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Isotropic Magnetic Exchange between Anisotropic Yb(III) Ions. Study of $Cs_3Yb_2Cl_9$ and $Cs_3Yb_2Br_9$ Crystals

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Despite the prevalent belief about a strong anisotropy of the magnetic exchange in rare-earth compounds, $Cs_3Yb_2Cl_9$ and $Cs_3Yb_2Br_9$ crystals are found to exhibit fully isotropic exchange coupling between Yb^{3+} ions. In this article, we attempt to reveal the physical origin of this surprising feature. Our theoretical consideration is based on a model of the kinetic exchange between two octahedrally coordinated Yb^{3+} ions in their ground Kramers doublet states. It is shown that a mechanism of kinetic exchange involving intercenter electron hopping between 4f orbitals of two Yb^{3+} ions in a face-shared binuclear unit results in fully isotropic antiferromagnetic exchange coupling, while a mechanism in which the electron jumps from the 4f to the 5d orbital gives rise to a highly anisotropic interaction. Comparison of these results with the experimental data along with qualitative arguments regarding the relative significance of these two contributions to the overall exchange indicate that, in face-shared Yb^{3+} binuclear units, the 4f ↔ 4f mechanism plays a dominant role.

1. Introduction

Exchange-coupled systems comprising ions with unquenched orbital angular momenta seem to be quite attractive in magnetochemistry because these compounds are the paradigm of strong magnetic anisotropy.[1−7] Most rare-earth-based compounds exhibit a very strong magnetic anisotropy,[8−12] that manifests itself in both local factors (anisotropy of the g tensor) and in the anisotropy of the orbitally dependent exchange.

A large amount of experimental data[13−15] in conjunction with a clear physical concept of the role of the orbital angular momentum created a firm conviction that strong exchange anisotropy is an inherent and common property of all rare-earth systems with unquenched orbital angular momenta. However, the rare-earth compounds $Cs_3Yb_2Cl_9$ and $Cs_3Yb_2Br_9$, which are formed by pairs of $YbCl_6$ octahedra sharing a face, seem to be an exception to this general rule. In fact, Güdel et al.[16] experimentally showed that the exchange interaction between Yb^{3+} ions in these compounds seems to be isotropic and can be described by a Heisenberg-type Hamiltonian acting within the lowest Kramers doublet of Yb^{3+} ions. This surprising result generated at least two theoretical questions: (1) Is this unexpected isotropy of the exchange coupling a consequence of some accidental com-

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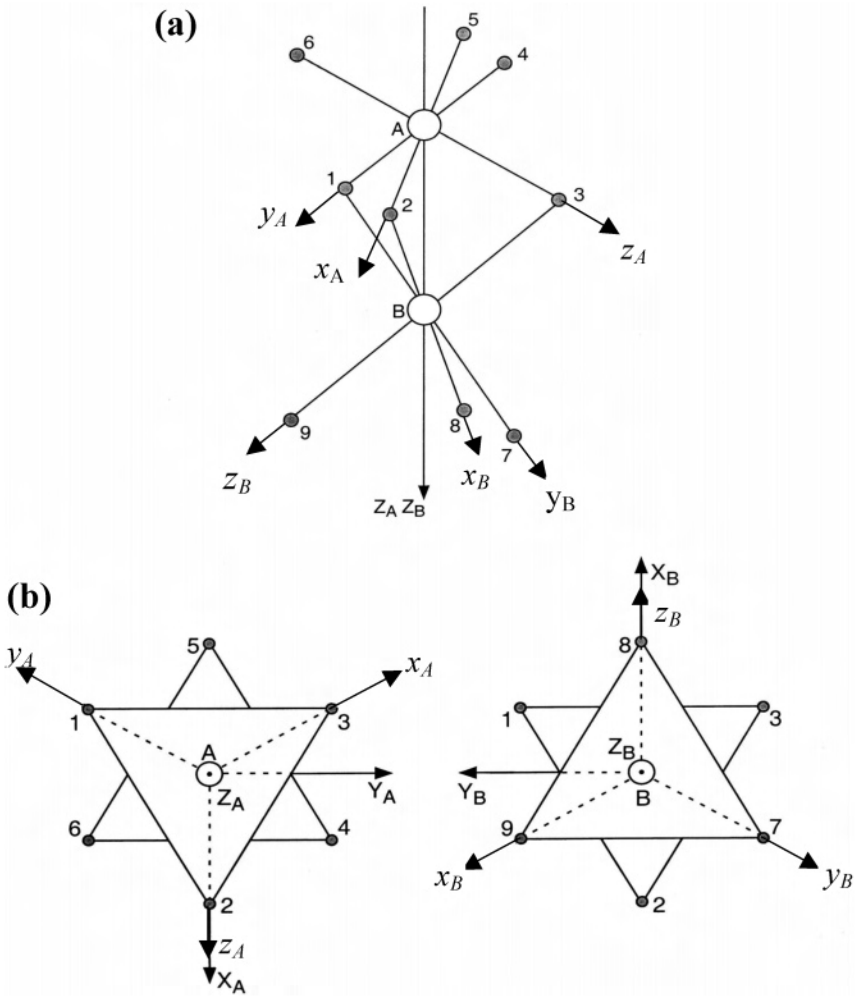

