Exchange–relativistic double-ion spin anisotropy: Tensor form, temperature dependence, and numerical value

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This paper presents the first consistent analysis of the tensor form, numerical value, and temperature dependence of the exchange–relativistic double-ion anisotropy in pairs of $3d$-ions of the S-type. In addition to the well-known quasidipole contribution, the anisotropy contains a number of new nondipole contributions of the same order of magnitude but with a characteristic temperature dependence. Microscopic calculations show that the contribution of the exchange-bound pair of Fe^{3+} ions to the effective anisotropy constant is on the order of 1 cm^{-1}, which exceeds the respective magnetodipole contribution. In contrast to established ideas, exchange–relativistic anisotropy has proved to be one of the most important sources of magnetic anisotropy and magnetoelastic coupling in magnetodielectrics based on $3d$-ions of the S-type, such as Fe^{3+}, Mn^{2+}, Cr^{3+}, and Ni^{2+}. A four-parameter formula for the temperature dependence of the magnetic-anisotropy and magnetoelastic-coupling constants is derived in the molecular field approximation. Finally, an explanation is given of the specific temperature behavior of the anisotropy constants in α-Fe_2O_3 and Cr_2O_3.

1. INTRODUCTION

Studying the nature and special features of spin anisotropy in systems with $3d$-ions is one of the classical problems of magnetism (the magnetic anisotropy problem) and microwave spectroscopy (the problem of the spin Hamiltonian).

The most complicated for analysis and, hence, the least studied is the double-ion spin anisotropy of the exchange-relativistic origin, an effect of third-order perturbation-theory terms linear in the exchange interaction of ions 1 and 2 and quadratic in the spin–orbit coupling for ions 1(2). Schematically,

$$V_{\text{an}}(1,2)\sim\frac{V_{\text{so}}(1)V_{\text{ex}}(12)V_{\text{so}}(2)}{\Delta E^2}+\frac{V_{\text{so}}(1)V_{\text{so}}(2)V_{\text{ex}}(12)}{\Delta E^2}+\frac{V_{\text{so}}(1)V_{\text{ex}}(12)V_{\text{so}}(1)}{\Delta E^2}+\frac{V_{\text{so}}(1)V_{\text{so}}(1)V_{\text{ex}}(12)}{\Delta E^2} \qquad (1)$$

plus terms that are Hermitian conjugate to the above terms and in which ion 1 is interchanged with ion 2.

Below we speak of contributions of four types I–IV corresponding to the terms in Eq. (1). For ions 1 and 2 with spins $S_1=S_2=1/2$ and orbit-nondegenerate ground states, the effective spin Hamiltonian (1) has the simple form

$$V_{\text{an}}(1,2)=\sum_{i,j}K_{ij}(1,2)S_{1i}S_{2j} \qquad (2)$$

with a traceless symmetric tensor K_{ij} of the anisotropy constants. The spin anisotropy of the form (2) considered as early as 1937 by Van Vleck[1] became known as quasidipole, or exchange anisotropy (anisotropic exchange). For the simplest case of $S_1=S_2=1/2$ this type of anisotropy was studied by Moriya[2] and Yosida.[3]

Historically a situation emerged in which the operator (2) was used without rigorous substantiation in the general case for any ions and spin values. The fairly simple temperature dependence of the corresponding contribution to the effective anisotropy constant, $\Delta K(T)\sim B_S^2(T)\sim m^2(T)$ (for equal spins) was considered in many papers, including the fundamental work on the widely known systems of the Cr_2O_3 and α-Fe_2O_3 type,[4,5] as "representative" of the double-ion anisotropy of dipole and exchange-relativistic origin and was widely used for separation and quantitative estimate of the contributions of various anisotropy mechanisms.

The situation changed little after publication of the paper of Nikiforov, Mitrofanov, and Men,[6] who obtained the general tensor form of the spin Hamiltonian V_{an} for any ions and spins. Because of elaborate calculations and the absence of analysis in Ref. 6 the paper has not influenced the standard practice of the simplified approach to exchange-relativistic anisotropy.

The numerical values of the exchange–relativistic anisotropy parameters strongly depend on the nature of the ground orbital state of the exchange-bound $3d$-ions. For instance, for ions with the ground states T_1 and T_2 the energy denominators in (1) are usually determined by the small splitting of the T_1 and T_2 states in a low-symmetry crystalline field (CF), which leads to larger effects than for ions with the ground states A_1, A_2, and E. In all cases, we believe, the relation most suitable for semiquantitative estimates is

$$K_{\rm an}\sim\eta\,\frac{\xi_{3d}^2 I}{\Delta E^2},$$

where ξ_{3d} is the one-electron spin-orbit coupling constant, I the exchange integral, and ΔE the energy of the lowest energy levels in the $3d$-ion that are mixed with the ground state via spin–orbit coupling. The factor η, which among other things allows for many contributions from third-order perturbation terms, may, as we shortly show, reach values of order ten. The approximate relation

$$K_{\rm an}\sim\left(\frac{\Delta g}{g}\right)^2 I,$$

with Δg the deviation of the g-factor from the purely spin value, introduced by Moriya,[2] has a greatly restricted sphere of application. Its unjustified use has led, among other things, to the conclusion about the insignificance of the exchange-relativistic contribution to the anisotropy of pairs of $3d$-ions of the S-type (ions with an orbit-nondegenerate ground state A_1 or A_2, for instance, Cr^{3+}, Mn^{2+}, Fe^{3+}, and Ni^{2+}), that is, ions of the greatest interest in studying magnetodielectrics.

The present paper is devoted mainly to S-ions. We show that rigorous analysis of $V_{\rm an}$ leads to a radical re-evaluation of many established ideas about the spin-orbit structure of exchange–relativistic anisotropy and the numerical value and temperature dependence of the respective contribution to the anisotropy constants.

2. THE EFFECTIVE SPIN HAMILTONIAN OF EXCHANGE-RELATIVISTIC ANISOTROPY. NONDIPOLE CONTRIBUTIONS

In establishing, analyzing, and numerically estimating the Hamiltonian of exchange-relativistic anisotropy we follow the method developed in Ref. 7, which considers one of the main exchange-relativistic effects of second-order perturbation theory, the Dzyaloshinskiĭ–Moriya antisymmetric exchange. The most convenient way to describe spin–orbit and especially exchange interactions in compounds based on $3d$-elements, which are characterized by a strong CF with a symmetry close to cubic (octahedral and tetrahedral), is to employ the method of double irreducible tensor operators[8] acting both in spin and orbit spaces.

According to Judd,[8] such operators have the form

$$\hat{W}^{a\gamma}_{\alpha\nu}(\Gamma\Gamma')=\sum_{\sigma\sigma'}\sum_{\mu\mu'}\begin{bmatrix}\frac{1}{2} & \frac{1}{2} & a\\ \sigma & -\sigma' & \alpha\end{bmatrix}\begin{bmatrix}\Gamma & \Gamma' & \gamma\\ \mu & -\mu' & \nu\end{bmatrix}$$
$$\times(-1)^{1/2+\sigma'+j(\Gamma')+\mu'}\hat{a}^{\dagger}_{f\Gamma\mu\sigma}\hat{a}_{f\Gamma'\mu'\sigma'},\qquad(3)$$

where $[\because]$ are the Clebsch–Gordan coefficients of the rotation group and the point group O_h (see Refs. 9–11), and $\hat{a}^{\dagger}$ and $\hat{a}$ are the electron creation and annihilation operators. In the space of the $|t_{2g}^{n_1}e_g^{n_2}SM_S\Gamma\mu\rangle$ functions, which describe the multielectron configurations of $3d$-ions in a strong cubic CF, the operators of the form (3) act according to the Wigner–Eckart theorem:[10]

$$\langle t_{2g}^{n_1}e_g^{n_2}SM_S\Gamma\mu|\hat{W}^{a\gamma}_{\alpha\nu}(\Gamma_i\Gamma_j)|t_{2g}^{n_1'}e_g^{n_2'}S'M_S'\Gamma'\mu'\rangle=(-1)^{S-M_S}$$
$$\times\begin{pmatrix}S & a & S'\\ -M_S & \alpha & M_S'\end{pmatrix}(-1)^{j(\Gamma)-\mu}$$
$$\times\left\langle\begin{matrix}\Gamma & \gamma & \Gamma\\ -\mu & \nu & \nu'\end{matrix}\right\rangle W^{(a\gamma)}_{S\Gamma;S'\Gamma'}(\Gamma_i\Gamma_j),\qquad(4)$$

where $(\because)$ and $\langle\because\rangle$ are the Wigner coefficients of the rotation group and the O_h group, respectively (see Ref. 9–11), and the $W^{(a\gamma)}$ are the reduced matrix elements (spectroscopic coefficients). Here in the single-particle case we have

$$W^{(a\gamma)}_{\frac{1}{2}\Gamma_i;\frac{1}{2}\Gamma_j}(\Gamma_i\Gamma_j)=-[a,\gamma]^{1/2},$$

with $[a]=2a+1$ and $[\Gamma]$ the degree of the representation.

