantitative evaluation to be performed independently by using diamagnetic analogs doped with ions of the magnetically concentrated substance [4].

The calculations have demonstrated that, when using from three to five fitting parameters with this form of the functions, there exist local minima along with the absolute minimum of the root-mean-square deviation.

As the first step, fitting was carried out for the field H_c by the least-squares method, and the following parameters were obtained: $B'_E = -4.96$, $C'_E = 5.22$, and $E'_C = -2.17$ kOe, with the root-mean-square deviation $\sigma_c = 0.004\sigma$ kOe being the absolute minimum. Then, the values of these parameters were substituted into the expression for H_A, and the other two constants were determined: $A'_E = 0.11$ and $D'_c = -8.51$ kOe, with the root-mean-square deviation $\sigma_A = 0.17$ kOe being the absolute minimum as well. Note that these results reflect the quantitative evaluation of the "single-ion" contributions corresponding to $D'_c = -8.5$ kOe and $E'_c = -0.8$ kOe determined by the EPR method [4]. The results of fitting are presented in Fig. 1a (version 1).

The next step was a combined fitting of the effective fields of the first and second-order anisotropy constants by the least-squares method, provided that $\sigma_A + \sigma_c = \min$. The solution was obtained for one of the local minima, which also reflected the quantitative evaluation of the parameters from the EPR data: $A'_E = 3.20$, $D'_c = -12.57$, $C'_E = 2.64$, $E'_c = -0.97$, and $B'_E = $
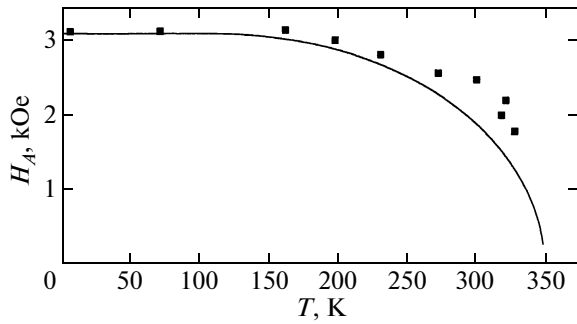
Fig. 2. Temperature dependence of the uniaxial anisotropy field for iron borate. Points are the experimental data taken from [14, 15], and the solid curve indicates the results of the calculations.
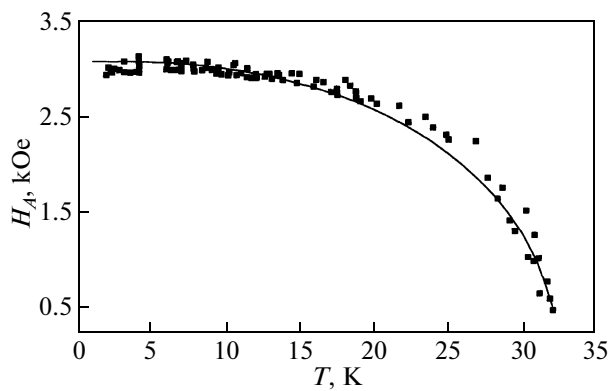
Fig. 3. Temperature dependence of the uniaxial anisotropy field for manganese carbonate. Points are the experimental data taken from [18, 19], and the solid curve indicates the results of the calculations.

-2.58 kOe with $\sigma_A + \sigma_c = 0.05$ kOe. The fitting results are presented in Fig. 1b (version 2).

Note that the fitting of the theoretical curves to the EPR experimental data using a sufficient number of parameters (three parameters) has demonstrated that the root-mean-square deviation has only one minimum [4]. Therefore, the EPR data are quite unambiguous, and the discrepancies with these data, which appear while performing the fitting of the temperature dependences, can be caused by the negative factors indicated above for the hematite.

The resulted solutions (Figs. 1a, 1b) only roughly reflect the values of the fitting parameters for hematite crystals. However, these solutions demonstrate that there exist anisotropic exchange contributions to the first- and second-order constants of the uniaxial anisotropy of the hematite.

Figure 2 presents the temperature dependence of the uniaxial anisotropy field H_A for FeBO$_3$ crystals. Here, the dipole and single-ion contributions of the second- and fourth-order terms are taken into account. The "single-ion" constants $D_c' = -0.05$ kOe and $E_c' = -0.5$ kOe were the fitting parameters. The value of $A_{dip}' = H_{A\,dip}(0) = 3.66$ kOe [16, 17] was used as a fixed parameter. From the EPR data [4], it follows that $D_c' = -0.84$ kOe and $E_c' = -0.2$ kOe.

Figure 3 shows the temperature dependence of the uniaxial anisotropy field H_A for crystals of manganese carbonate MnCO$_3$. The theoretical temperature dependence is described by the expressions for two mechanisms (the dipole mechanism and the "single-ion" mechanism) with the fitting parameters $D_c' = -0.75$ kOe and a fixed value equal to the calculated dipole anisotropy field $A_{dip}' = 3.82$ kOe. From the EPR data [4], it follows that the value including the contribution from the "single-ion" mechanism [4] and corresponding to D_c' is equal to -0.98 kOe. Based on the results thus obtained in combination with the studies [3, 4], a general method can be formulated for evaluating the magnetic anisotropy in the crystals with ions in the S state. This method is based on the measurements of the spin-Hamiltonian constants for single and paired ions in diamagnetic analogs [3, 4], on the dipole calculation, and on the investigation of the temperature dependence of the anisotropy fields in the magnetically concentrated crystals.

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Translated by N. Pomortseva