Figure 1. Schematic structure of $Cs_3Yb_2Cl_9$ and $Cs_3Yb_2Br_9$ compounds: (a) tetragonal coordinate frames, and (b) local trigonal frames.

pensation of the contributions coming from the microscopic parameters of the system (electron-transfer integrals contributing to the kinetic exchange, intra-atomic Coulomb energies, etc.), or there is a definite underlying physical reason giving rise to the observed isotropic exchange? (2) If such a physical reason does exist, of what does this reason consist and under what physical conditions does the exchange appears to be isotropic (structure, exchange mechanisms, etc.)? The aim of the present study is to shed light on these questions on the basis of the microscopic theory of magnetic exchange.

2. Ground State of the Yb^{3+} Pair

In $Cs_3Yb_2Cl_9$ and $Cs_3Yb_2Br_9$ crystals, the octahedrally coordinated Yb^{3+} ions form face-shared dimers of approximately D_{3h} symmetry.[17] Because the local trigonal crystal field is unable to produce an appreciable anisotropy of the g tensor,[16] we will exclude this field from consideration and focus on the kinetic exchange problem in the idealized system built from two perfect octahedral Yb^{3+} sites (Figure 1). The cubic crystal field splits the $^2F_{7/2}$ ground term of Yb^{3+} ions into two Kramers doublets, Γ_6 and Γ_7, and a quadruplet, Γ_8, in such a way that the Kramers doublet Γ_6 proves to be the ground state (Figure 2). The energy gap between the ground and excited states was shown to exceed considerably the exchange interaction ($J = -2.87$ cm^{-1}),[16] so we will focus on the Kramers doublet Γ_6. Considering symmetry-adapted combinations of the spherical harmonics $Y_{4m}(\vartheta\varphi)$ one can build the wave functions of the Kramers doublet from the $^2F_{7/2}$ manifold. We will use an alternative approach that is more appropriate for the problem of magnetic exchange. Let us note that the 4f atomic level is split in the cubic crystal field into two triplets, T_1 and T_2,

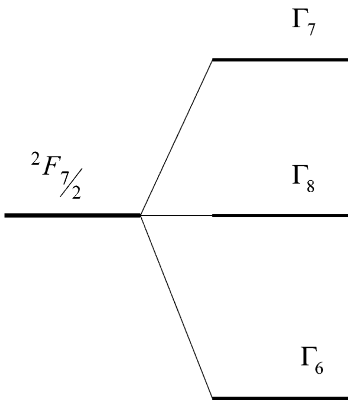

Figure 2. Cubic crystal field splitting of the ground term of the Yb^{3+} ion.

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and a singlet, A_2. Simple group-theoretical arguments show that Γ_6 arises from the T_1 orbital triplet only when the latter is coupled to the spin state with $S = {}^1/_2$ (Γ_6). This means that only T_1 states contribute to the ground Kramers doublets. To make the calculations simpler and more transparent, we will consider the Γ_6 state that originates from the hole configuration f^1, instead of that coming from the electronic configuration f^{13}. The validity of this hole formalism will be justified later.