In terms of double irreducible tensor operators the Hamiltonian of spin–orbit coupling is

$$V_{\rm so}=\sum_{\Gamma_i\Gamma_j}\langle\Gamma_i\|\zeta\|\Gamma_j\rangle\sum_q(-1)^q\hat{W}^{1T_1}_{q-q}(\Gamma_i\Gamma_j),\qquad(5)$$

where $\langle e_g\|\zeta\|e_g\rangle=0$, $\langle e_g\|\zeta\|t_{2g}\rangle=\langle t_{2g}\|\zeta\|e_g\rangle^*$, and

$$\langle e_g\|\zeta\|t_{2g}\rangle\approx-3\sqrt{2}\zeta_{3d},\quad\langle t_{2g}\|\zeta\|t_{2g}\rangle\approx3\zeta_{3d},\qquad(6)$$

where ζ_{3d} is the one-electron spin–orbit coupling constant.

The Hamiltonian of the exchange interaction of two ions with electron configurations of the $t_{2g}^{n_1}e_g^{n_2}$ type has a more complicated form:[7]

$$\hat{V}_{\rm ex}(1,2)=\sum I(f_1\Gamma_1\Gamma_1'f_2\Gamma_2\Gamma_2'|\gamma_1\gamma_2\gamma\nu)$$
$$\times[\hat{W}^{a\gamma_1}(\Gamma_1\Gamma_1')\hat{W}^{a\gamma_2}(\Gamma_2\Gamma_2')]^{\gamma}_{\nu},\qquad(7)$$

with

$$[\hat{W}^{a\gamma_1}\times\hat{W}^{a\gamma_2}]^{\gamma}_{\nu}=\sum_{\alpha\nu_1\nu_2}\begin{bmatrix}\gamma_1 & \gamma_2 & \gamma\\ \nu_1 & \nu_2 & \nu\end{bmatrix}(-1)^{\alpha}\hat{W}^{a\gamma_1}_{\alpha\nu_1}\hat{W}^{a\gamma_2}_{-\alpha\nu_2}$$

the scalar product of double tensors in the spin space and the tensor product (of rank γ) of the same tensors in the orbital space. The exchange parameters I that allow for potential and kinetic exchange, according to Anderson,[12] have the form

$$I(f_1\Gamma_1\Gamma_1'f_2\Gamma_2\Gamma_2'|\gamma_1\gamma_2\gamma\nu)$$
$$=\sum[\gamma_1\gamma_2]^{1/2}$$
$$\times\begin{bmatrix}\gamma_1 & \gamma_2 & \gamma\\ \nu_1 & \nu_2 & \nu\end{bmatrix}^*(-1)^{j(\Gamma_1)-\mu_1}\left\langle\begin{matrix}\Gamma_1 & \gamma_1 & \Gamma_1'\\ -\mu_1 & \nu_1 & \mu_1\end{matrix}\right\rangle$$
$$\times(-1)^{j(\Gamma_2)-\mu_2}\left\langle\begin{matrix}\Gamma_2 & \gamma_2 & \Gamma_2'\\ -\mu_2 & \nu_2 & \mu_1\end{matrix}\right\rangle$$

$$\times\left\{\frac{b(f_1\Gamma_1\mu_1|f_2\Gamma_2'\mu_2')b(f_2\Gamma_2\mu_2|f_1\Gamma_1'\mu_1')}{U}\right.$$

$$\left.-\tfrac{1}{2}F(f_1\Gamma_1\mu_1f_2\Gamma_2\mu_2|f_2\Gamma_2'\mu_2'f_1\Gamma_1'\mu_1')\right\}, \qquad (8)$$

where we have employed the standard notation for Heisenberg exchange integrals F, the transport integral b, and the average transport energy U.

Without writing the cumbersome general expressions for the effective operator of exchange-relativistic anisotropy, which emerges in third-order perturbation theory, we analyze the spin-operator structure and consider combinations of spin-operator products corresponding to four distinctly different perturbation-theory contributions I–IV. Via the well-known[10] relations of the theory of angular momentum these products can be transformed to tensor products of the following form:
I.

$$\hat{V}^1_{q_1}(S_1)(\hat{V}^a(S_1)\hat{V}^a(S_2))\hat{V}^1_{q_1}(S_2)$$

$$=\sum_{k_1k_2k}(-1)^{a+k+2S_1+2S_2}[k_1,k_2]\begin{Bmatrix}1 & k_1 & 1\\ k_2 & 1 & k\end{Bmatrix}$$

$$\times\begin{Bmatrix}1 & a & k_1\\ S_1 & S_1 & S_1'\end{Bmatrix}\begin{Bmatrix}1 & a & k_2\\ S_2 & S_2 & S_2'\end{Bmatrix}\begin{bmatrix}1 & 1 & k\\ q_1 & q_2 & q\end{bmatrix}$$

$$\times[\hat{V}^{k_1}(S_1)\times\hat{V}^{k_2}(S_2)]^k_q, \qquad (9)$$

II.

$$\hat{V}^1_{q_1}(S_1)\hat{V}^1_{q_2}(S_2)(\hat{V}^a(S_1)\hat{V}^a(S_2))$$

$$=\sum_{k_1k_2k}(-1)^{k_2+1+k+2S_1+2S_2}[k_1,k_2]\begin{Bmatrix}1 & k_1 & 1\\ k_2 & 1 & k\end{Bmatrix}$$

$$\times\begin{Bmatrix}1 & a & k_1\\ S_1 & S_1 & S_1'\end{Bmatrix}\begin{Bmatrix}1 & a & k_2\\ S_2 & S_2 & S_2'\end{Bmatrix}\begin{bmatrix}1 & 1 & k\\ q_1 & q_2 & Q\end{bmatrix}$$

$$\times[\hat{V}^{k_1}(S_1)\times\hat{V}^{k_2}(S_2)]^k_Q \qquad (10)$$

(the difference from (9) is only in the phase $(-1)^{k_2+a+1}$ under the summation sign),
III.

$$\hat{V}^1_{q_1}(S_1)(\hat{V}^a(S_1)\hat{V}^a(S_2))\hat{V}^1_{q_2}(S_2))$$

$$=\sum_{k_1k_2}(-1)^{S_1'-S_1+a+1}[k_1]\begin{Bmatrix}k_1 & a & k\\ S_1 & S_1'' & 1\\ S_1 & S_1' & 1\end{Bmatrix}\begin{bmatrix}1 & 1 & k\\ q_1 & q_1 & Q\end{bmatrix}$$

$$\times[\hat{V}^{k_1}(S_1)\times\hat{V}^a(S_2)]^k_Q, \qquad (11)$$

IV.

$$\hat{V}^1_{q_1}(S_1)\hat{V}^1_{q_2}(S_1)(\hat{V}^a(S_1)\hat{V}^a(S_2))$$

$$=\sum_{k_1k}(-1)^{S_1''-S_1}[k_1]\begin{Bmatrix}1 & 1 & k\\ S_1 & S_1'' & S_1'\end{Bmatrix}\begin{Bmatrix}a & k_1 & k\\ S_1 & S_1'' & S_1\end{Bmatrix}$$

$$\times\begin{bmatrix}1 & 1 & k\\ q_1 & q_2 & q\end{bmatrix}[\hat{V}^{k_1}(S_1)\times\hat{V}^a(S_2)]^k_q, \qquad (12)$$

where $\{\substack{\cdots\\\cdots}\}$ is a $6j$-symbol, $\{\substack{\cdots\\\cdots\\\cdots}\}$ a $9j$-symbol,[10] and the operators $\hat{V}^k_q(S)$ act according to the Wigner–Eckart theorem,

$$\langle SM|V^k_q(S)|S'M'\rangle=(-1)^{S-M}\begin{pmatrix}S & k & S'\\ -M & q & M'\end{pmatrix},$$

with the values of S and S' determined in accordance with perturbation theory. The spin-operator products on the left- and right-hand sides of Eqs. (9)–(12) are projected on the space of spin functions of the ground state of the ions. The absence on the right-hand side of these equations of summation over $S_{1,2}'$ and $S_{1,2}''$, the spins of the intermediate (excited) states of ions in a pair, is an indication that in calculating the operator-product matrix on the left-hand side there emerges summation only over the projections of the intermediate spins.