Henceforth, we will not consider very weak component of the trigonal field, but we will use the trigonal one-electron 4f basis of T_1 type described in Appendix I. This basis is defined with respect to the local trigonal frames shown in Figure 1b together with the corresponding cubic ones (Figure 1a). Because only the Γ_6 state is present in the f^1 pattern, the wave functions for this doublet can be found using the Clebsch−Gordan expansion for the O group.[18] This leads to the following expressions for the wave functions in terms of the complex trigonal T_1 states

$$\begin{aligned} \varphi^{+}_{\Gamma_6} &\equiv [+] = \sqrt{\frac{2}{3}}\, f_{a_+}|{\downarrow}\rangle - \frac{1}{\sqrt{3}}\, f_{a_o}|{\uparrow}\rangle, \\ \varphi^{-}_{\Gamma_6} &\equiv [-] = \sqrt{\frac{2}{3}}\, f_{a_-}|{\uparrow}\rangle - \frac{1}{\sqrt{3}}\, f_{a_o}|{\downarrow}\rangle \end{aligned} \tag{1}$$

where $|{\uparrow}\rangle$ and $|{\downarrow}\rangle$ are "spin-up" and "spin-down" functions, respectively; we use the shorthand notations $f_{T_1 a_o} \equiv f_{a_o}$ and $f_{T_1 a_{\pm 1}} \equiv f_{a_\pm}$ for the complex trigonal basis. The wave functions of the Kramers doublet satisfy the same Hermitian conjugation relation as the spin-${}^1/_2$ functions $|{\uparrow}\rangle$ and $|{\downarrow}\rangle$, that is

$$(\varphi^{+}_{\Gamma_6})^* = \varphi^{-}_{\Gamma_6}, \quad (\varphi^{-}_{\Gamma_6})^* = -\varphi^{+}_{\Gamma_6} \tag{2}$$

The four states describing the ground $(\Gamma_6)_A \otimes (\Gamma_6)_B$ manifold of the pair are

$$\begin{aligned} |g_1\rangle &\equiv |[+]_A[+]_B\rangle = \\ &\frac{2}{3}|\bar{f}^{A}_{a_+}\, \bar{f}^{B}_{a_+}| + \frac{1}{3}|f^{A}_{a_o}\, f^{B}_{a_o}| - \frac{\sqrt{2}}{3}(|\bar{f}^{A}_{a_+}\, f^{B}_{a_o}| + |f^{A}_{a_o}\, \bar{f}^{B}_{a_+}|) \\ |g_2\rangle &\equiv |[+]_A[-]_B\rangle = \\ &\frac{2}{3}|\bar{f}^{A}_{a_+}\, f^{B}_{a_-}| + \frac{1}{3}|f^{A}_{a_o}\, \bar{f}^{B}_{a_o}| - \frac{\sqrt{2}}{3}(|\bar{f}^{A}_{a_+}\, \bar{f}^{B}_{a_o}| + |f^{A}_{a_o}\, f^{B}_{a_-}|) \\ |g_3\rangle &\equiv |[-]_A[+]_B\rangle = \\ &\frac{2}{3}|f^{A}_{a_-}\, \bar{f}^{B}_{a_+}| + \frac{1}{3}|\bar{f}^{A}_{a_o}\, f^{B}_{a_o}| - \frac{\sqrt{2}}{3}(|f^{A}_{a_-}\, f^{B}_{a_o}| + |\bar{f}^{A}_{a_o}\, \bar{f}^{B}_{a_+}|) \\ |g_4\rangle &\equiv |[-]_A[-]_B\rangle = \\ &\frac{2}{3}|f^{A}_{a_-}\, f^{B}_{a_-}| + \frac{1}{3}|\bar{f}^{A}_{a_o}\, \bar{f}^{B}_{a_o}| - \frac{\sqrt{2}}{3}(|f^{A}_{a_-}\, \bar{f}^{B}_{a_o}| + |\bar{f}^{A}_{a_o}\, f^{B}_{a_-}|) \end{aligned} \tag{3}$$

where we use the conventional shorthand notations of the spin−orbitals $f_{a_+}|{\uparrow}\rangle \equiv f_{a_+}$, $f_{a_+}|{\downarrow}\rangle \equiv \bar{f}_{a_+}$, etc., and $|\cdot\cdot|$ is the symbol of Slater determinant.