Equations (9)–(12) form the basis for introducing the effective spin operator of second-order exchange–relativistic double-ion anisotropy (the term with $k=2$).

For ions 1 and 2 with orbit-nondegenerate ground states (such ions as Fe^{3+}, Mn^{2+}, Cr^{3+}, and Ni^{2+}) the effective spin operator V_{an} has the general form

$$\hat{V}_{an}=\sum_{k_1k_2}(P^2(1k_1,2k_2)\cdot[\hat{V}^{k_1}(S_1)\times\hat{V}^{k_2}(S_2)]), \qquad (13)$$

where the $P^2_q(1k_1,2k_2)$ are tensor constants.[1)] In addition to the well-known standard quasidipole terms ($k_1=k_2=1$), V_{an} contains a number of new "nondipole" terms with $k_1k_2=20(02),22$ (mechanisms I and II) and with $k_1k_2=13(31)$ (mechanisms III and IV). In the general case purely orbital exchange ($a=0$) yields a contribution to the term with $k_1=k_2=1$ (mechanisms I and II) and the term with $k_1=2$, $k_2=0$ or $k_1=0$, $k_2=2$ (mechanisms III and IV). An important consequence of Eqs. (9)–(12) is the presence of the well-known dependence of the parameters $P^2(k_1k_2)$ on the values of k_1 and k_2 at certain values of the intermediate spins for each of the four types of perturbation-theory contributions. This enables the ratio of the values of the $P^2(k_1k_2)$ parameters for the quasidipole and nondipole contributions to be found for each type of ion pairs.

3. THE ENERGY OF THE EXCHANGE-RELATIVISTIC DOUBLE-ION ANISOTROPY, ALLOWING FOR NONDIPOLE CONTRIBUTIONS

With magnetic substances the molecular field approximation provides a simple way of going from $\hat{V}_{\rm an}$ to the anisotropy energy. Here[13]

$$\langle V_q^k(S)\rangle_T=\langle V_0^k(S)\rangle_T C_q^k(\mathbf{S}),\quad \langle V_q^k\rangle=\langle V_q^k\rangle_0\rho_k(T), \tag{14}$$

where C_q^k is a spherical tensor harmonic, $\langle V_q^k\rangle$ the thermodynamic average, with

$$\langle V_0^k\rangle_0=\begin{pmatrix} S & k & S\\ -S & 0 & S\end{pmatrix},$$

and $\rho_k(T)$ the characteristic temperature factor determining the temperature dependence of averages for tensors of rank k (Ref. 13):

$$\rho_0=1,\quad \rho_1=B_S(T)=\frac{\langle S_z\rangle}{S},\quad \rho_2=\frac{\langle 3S_z^2-S(S+1)\rangle}{S(2S-1)},$$
$$\rho_3=-\frac{[3S(S+1)-1]\langle S_z\rangle+S\langle S_z^3\rangle}{S(S-1)(2S-1)},\quad \rho_k(T=0)=1. \tag{15}$$

Allowing for (13) and (14), we can write

$$E_{\rm an}=\sum_{1,2}\sum_{k_1k_2}\langle V_0^{k_1}\rangle_0\langle V_0^{k_2}\rangle_0\rho k_1\rho k_2(P^2(1k_1,2k_2)$$
$$\cdot[C^{k_1}(\mathbf{S}_1)\times C^{k_2}(\mathbf{S}_2)]^2). \tag{16}$$

The nontrivial tensor products of harmonics at $k_1=k_2=2$ or $k_1=3$ and $k_2=1$ can be simplified by employing, for instance, the following relations:

$$[C^2(\mathbf{S}_1)\times C^2(\mathbf{S}_2)]_q^2=-\frac{3\sqrt{3}}{\sqrt{7}}\Big\{(C^1(\mathbf{S}_1)C^1(\mathbf{S}_2))$$
$$\times[C^1(\mathbf{S}_1)\times C^1(\mathbf{S}_2)]_q^2$$
$$-\frac{\sqrt{2}}{3\sqrt{3}}(C_q^2(\mathbf{S}_1)+C_q^2(\mathbf{S}_2))\Big\}, \tag{17}$$

$$[C^3(\mathbf{S}_1)\times C^1(\mathbf{S}_2)]_q^2=-\frac{5}{\sqrt{21}}\Big\{\frac{\sqrt{6}}{5}[C^1(\mathbf{S}_1)\times C^1(\mathbf{S}_2)]_q^2$$
$$-(C_1^1(\mathbf{S}_1)C_1^1(\mathbf{S}_2))C_q^2(\mathbf{S}_1)\Big\}. \tag{18}$$

By going from spins $\mathbf{S}_1$ and $\mathbf{S}_2$ to the base vectors of the magnetic structure, isolating the principal vector (for instance, the antiferromagnetism vector in two-sublattice antiferromagnets), and substituting

$$[C^{k_1}(\mathbf{S}_1)\times C^{k_2}(\mathbf{S}_2)]_q^2=\pm\begin{bmatrix} k_1 & k_2 & 2\\ 0 & 0 & 0\end{bmatrix}C_q^2(\mathbf{1}) \tag{19}$$

(the "minus" is chosen if the ions 1 and 2 belong to different sublattices for odd $k_1(k_2)$, and the "plus" in other cases), for collinear or weakly collinear magnetic substances instead of (16) we can obtain the following expression for the effective anisotropy energy:

$$E_{\rm an}=(P^2C^2(\mathbf{1}))=\tfrac{1}{2}P_0^2(3l_z^2-1)+\frac{\sqrt{3}}{2\sqrt{2}}\Re P_2^2(l_x^2-l_y^2)+\dots. \tag{20}$$

For the tensor of the effective magnetic anisotropy constants we have

$$P_q^2=\sum_{1,2}\sum_{k_1k_2}\pm P_q^2(k_1k_2)$$
$$\times\langle V_0^{k_1}\rangle_0\langle V_0^{k_2}\rangle_0\rho k_1\rho k_2\begin{bmatrix} k_1 & k_2 & 2\\ 0 & 0 & 0\end{bmatrix}. \tag{21}$$

An important factor that makes it possible to substantially lower the number of various parameters in the expression for the constant P_q^2 is the known dependence of the $P_q^2(k_1k_2)$ on the spin quantum numbers in the ground and excited states of an ion pair and the indices k_1 and k_2. For instance, at $a=1$, for type-I contributions we have

$$P_q^2(k_1k_2)=[k_1,k_2]\begin{Bmatrix} 1 & k_1 & 1\\ k_2 & 1 & 2\end{Bmatrix}\begin{Bmatrix} 1 & 1 & k_1\\ S_1 & S_1 & S_1'\end{Bmatrix}$$
$$\times\begin{Bmatrix} 1 & 1 & k_2\\ S_2 & S_2 & S_2'\end{Bmatrix}P_q^2(\mathrm{I}) \tag{22}$$

with k_1k_2 values equal to 11, 22, 20, and 02.

For type-II contributions we have

$$P_q^2(k_1k_2)=(-1)^{k_2}[k_1k_2]\begin{Bmatrix} 1 & k_1 & 1\\ k_2 & 1 & 2\end{Bmatrix}\begin{Bmatrix} 1 & 1 & k_1\\ S_1 & S_1 & S_1'\end{Bmatrix}$$
$$\times\begin{Bmatrix} 1 & 1 & k_2\\ S_2 & S_2 & S_2'\end{Bmatrix}P_q^2(\mathrm{II}) \tag{23}$$

with the same values of k_1 and k_2 [the difference from (22) is only in the phase $(-1)^{k_2}=(-1)^{k_1}$].

For type-III contributions that allow for $V_{\rm so}(1)$ we have

$$P_q^2(k_1k_2)=[k_1]\begin{Bmatrix} k_1 & 1 & 2\\ S_1 & S_1'' & 1\\ S_1 & S_1' & 1\end{Bmatrix}\delta_{k_21}P_q^2(\mathrm{III}) \tag{24}$$

with k_1k_2 values equal to 11 and 31 [allowing for $V_{\rm so}(2)$ yields a similar result, in which, however, k_1 and k_2 change places, as do S_1 and S_2].

Finally, for type-IV contributions that allow for $V_{\rm so}(1)$ we have

$$P_q^2(k_1k_2)=[k_1]\begin{Bmatrix} 1 & k_1 & 2\\ S_1 & S_1'' & S_1\end{Bmatrix}P_q^2(\mathrm{IV})\delta_{k_21} \tag{25}$$

with k_1k_2 values equal to 11 and 31 (allowing for $V_{\rm so}(2)$ yields a similar result, in which, however, k_1 and k_2 change places, as do S_1 and S_2).

Naturally, $P_q^2(\mathrm{I})$, $P_q^2(\mathrm{II})$, $P_q^2(\mathrm{III})$, and $P_q^2(\mathrm{IV})$ depend on S_1, S_1', S_2, and S_2'. Equations (22)–(25) make it possible in each case of a definite ion pair to establish the

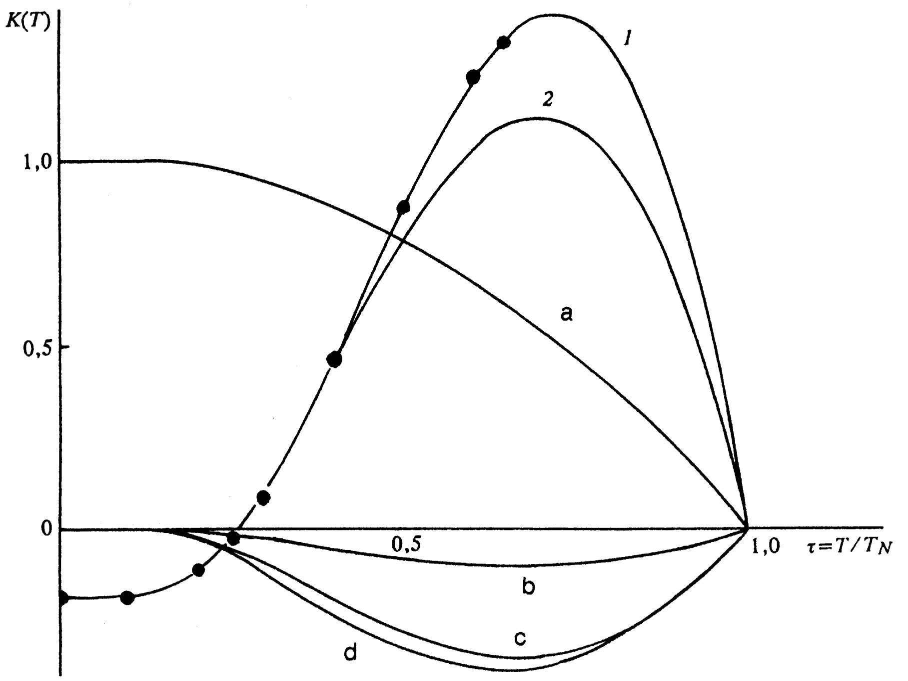

FIG. 1. The temperature dependence of the second-order magnetic anisotropy constant in hematite α-Fe_2O_3: the ● stand for the experimental data of Ref. 17, curve *I* represents the result of processing the experimental data by the four-parameter formula (26) with allowance for exchange–relativistic contributions, and curve *II* the result of processing the experimental curve without allowing for exchange–relativistic anisotropy. Curves a, b, c, and d represent the temperature dependence of the factors determining the temperature behavior of the dipole or "quasidipole" anisotropy (curve a: ρ_1^2), and also the deviation from this behavior for the nondipole 20-(02)-contribution (curve b: $\rho_2-\rho_1^2$), the 22-contribution (curve c: $\rho_2^2-\rho_1^2$), and the 13-(31)-contribution (curve d: $\rho_2\rho_3-\rho_1^2$).

relative value of the standard quasidipole contribution ($k_1=k_2=1$) and nontrivial tensor contributions ($k_1k_2=20,02,22,13,31$) to the constant of second-order effective magnetic anisotropy.

In all cases of magnetic substances with equivalent spins, the temperature dependence of the effective constant (or constants) of second-order exchange–relativistic anisotropy may generally, according to Eq. (21), be represented in the following form:

$$K(T)=K(0)\rho_1^2+K_{20}(\rho_2-\rho_1^2)+K_{22}(\rho_2^2-\rho_1^2)+K_{13}(\rho_1\rho_3-\rho_1^2), \qquad (26)$$

where for convenience we have introduced the differences $\rho^2-\rho_1^2$, etc., which vanish at $T=0$ K and at $T=T_N(T_c)$ (see Figs. 1 and 2). The constant K_{11} of ordinary quasidipole anisotropy is determined in this case via the relation $K_{11}=K(0)-K_{20}-K_{22}-K_{13}$.

The subscripts m and n on the constants K_{mn} indicate the rank of spin operators in the effective spin Hamiltonian of anisotropy, with $K_{20}=K_{02}$ and $K_{31}=K_{13}$ for equal spins. Allowing for second-order magnetodipole and single-ion anisotropy only leads to the renormalization of constants $K(0)$ and K_{20}, respectively, so that Eq. (26) serves as a universal four-parameter formula for the temperature de-

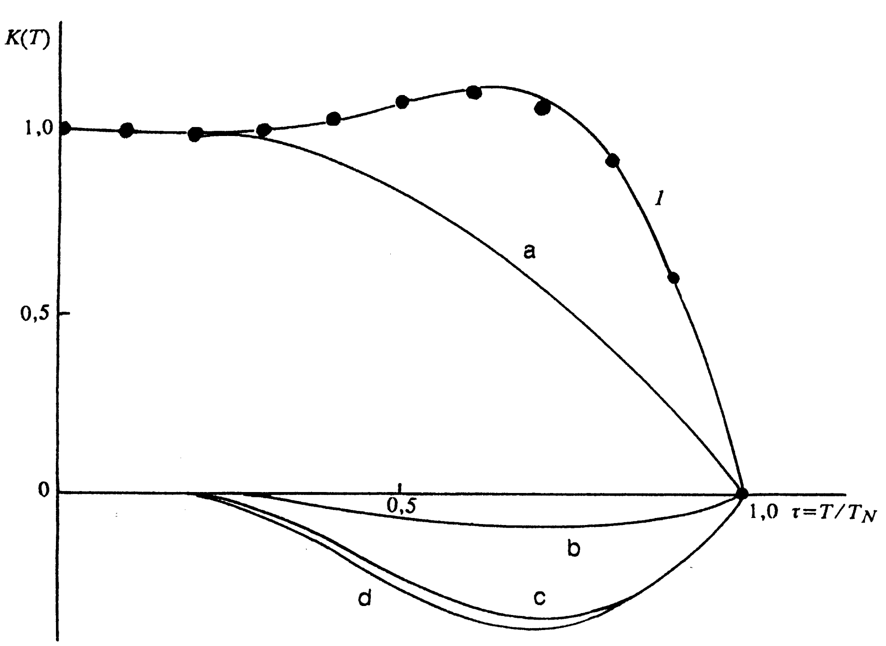

FIG. 2. The temperature dependence of the second-order magnetic anisotropy constant in the ferromagnet Cr_2O_3: the ● stand for the experimental data of Ref. 4, and curve *I* represents the result of processing the experimental data by formula (26) with allowance for exchange-relativistic contributions. Curves a, b, c, and d are the same as in Fig. 1 for $S_1=S_2=3/2$.

pendence of the effective second-order magnetic anisotropy constant.

4. EXCHANGE–RELATIVISTIC ANISOTROPY IN A PAIR OF *S*-TYPE 3*d*-IONS

4.1. Exchange–relativistic anisotropy in a pair of 3*d*-ions. The temperature dependence of the effective anisotropy constants

For $3d^5$-ions, such as Fe^{3+} and Mn^{2+}, the ground Hund state corresponds to the maximum spin value of $S=5/2$, while in processes I–IV only excited quartic states with $S'=S''=3/2$ participate.