3. Effective Exchange Hamiltonian for a Kramers Doublet Pair

Kinetic exchange appears as a second-order contribution to intercenter one-electron (one-hole) transfer.[19,20] The effective exchange operator acting within the space of the direct product of the one-center Kramers doublet functions (the states $|g_k\rangle$) is defined by the matrix $\hat{H}_{\mathrm{eff}}$ with the complex matrix elements

$$\langle g_{k'}||g_k\rangle = -\sum_n \frac{1}{E_n - E_g}\langle g_{k'}|h|e_n\rangle\langle e_n|h|g_k\rangle \tag{4}$$

where h is the one-electron part of the Hamiltonian that includes the kinetic energy and the attraction between the electrons and alien nuclei. The sum in eq 4 runs over the excited charge-transfer (CT) states in which one electron is transferred from site A (B) to site B (A).

An equivalent way to express this exchange interaction between the two lowest-lying Kramers doublets consists of using an effective pseudo-spin-${}^1/_2$ Hamiltonian, which in the case of axial symmetry can be expressed as

$$\hat{H}_{\mathrm{eff}} = -2J_{\perp} s^{A}_{Z}\, s^{B}_{Z} - 2J_{\|}(s^{A}_{X}\, s^{B}_{X} + s^{A}_{Y}\, s^{B}_{Y}) = \begin{array}{c} \begin{array}{cccc} \alpha_A\alpha_B & \alpha_A\beta_B & \beta_A\alpha_B & \beta_A\beta_B \end{array} \\ \begin{pmatrix} -J_{\|}/2 & 0 & 0 & 0 \\ 0 & J_{\|}/2 & -J_{\perp} & 0 \\ 0 & -J_{\perp} & J_{\|}/2 & 0 \\ 0 & 0 & 0 & -J_{\|}/2 \end{pmatrix} \end{array} \tag{5}$$

To calculate the effective exchange parameters $J_{\|}$ and $J_{\perp}$, one has to compare this matrix with the matrix elements given by eq 4. In general, in eq 4, the matrix is not traceless, but by extracting the unit part, one can obtain the traceless matrix

$$\hat{H}_{\mathrm{eff}} = \begin{array}{c} \begin{array}{cccc} |g_1\rangle & |g_2\rangle & |g_3\rangle & |g_4\rangle \end{array} \\ \begin{pmatrix} w_1 & 0 & 0 & 0 \\ 0 & w_2 & w_3 & 0 \\ 0 & w_3 & w_2 & 0 \\ 0 & 0 & 0 & w_1 \end{pmatrix} \end{array} = \frac{1}{2}(w_1 + w_2)\mathbf{I} + \begin{array}{c} \begin{array}{cccc} |g_1\rangle & |g_2\rangle & |g_3\rangle & |g_4\rangle \end{array} \\ \begin{pmatrix} \frac{1}{2}(w_1 - w_2) & 0 & 0 & 0 \\ 0 & -\frac{1}{2}(w_1 - w_2) & w_3 & 0 \\ 0 & w_3 & -\frac{1}{2}(w_1 - w_2) & 0 \\ 0 & 0 & 0 & \frac{1}{2}(w_1 - w_2) \end{pmatrix} \end{array} \tag{6}$$

where $\mathbf{I}$ is a 4 × 4 unit matrix. By comparing the traceless part of the matrix in eq 6 with the matrix in eq 5, one obtains

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the following relationships between the parameters of the effective pseudo-spin-$^1/_2$ Hamiltonian and the second-order matrix elements of the kinetic exchange

$$J_{\parallel} = w_2 - w_1, \quad J_{\perp} = -w_3 \tag{7}$$

Because the matrix elements $\langle g_{k'}|h|e_n\rangle$ connecting the ground state with the excited states are proportional to the one-hole intercenter matrix elements (transfer integrals), the nonzero matrix elements w_1, w_2, and w_3 (and thus, the effective exchange parameters) represent the bilinear forms of the transfer integrals. Our aim is to find explicit expressions of the second-order matrix elements in terms of the transfer integrals allowed by the trigonal overall symmetry of the system. To do so, one must specify the types of the electron-transfer processes that determine the different mechanisms of kinetic exchange. In the next section, we will derive the effective pseudo-spin-$^1/_2$ Hamiltonian related to two main mechanisms of the kinetic superexchange.