Allowing for Eqs. (30)–(33) in a pair of 3*d*-ions, we can easily obtain the following formula for the exchange-relativistic contribution to the constant of effective second-order magnetic anisotropy in Fe^{3+}- and Mn^{2+}-based antiferromagnets:

$$\begin{aligned} P_q^2= & \left[\pm\rho_1^2(T)+\left(\frac{4}{3}\rho_2(T)-\frac{1}{3}\rho_2^2(T)\right)\right]\sum P_q^2(\mathrm{I}) \\ & +\left[\pm\rho_1^2(T)-\left(\frac{4}{3}\rho_2(T)\right.\right. \\ & \left.\left.-\frac{1}{3}\rho_2^2(T)\right)\right]\sum P_q^2(\mathrm{II})+\left[\pm\rho_1\left(\rho_1+\frac{3}{2}\rho_3\right)\right. \\ & \left.+\varkappa\rho_2\right]\sum P_q^2(\mathrm{III}) \\ & \pm\rho_1(\rho_1-\rho_3)\sum P_q^2(\mathrm{IV}), \end{aligned} \tag{27}$$

where the upper signs are chosen for the contribution of intrasublattice exchange, the lower signs for the contribution of intersublattice exchange, and summation is over lattices. The parameter $\varkappa$ determines the relative value of the unique contribution to P_q^2 of the purely orbital $(a=0)$ exchange $Fe_1^{3+}({}^4T_1)$-$Fe_2^{3+}({}^6A_1)$, which appears only in the type-III mechanism.

In the contributions of all four processes I–IV only the first term corresponds to the known quasidipole exchange-relativistic anisotropy $(k_1=k_2=1)$. The other terms describe the contributions of nondipole exchange-relativistic anisotropy not allowed for in standard approaches to the analysis of V_{an}. The values not only prove to be of the same order of magnitude as the quasidipole contribution but may even exceed it. Naturally this leads to a radical transformation of the nature of the temperature dependence of the total exchange-relativistic contribution to the magnetic anisotropy constant.

A remark is in order. At $T=0$ K the nondipole 20-, 02-, and 22-contributions to the magnetic anisotropy constant for type-I and type-II processes coincide in absolute value with the quasidipole 11-contribution, which results in compensation of the total contribution of type-I (type-II) processes for intersublattice (intrasublattice) exchange or in doubling of the quasidipole contribution in the opposite case. For the type-IV mechanism, at $T=0$ K the quasidipole 11-contribution and the nondipole 13- and 31-contributions balance each other exactly in both intrasublattice and intersublattice interactions. All these compensation effects are related to the property of exchange interaction to conserve the projection of the total spin angular momentum of a pair. The contribution of the type-I (type-II) mechanism for intersublattice (intrasublattice) exchange is small for finite temperatures, too:

$$-\rho_1^2(T)+\tfrac{4}{3}\rho_2(T)-\tfrac{1}{3}\rho_2^2(T)<0.02.$$

Hence, the contribution of the type-I (type-II) mechanism for intrasublattice (intersublattice) exchange is practically twice the quasidipole contribution:

$$\rho_1^2(T)+\tfrac{4}{3}\rho_2(T)-\tfrac{1}{3}\rho_2^2(T)\approx 2\rho_1^2(T).$$

Thus, for weakly anisotropic magnetic substances based on $3d^5$-ions, the temperature dependence of the effective anisotropy constant can be represented fairly accurately by the following three-parameter formula:

$$K(T)\approx K(0)\rho_1^2(T)+K_{20}(\rho_2-\rho_1^2)+K_{13}(\rho_1\rho_3-\rho_1^2), \tag{28}$$

where K_{20} actually determines only the contribution of the ordinary single-ion anisotropy and the 20-(02-) contribution of spinless exchange, and $K_{11}^{*}=K(0)-K_{20}-K_{13}$ reflects the total contribution of magnetodipole and quasidipole exchange-relativistic anisotropy and also the nondipole 20,02,22 contributions determined by the ordinary spin-dependent part of exchange.

4.2. Microscopic calculation of exchange–relativistic anisotropy in a pair of 3*d*-ions

A quantitative calculation of the parameters of exchange–relativistic anisotropy is extremely lengthy and complicated even in the fairly simple case of $3d^5$-ion pairs. For its practical realization we chose a model with the following approximations:

1. The local CF's for both ions in a pair are assumed cubic and equivalent, with the $C_4(O_z)$ axis directed along the pair's symmetry axis. This automatically leads to a collinear geometry of exchange (superexchange) in the Fe^{3+}—Fe^{3+} pair. Moreover, in the selected system of coordinates, of all the anisotropy parameters only the parameter $P_0^2(k_1k_2)$ remains nonzero.
2. The wave functions of the three quartic states ${}^4T_{1g}$ acting as intermediate states in processes I–IV are found with allowance for configuration mixing, the values of the parameters being $10Dq=12\,200$ cm^{-1}, $B=700$ cm^{-1}, and $C=2600$ cm^{-1} (Ref. 7), which is characteristic of octahedral FeO_6^{9-} complexes in ferrite-type compounds.
3. Approximation (6) is used to calculate one-electron spin–orbit coupling constants.
4. The exchange interaction of ions takes into account the greatest kinetic-exchange contribution.

Below we give the explicit expressions obtained from calculations for the parameters

$$K_{k_1k_2}=P_0^2(k_1k_2)\langle V_0^{k_1}\rangle\langle V_0^{k_2}\rangle\begin{bmatrix}k_1 & k_2 & 2\\ 0 & 0 & 0\end{bmatrix}, \tag{29}$$

which represent the k_1k_2-contribution of the pair of $3d^5$-ions considered to the anisotropy constant $P_0^2(T=0)$ on the assumption that both ions belong to the same sublattice of the antiferromagnet.

Type-I mechanism:

$$K_{11}(\mathrm{I})=\frac{\xi_{3d}^2}{2}\left\{\left[\frac{1}{4}(k_1-k_3)^2+\frac{1}{2}(k_1+k_3)^2\right]\frac{b_{\sigma\sigma}b_{\pi\pi}}{U}-\frac{4}{3}k_2^2\frac{b_{\pi\pi}^2}{U}\right\},$$

$$K_{20}=K_{02}=\tfrac{2}{3}K_{11},\quad K_{22}=-\tfrac{1}{3}K_{11},\quad K_{13}=K_{31}=0. \qquad (30)$$

Type-II mechanism:

$$K_{11}(\mathrm{II})=\frac{\xi_{3d}^2}{2}\left\{\left[\frac{1}{4}(k_1-k_3)^2-\frac{1}{2}(k_1+k_3)^2\right]\frac{b_{\sigma\sigma}b_{\pi\pi}}{U}+\frac{4}{3}k_2^2\frac{b_{\pi\pi}^2}{U}\right\},$$

$$K_{20}=K_{02}=-\tfrac{2}{3}K_{11},\quad K_{22}=\tfrac{1}{3}K_{11},\quad K_{13}=K_{31}=0. \qquad (31)$$

Type-III mechanism:

$$K_{11}(\mathrm{III})=-\frac{\xi_{3d}^2}{5}\left[(k_1^2+k_3^2)\frac{b_{\sigma\sigma}^2}{U}+\frac{4}{3}(k_1^2+k_3^2-k_2^2)\frac{b_{\pi\pi}^2}{U}\right],$$

$$K_{20}=K_{02}=-\frac{\xi_{3d}^2}{2}\left[(k_1^2-k_3^2)\frac{b_{\sigma\sigma}^2}{U}+\frac{4}{3}(k_1^2+k_3^2)\frac{b_{\pi\pi}^2}{U}\right], \qquad (32)$$

$$K_{13}=K_{31}=\tfrac{3}{4}K_{11},\quad K_{22}=0.$$

Type-IV mechanism:

$$K_{11}(\mathrm{IV})=\frac{2\xi_{3d}^2}{5}\left(k_\sigma\frac{b_{\sigma\sigma}^2}{U}+2k_\pi\frac{b_{\pi\pi}^2}{U}\right),$$

$$K_{13}=K_{31}=-\tfrac{1}{2}K_{11},\quad K_{20}=K_{02}=K_{22}=0. \qquad (33)$$

The parameters $b_{\sigma\sigma}$ and $b_{\pi\pi}$ in Eqs. (30)–(33) are integrals of the transfer of a $3d$-electron between Fe^{3+}-Fe^{3+} centers with allowance for σ- and π-bonds, respectively. These parameters determine the contribution of kinetic exchange to the superexchange integral for the 180°-geometry of the Fe^{3+}—intermediate anion—Fe^{3+} bond:[7]

$$I(\mathrm{Fe}^{3+}\mathrm{Fe}^{3+})=-\frac{1}{25}\left(\frac{b_{\sigma\sigma}^2}{U}+\frac{b_{\pi\pi}^2}{U}\right). \qquad (34)$$

Analyses of the experimental and calculated data on systems of the orthoferrite RFeO_3 type done in Refs. 7 and 14 put for the 180°-superexchange Fe^{3+}—O^{2-}—Fe^{3+} bond in ferrite systems the value of the integral $I(\mathrm{Fe}^{3+}\mathrm{Fe}^{3+})$ at approximately 20 cm^{-1}, with the predominant contribution of the σ-bond, $b_{\sigma\sigma}^2\sim(2-3)b_{\pi\pi}^2$, which in turn yields $b_{\sigma\sigma}^2U^{-1}\sim 300$–$400$ cm^{-1} and $b_{\pi\pi}^2U^{-1}\sim 150$–$200$ cm^{-1}.

The parameters k_1, k_2, k_3, k_σ, and k_π in Eqs. (30)–(33) are determined by the coefficients of mixing of states with the same symmetry and the energies of the excited ${}^4T_1$ and ${}^4E$ states:

$$k_i=\sum_j\frac{1}{\Delta E(i^4T_1)}\left(\alpha_1^i+\alpha_3^j-\frac{1}{\sqrt{2}}\alpha_2^j\right)\alpha_i^j, \qquad (35)$$

$$k=\sum_{ij}\frac{1}{\Delta E(i^4T_1)\Delta E(j^4E)}\left(\alpha_1^i+\alpha_3^j-\frac{1}{\sqrt{2}}\alpha_2^i\right)\times\left[(\alpha_1^i+\alpha_3^i)\left(\beta_1^j+\frac{\sqrt{3}}{2}\beta_2^j\right)+\frac{1}{\sqrt{2}}\alpha_2^i\beta_1^j\right]\times\begin{cases}\sqrt{3}\beta_2^j & \text{if } k=k_\sigma,\\ \beta_1^j & \text{if } k=k_\pi.\end{cases} \qquad (36)$$

Here the α_i^j are the interconfiguration-mixing coefficients for the ${}^4T_1$ states,

$$|i^4T_1\rangle=\alpha_1^i|t_{2g}^4e_g^{1}\,{}^4T_1\rangle+\alpha_2^i|t_{2g}^3e_g^{2}\,{}^4T_1\rangle+\alpha_3^i|t_{2g}^2e_g^{3}\,{}^4T_1\rangle,$$

and the β_i^j are the mixing coefficients for two ${}^4E$ states of the $t_{2g}^3e_g^2$ configuration of different origin,

$$|i^4E\rangle=\beta_1^i|(t_{2g}^3)^2E(e_g^2)^3A_2;{}^4E\rangle+\beta_2^i|(t_{2g}^3)^4A_2(e_g^2)^1E;{}^4E\rangle.$$

For the chosen CF parameters and the Racah parameters for Fe^{3+} ions,[7]

$$k_1\simeq-1.0\times10^{-4}\ \mathrm{cm},\quad k_2\simeq0.2\times10^{-4}\ \mathrm{cm},$$

$$k_3\simeq-0.4\times10^{-4}\ \mathrm{cm},$$

$$E(1^4T_1)=1.0\times10^{4}\ \mathrm{cm}^{-1},$$

$$E(2^4T_1)=3.0\times10^{4}\ \mathrm{cm}^{-1},$$

$$E(3^4T_1)=3.7\times10^{4}\ \mathrm{cm}^{-1},$$

$$k_\sigma=-0.7\times10^{-8}\ \mathrm{cm}^{-2},\quad E(1^4E)=2.0\times10^{4}\ \mathrm{cm}^{-1},$$

$$E(2^4E)=2.5\times10^{4}\ \mathrm{cm}^{-1},$$

$$k_\pi=-0.5\times10^{-8}\ \mathrm{cm}^{-2}.$$

Thus, Eqs. (30)–(33) make possible a fairly accurate estimate of K_{11}. For instance, at $\xi\approx400$ cm^{-1}, which is characteristic of a Fe^{3+} ion with allowance for approximately a ten percent drop in the spin-orbit coupling constant in the crystal,

$$K_{11}(\mathrm{I})\approx0.2\ \mathrm{cm}^{-1},\quad K_{11}(\mathrm{III})\approx-0.2\ \mathrm{cm}^{-1},$$

$$K_{11}(\mathrm{II})\approx-0.1\ \mathrm{cm}^{-1},\quad K_{11}(\mathrm{IV})\approx-0.2\ \mathrm{cm}^{-1}. \qquad (37)$$

For the total contribution of the pair of Fe^{3+} ions to the effective anisotropy constant P_0^2 at $T=0$ K in our model we obtained the following:

$$P_0^2(\pi)=\begin{cases}2K_{11}(\mathrm{I})+\frac{5}{2}K_{11}(\mathrm{III})\approx -0.9\ \mathrm{cm}^{-1}\\ \quad\text{(identical sublattices)},\\ 2K_{11}(\mathrm{II})-\frac{5}{2}K_{11}(\mathrm{III})\approx -0.1\ \mathrm{cm}^{-1}\\ \quad\text{(distinct sublattices)}.\end{cases}$$

Allowing only for the quasidipole contribution, we get

$$P_0^2(\pi)=\begin{cases}K_{11}(\text{total})\approx -0.3\ \mathrm{cm}^{-1}\ \text{(identical sublattices)},\\ -K_{11}(\text{total})\approx +0.3\ \mathrm{cm}^{-1}\ \text{(distinct sublattices)}.\end{cases}$$

The ordinary magnetodipole contribution of the pair of Fe^{3+} ions considered to P_0^2 is

$$P_0^2|_{\mathrm{md}}=\pm\frac{2g\beta S}{R^3}\approx\pm 0.4\ \mathrm{cm}^{-1}$$

at $R\approx 4$ Å. Thus, the exchange–relativistic contribution of the pair of Fe^{3+} ions to the magnetic anisotropy constant can exceed the respective magnetodipole contribution.

In contrast to the magnetodipole interaction, exchange-relativistic anisotropy in the event of noncollinear superexchange geometry is not an axisymmetric interaction. For a pair of $3d$-ions of the S-type the principal axes of the tensor of the effective spin anisotropy constants lie in the superexchange-bond plane, and the symmetry of V_{an} is generally higher than the crystal symmetry of the respective bond. In the simplest case where only the Fe^{3+}—O^{2-} σ-bond is taken into account, the direction of the radius vector $\mathbf{R}_{12}$ of the Fe_1^{3+}—Fe_2^{3+} bond serves as the principal axis of the tensor of the anisotropy constants P_q^2, with

$$P_0^2(\theta)=\frac{1-3\cos\theta}{2}P_0^2(\pi),$$

$$P_{\pm 1}^2(\theta)=0,$$

$$P_{\pm 2}^2(\theta)=\sqrt{\tfrac{3}{8}}\,(1+\cos\theta)P_0^2(\pi), \tag{38}$$

where θ is the angle of the superexchange bond Fe_1^{3+}—O^{2-}—Fe_2^{3+}. Note that if we allow only for the Fe^{3+}—O^{2-} σ-bond, only type-III and type-IV mechanisms contribute to exchange–relativistic anisotropy.

Equations (38) serve as a good illustration of the dependence of effective anisotropy constants on the angle of the superexchange bond.