4. Kinetic Exchange Due to 4f ↔ 4f Transfer

The first exchange mechanism involves the charge-transfer states in which one hole is transferred from the 4f shell of one ion to the 4f shell of another. Because the $4f^2$ CT configurations have a complicated energy pattern, some assumptions should be made. We will not take into account the multiplet structure of the CT states, thus neglecting both the exchange interaction between two electrons (holes) of the CT f^2 configuration and the spin−orbit and crystal field splitting of the CT states. We thus assume that all CT states have the same energy U_{ff} that can be roughly estimated as the spherical part $F^0(4f,4f)$ of the Coulomb interaction between two 4f electrons (or holes). Because no intracenter exchange is assumed between 4f electrons in the CT states, only the transfer processes between the t_1 orbitals involved in the ground Kramers doublets should be considered. The remaining transfer processes (for example, those connecting t_1 and t_2 orbitals) result only in a shift of the energy pattern as a whole, so we will not consider them. The transfer integrals of the 4f ↔ 4f type, allowed by the trigonal symmetry, that contribute to the exchange splitting are the following

$$\begin{aligned} t_a &= \langle f^{A}_{T_1 a}|h|f^{B}_{T_1 a}\rangle = \langle f^{A}_{a_o}|h|f^{B}_{a_o}\rangle \\ t_e &= \langle f^{A}_{T_1\theta}|h|f^{B}_{T_1\theta}\rangle = \langle f^{A}_{T_1\epsilon}|h|f^{B}_{T_1\epsilon}\rangle = \langle f^{A}_{a_+}|h|f^{B}_{a_+}\rangle = \langle f^{A}_{a_-}|h|f^{B}_{a_-}\rangle \end{aligned} \tag{8}$$

The parameter t_a can be associated with the through-space direct $\sigma-\sigma$ interaction, whereas the interaction with the participation of the t_e transfer is an indirect one that occurs through the Cl ligands. Similar transfer processes were previously mentioned both for trigonal exchange-coupled and mixed-valence dimers of transition metal ions.[2,21,22]

The nonzero matrix elements connecting the states $|g_i\rangle$ belonging to the ground manifold with the excited states are given in the Appendix II. By substituting these results into eq 4, we find

$$w_1 = -\frac{4}{9U_{ff}}(t_a - t_e)^2, \quad w_2 = -\frac{2}{3U_{ff}}(t_a^{\,2} + 2t_e^{\,2}), \quad w_3 = \frac{2}{9U_{ff}}(t_a + 2t_e)^2 \tag{9}$$

Finally, by combining these results with eq 7, we obtain that $J_{\parallel}$ is equal to $J_{\perp}$ with the following expression for these exchange components

$$J_{\parallel} = J_{\perp} \equiv J = -\frac{2}{9U_{ff}}(t_a + 2t_e)^2 \tag{10}$$

Therefore, we arrive at the important conclusion that the kinetic exchange mechanism associated with 4f ↔ 4f transfer processes gives rise to the following isotropic Heisenberg interaction between two pseudo-spins-$^1/_2$

$$H_{\mathrm{eff}} = -2J\mathbf{s_A}\mathbf{s_B} \tag{11}$$

Because $J < 0$, the exchange interaction in this case proves to be antiferromagnetic.

5. Kinetic Exchange Due to 4f ↔ 5d Transfer

The second mechanism of kinetic exchange proposed by Goodenough[23] involves electron transfer from the 4f orbital of one rare-earth ion to the 5d orbital of another. Now, along with the 4f orbitals of T_1 type, we have to use the 5d orbitals that are transformed as the bases of T_2 and E representations in the *O* group. The real and complex trigonal forms of these orbitals are given in Appendix III.

As distinguished from the mechanism considered above. this mechanism demands the inclusion of the intracenter exchange interaction between 4f and 5d electrons in the CT states. Here we will use a simplified model proposed in ref 24. Within this model, the intraionic Coulomb repulsion between 4f and 5d electrons is approximated by one parameter U_{fd} that is assumed to include the spherical term $F^0(4f,5d)$ and the energy difference Δ_{fd} between the 4f and 5d orbitals (this difference approximated by the energy gap between the centers of gravity of the levels originating from $4f^{\,12}5d^1$ and $4f^{\,13}$ configurations is found to be ~13.5 eV[25]). The intracenter exchange is approximated by the single exchange integral $J_{fd} \approx G^1(4f,5d)$. For free Yb^{3+} ions, this value is ~1.5 eV.[25] This exchange discriminates the energies of spin triplets and spin singlets; the corresponding energy gap is equal to J_{fd}. In addition, the cubic crystal field splitting of the 5d levels, which is on the order of $10Dq \approx 2-3$ eV, is taken into account. At the same time, the spin−orbit splitting in the CT states is neglected, as is the cubic crystal field splitting of the 4f level (~100 cm^{-1}).