The total contribution to the effective anisotropy constant is in some cases a result of competition between several terms with different signs. For instance, in the case of the given pair of ions belonging to different sublattices,

$$P_0^2=-2K_{11}(\mathrm{II})-\tfrac{5}{2}K_{11}(\mathrm{III})+2K_{20}(\mathrm{III})$$

$$\approx +0.2+0.5-0.8=-0.1\ \mathrm{cm}^{-1}.$$

The microscopic model calculation conducted is of only semiquantitative, but it provides a reliable means for establishing the order of magnitude (0.1–1 cm^{-1}) both of separate quasidipole or nondipole contributions of the exchange-bound pair of Fe^{3+} ions to the anisotropy constant and of the total contribution of one or another perturbation-theory mechanism. Note the unexpectedly large 20-(02-) contribution of the purely orbital spinless exchange (type-III) mechanism), equivalent to single-ion anisotropy in both the spin-orbit structure and the temperature dependence.

The total contribution of the type-IV mechanism, "frozen" at $T=0$ K, may reach a sizable value (of the order of 0.1 cm^{-1}) at relative temperatures $\tau=T/T_N\sim 0.6$–0.7, although at the same time the contributions of the other mechanisms drop by a factor of two.

In conclusion we note the exceptionally strong dependence of the resulting exchange–relativistic contribution to the anisotropy on the type of exchange (intrasublattice or intersublattice), which is primarily a consequence of allowing for nondipole (20)-(02-) contributions.

4.3. The exchange–relativistic contribution to magnetoelastic coupling

The large value of the exchange–relativistic anisotropy in the pair of Fe^{3+} ions and the strong dependence of P_0^2 on the distance between the cation and the intermediate anion and on the superexchange-bond angles indicate that the exchange–relativistic contribution to magnetoelastic coupling is large even when the total exchange–relativistic contribution to the effective magnetic anisotropy constant is negligible.

For numerical estimates we consider a model antiferromagnet of the orthoferrite $RFeO_3$ type with an ideal perovskite structure. Assuming that the dependence on the cation–anion separation of P_0^2 coincides with that of the exchange integral in the pair of Fe^{3+} ions and employing the Bloch empirical law[16]

$$\frac{\partial\ln P_0^2}{\partial\ln R}\approx\frac{\partial\ln I}{\partial\ln R}\approx-\alpha\quad(\alpha\sim 10),$$

we arrive at the following expressions for the magnetostriction constants λ_{100} and λ_{111} of the model perovskite and for the magnetoelastic coupling constants:

$$\Delta\lambda_{100}(T=0)=\frac{\alpha P_0^2N_0}{3(C_{11}-C_{12})},\quad \Delta a_1=-\frac{3}{2}\alpha P_0^2(0)N_0,$$

$$\Delta\lambda_{111}(T=0)=\frac{P_0^2N_0}{C_{44}},\quad \Delta a_2=3P_0^2N_0,$$

where N_0 is the number of Fe^{3+} ions per unit volume, and C_{11}, C_{12}, and C_{14} are elastic constants. Assuming that N_0, C_{11}, C_{12}, and C_{14} are characteristic of orthoferrites of the $YFeO_3$ type and allowing for the intersublattice nature of the nearest neighbor exchange and the estimates of $P_0^2(0)$, we find

$$\Delta\lambda_{100}(T=0)\approx 10^{-6}\alpha P_0^2,$$

$$\Delta a_1\approx -6\times 10^6\alpha P_0^2\ \mathrm{erg\ cm}^{-3},$$

$$\Delta\lambda_{111}(T=0)=3\times 10^{-6}\alpha P_0^2;\quad \Delta a_2\approx 10^7P_0^2\ \mathrm{erg\ cm}^{-3}$$

(here P_0^2 is measured in units of cm^{-1}), which at $P_0^2 \sim 1$ cm^{-1} is of the same order of magnitude as the experimental data on orthoferrites.[16] This fact suggests that exchange–relativistic anisotropy, like single-ion anisotropy, is one of the most important mechanisms of the magnetoelasticity of orthoferrites.

Note that the magnetoelastic constants of weakly anisotropic magnetic materials based on $3d$-ions of the S-type, and also the anisotropy constants, follow a four-parameter temperature dependence of the type (26).

4.4. The features of exchange–relativistic anisotropy in a pair of $3d^3$- or $3d^8$-ions

For $3d^3$-ions, such as Cr^{3+}, Mn^{4+}, and V^{2+}, the situation with parametrization of exchange-relativistic anisotropy is somewhat worse than in the case of pairs of $3d^5$-ions, since spin $S=3/2$ is characteristic not only of the ground Hund term but also of a number of excited states. Thus, the values of the intermediate spin in perturbation-theory sums can be both $S=3/2$ and $S=1/2$. For instance, for type-I perturbation-theory processes one must introduce several terms in accordance with the values of the intermediate spin of ions 1 and 2. Here calculations by formulas (21) and (22) yield for the contribution of the spin-dependent part of the exchange to the effective magnetic anisotropy constant the following

$$\begin{aligned} P_1^2 = & \left(\pm \rho_1^2(T) - \frac{4}{3} \rho_2(5+\rho_2) \right) P_q^2\left(\frac{3}{2}\frac{3}{2} \right) \\ & + \left(\pm \rho_1^2(T) + \frac{4}{3} \rho_2(T) - \frac{1}{3} \rho_2^2(T) \right) P_q^2\left(\frac{1}{2}\frac{1}{2} \right) \\ & + \left(\pm \rho_1^2(T) + \frac{1}{6} \rho_2(T) + \frac{2}{3} \rho_2^2(T) \right) P_q^2\left(\frac{3}{2}\frac{1}{2} + \frac{1}{2}\frac{3}{2} \right), \end{aligned} \tag{39}$$

where the values $S_1' S_2'$ in the parameters P_q^2 point directly to the relation between the respective term and the contribution of one or another excited states.

Clearly, in some terms the nondipole contributions may considerably exceed the ordinary quasidipole contribution. Without going into a detailed analysis of type-II to type-IV contributions, we can nevertheless draw a general conclusion that the situation with pairs of $3d^3$-ions is on the whole similar to that with pairs of $3d^5$-ions.

Note that in contrast to pairs of $3d^5$-ions, the spinless ($a=1$) and, therefore, purely orbital part of the exchange interaction for pairs of $3d^3$-ions yields an exchange–relativistic contribution not only to terms with $k_1k_2=20\ 02$ (of the single-ion anisotropy type) but to terms with $k_1k_2=11$ of the quasidipole type.

For S-type ions with a $3d^8$ configuration (Ni^{2+} and Cu^{3+}) the principal difference lies in the absence in the spin Hamiltonian (13), and hence in formula (26) for the effective magnetic anisotropy constants, of nondipole 13-(31-) contributions. This is related to the magnitude of the spin in the ground state of $3d^6$-ions ($S=1$) and to the restrictions imposed on k_1 and k_2, namely, $k_1 \leqslant 2S$ and $k_2 \leqslant 2S$ (the triangle rule).

4.5. Contribution of states with charge transfer to exchange–relativistic anisotropy

Above we estimated the contribution to exchange–relativistic anisotropy of the excited states of Fe^{3+} ions (more precisely, complexes of the FeO_6^{9-} type) within the $3d^5$-configuration. However, complexes of the FeO_6^{9-} type contain low-energy excited states with anion-cation charge transfer, say, states of the configuration $t_{2g}^4 e_g^2 t_{-1g}^1$ (here t_{-1g} is an "oxygen hole") with an energy of approximately 2.5 eV (Ref. 14). Among the states of this configuration there are ${}^4T_{1g}$ and ${}^6T_{1g}$, which are mixed, via spin–orbit coupling and exchange, with the ${}^6A_{1g}$ term of the $t_{2g}^3 e_g^2$ configuration, the ground state of the complex. Generally, allowing for quartic states leads, as before, to the same expression (27) for the contribution to the anisotropy constant.

${}^6T_{1g}$ states with the same spin multiplicity as the ground Hund state ${}^6A_{1g}$ can also be treated via Eqs. (30)–(33). This yields an expression similar to (27) for the contribution of spin-dependent exchange to the effective anisotropy constant:

$$\begin{aligned} \Delta P_q^2 = & \left[\pm \rho_1^2 - \left(\frac{56}{3} \rho_2 + \frac{16}{3} \rho_2^2 \right) \right] \sum \Delta P_q^2(\mathrm{I}) \\ & + \left[\pm \rho_1^2 + \left(\frac{56}{3} \rho_2 + \frac{16}{3} \rho_2^2 \right) \right] \sum \Delta P_q^2(\mathrm{II}) \\ & \pm \left(\rho_1^2 + \frac{18}{37} \rho_1 \rho_3 \right) \sum \Delta P_q^2(\mathrm{III}) \\ & \pm \left(\rho_1^2 + \frac{9}{16} \rho_1 \rho_3 \right) \sum \Delta P_q^2(\mathrm{IV}) \end{aligned} \tag{40}$$

(summation is over lattices).

Note the unusually high relative value of the nondipole 20-, 02-, and 22-contributions of the type-I and type-II mechanisms. Their total contribution at $T=0$ K exceeds the ordinary quasidipole 11-contribution by a factor of 22! The purely orbital spinless exchange ($a=0$) in a pair of complexes, with allowance for states with charge transfer, yields a nondipole 20-, 02-contribution (of the single-ion type) and an ordinary quasidipole 11-contribution.

To estimate the numerical value of the exchange-relativistic contribution of states with charge transfer to the anisotropy constants a fairly difficult problem. The matrix elements of V_{so} sandwiched between states of the $3d^5$ and $3d^6\underline{L}$ (here $\underline{L}$ is an "oxygen" hole),

$$\langle 3d | V_{\mathrm{so}} | 2p \rangle \sim S_{3d-2p} \langle 3d | V_{\mathrm{so}} | 3d \rangle$$

(with the overlap integral $S_{3d-2p} \leqslant 0.1$), are smaller by a factor of approximately 10 than the matrix elements of V_{so} used earlier in our microscopic calculations. If we allow for states with charge transfer, various exchange parameters may increase, for one thing, because of the appearance in them of integrals of cation–anion transfer instead of integrals of cation–cation transfer.

Thus, we may conclude that excited states with charge transfer in FeO_6^{9-} complexes can noticeably participate in forming exchange–relativistic anisotropy. Most likely the 20-, 02-contributions, which renormalize the contribution of single-ion anisotropy, will have the largest value.

4.6. Exchange–relativistic anisotropy in α-Fe_2O_3 and Cr_2O_3 antiferromagnets

The above estimates point to the possibility of a large exchange-relativistic contribution to magnetic anisotropy. The real magnitude of this contribution in any magnetic substance of the form of various $3d$-oxides, fluorides, etc., is determined chiefly by two factors: (a) the spatial geometry of superexchange bonds and the number of such bonds, and (b) the type of exchange (intrasublattice or intersublattice). Incidentally, in the case of magnetodipole anisotropy the main factor determining the size of the contribution to the magnetic anisotropy is the extent to which the sublattice of local magnetic moments (the $3d$-sublattice) is noncubic. For single-ion anisotropy the basic factor is usually the extent to which the immediate anion environment is noncubic.

The numerical value of the constants of effective magnetic anisotropy of exchange-relativistic origin is largely determined by the nature of the exchange (superexchange) interaction of ions from different magnetic sublattices, the superexchange geometry and the magnitude of various exchange parameters, reaching in favorable situations values exceeding 1 cm^{-1} per ion.

Strong noncubic distortions of FeO_6^{9-} clusters and the Fe^{3+} sublattice proper and the existence of a large number of nonequivalent and noncollinear superexchange Fe^{3+}—O^{2-}—Fe^{3+} bonds make hematite α-Fe_2O_3 a system with a potentially large exchange–relativistic contribution to the anisotropy constant. A similar situation is realized in the antiferromagnet Cr_2O_3. Total neglect of the exchange–relativistic contribution to the anisotropy of these systems has led to difficulties in describing their magnetic behavior.[4,5,17] First of all, in both cases we are forced to assume a great change (with sign reversal) in the value of the single-ion contribution to anisotropy in comparison to the respective contribution in isomorphic systems Al_2O_3: Cr^{3+}, Fe^{3+} (Ref. 18). For Cr^{3+} all attempts to describe the special features of the temperature dependence of the effective anisotropy constant[4] proved futile (see Fig. 2), for α-Fe_2O_3 a strong discrepancy was also observed between theoretical and experimental data.[17]

It is easy, however, to describe the results of experiments[4,5,17] using the general formula (26). Figures 1 and 2 depict the results of processing the data on the temperature dependence of second-order anisotropy constants $K(T)$ for, respectively, hematite α-Fe_2O_3 and Cr_2O_3 by employing the four-parameter formula (26). In contrast to the authors of Ref. 17, in hematite we allowed for the renormalization of the second-order anisotropy constant caused by the contribution of fourth-order anisotropy, as a result of which $|K(0)|$ was found to increase by approximately one-third. The calculated curves were obtained for the following parameter values:

$$\alpha\text{-}Fe_2O_3{:}K(0) = -4.4\times10^{-2}\ cm^{-1}/\text{ion},$$

$$K_{20} = -2.82\ cm^{-1}/\text{ion},$$

$$K_{22} = -1.90\ cm^{-1}/\text{ion},\quad K_{13} = 1.60\ cm^{-1}/\text{ion},$$

$$K_{11} = K(0) - K_{20} - K_{22} - K_{13} = 3.08\ cm^{-1}/\text{ion};$$

$$Cr_2O_3{:}K(0) = 2.5\times10^{-2}\ cm^{-1}/\text{ion},$$

$$K_{20} = -0.19\ cm^{-1}/\text{ion},$$

$$K_{13} = 0.14\ cm^{-1}/\text{ion},\quad K_{22} = 0,$$

$$K_{11} = K(0) - K_{20} - K_{13} - K_{22} = 7.3\cdot10^{-2}\ cm^{-1}/\text{ion}.$$

Comparing these values with the calculated magnetodipole contribution,[4,5]

$$\alpha\text{-}Fe_2O_3{:}K_{11}^{md} \approx -1.1\ cm^{-1}/\text{ion},$$

$$Cr_2O_3{:}K_{11}^{md} \approx 6\times10^{-2}\ cm^{-1}/\text{ion},$$

and the value of the single-ion contribution known for the impurity ions Fe^{3+} and Cr^{3+} in Al_2O_3 (Ref. 18),

$$\alpha\text{-}Fe_2O_3{:}K_{20}^{sia} \approx -1.1\ cm^{-1}/\text{ion},$$

$$Cr_2O_3{:}K_{20}^{sia} \approx 0.43\ cm^{-1}/\text{ion},$$

we can deduce that in both cases the quasidipole and nondipole contributions of the exchange–relativistic origin to the anisotropy constant are considerable.

The fairly small value of the K_{mn} parameters for Cr_2O_3 in comparison to that for α-Fe_2O_3 is the result of the following three factors:

(a) the smaller value of the Cr^{3+}-ion spin: $S_{Cr}/S_{Fe} = 3/5$;

(b) the smaller value of the spin–orbit coupling constant: $\zeta_{3d}(Cr^{3+}) \approx 1/2\zeta_{3d}(Fe^{3+})$; and

(c) the absence in Cr^{3+} ions and the presence in Fe^{3+} ions of e_g-electrons, which participate in the strongest cation–anion σ-bond.

5. CONCLUSION

Exchange–relativistic double-ion anisotropy consists, in addition to the standard quasidipole contribution, of a number of new "nondipole" contributions with a different temperature but a comparable numerical value. Within the molecular field approximation we derived a universal four-parameter formula for the temperature dependence of the constant of second-order anisotropy in weakly anisotropic magnetic substances. Numerical estimates show that in favorable circumstances the contribution of an exchange-bound pair of $3d$-ions of the S-type to the anisotropy constant can reach values of order 1 cm^{-1}.

Our results can find application not only in explaining the numerical values and temperature dependence of magnetic-anisotropy and magnetoelastic-coupling constants. For instance, lately there has been a new surge of interest in magnetic anisotropy mechanisms in connection with the appearance of a number of papers investigating the magnetoelectric effect, including studies of this effect in the antiferromagnet Cr_2O_3 (Refs. 19 and 20). As with the magnetic anisotropy constant, the separation of the contributions in the magnetoelectric susceptibility is in many respects based on the different nature of the temperature dependence of single-ion, double-ion, and other mechanisms of the magnetoelectric effect.[21–23] Here instead of the total spin Hamiltonian of the exchange–relativistic magnetoelectric interaction of type (13) a simplified form of type (2) is employed, which generally leads to incorrect conclusions concerning the relative role of various mechanisms of the magnetoelectric effect.

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[1] Strictly speaking, the tensor $P_q^2(1k_1,2k_2)$ of the anisotropy parameters is not a true irreducible tensor of rank 2 in the rotation group.

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