Strictly speaking, within the hole formalism, one should consider the ground-state configuration $(4f^15d^{10})_A - (4f^1$-$5d^{10})_B$ (*g*) and the two CT excited-state configurations $(4f^1$-

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$5d^9)_A$ − $(4f^25d^{10})_B$ and $(4f^25d^{10})_A$ − $(4f^15d^9)_B$ (*e*). It is possible to show, however, that, in the framework of the described simple model, the results will not be affected if, instead of these configurations, one considers simpler ones, namely, $(4f^1)_A - (4f^1)_B$ (g') and $(4f^15d^1)_A - (4f^2)_B$, $(4f^2)_A - (4f^15d^1)_B$ (e'). The detailed proof of this statement is given in Appendix IV.

The following transfer integrals of 4f ↔ 5d type are allowed by the trigonal symmetry

$$\beta_a = \langle f^{\mathrm{A}}_{\mathrm{T}_1 a}|h|d^{\mathrm{B}}_{\mathrm{T}_2 a}\rangle = \langle f^{\mathrm{A}}_{a_o}|h|d^{\mathrm{B}}_{x_o}\rangle$$

$$\beta_e = \langle f^{\mathrm{A}}_{\mathrm{T}_1\theta}|h|d^{\mathrm{B}}_{\mathrm{T}_2\theta}\rangle = \langle f^{\mathrm{A}}_{\mathrm{T}_1\epsilon}|h|d^{\mathrm{B}}_{\mathrm{T}_2\epsilon}\rangle = \langle f^{\mathrm{A}}_{a_+}|h|d^{\mathrm{B}}_{x_+}\rangle = \langle f^{\mathrm{A}}_{a_-}|h|d^{\mathrm{B}}_{x_-}\rangle \quad (12)$$

$$\beta'_e = \langle f^{\mathrm{A}}_{\mathrm{T}_1\theta}|h|d^{\mathrm{B}}_{\mathrm{E}\theta}\rangle = \langle f^{\mathrm{A}}_{\mathrm{T}_1\epsilon}|h|d^{\mathrm{B}}_{\mathrm{E}\epsilon}\rangle = \langle f^{\mathrm{A}}_{a_+}|h|d^{\mathrm{B}}_{u_+}\rangle = \langle f^{\mathrm{A}}_{a_-}|h|d^{\mathrm{B}}_{u_-}\rangle$$

The wave functions of the CT states that are connected to the ground manifold by these transfer processes and the corresponding excitation energies are reported in Table 1. The nonzero matrix elements connecting the ground manifold with these CT states of the $(4f^15d^1)_A$ configuration are given in Appendix V. Using these results, one can calculate the complex matrix elements in eq 4. Multiplying the obtained matrix elements by the factor 2 to take into account the CT states belonging to the $(4f^15d^1)_B$ configuration, we obtain

$$w_1 = -\frac{2(\beta_a{}^2 + \beta_e{}^2)}{9(U_{\mathrm{fd}} - 4D\mathrm{q})} - \frac{2(2\beta_a{}^2 + 5\beta_e{}^2)}{9(U_{\mathrm{fd}} - J_{\mathrm{fd}} - 4D\mathrm{q})} - \frac{2\beta'^2_e}{9(U_{\mathrm{fd}} + 6D\mathrm{q})} - \frac{10\beta'^2_e}{9(U_{\mathrm{fd}} - J_{\mathrm{fd}} + 6D\mathrm{q})}$$

$$w_2 = -\frac{(\beta_a{}^2 + 4\beta_e{}^2)}{9(U_{\mathrm{fd}} - 4D\mathrm{q})} - \frac{(5\beta_a{}^2 + 8\beta_e{}^2)}{9(U_{\mathrm{fd}} - J_{\mathrm{fd}} - 4D\mathrm{q})} - \frac{4\beta'^2_e}{9(U_{\mathrm{fd}} + 6D\mathrm{q})} - \frac{8\beta'^2_e}{9(U_{\mathrm{fd}} - J_{\mathrm{fd}} + 6D\mathrm{q})} \quad (13)$$

$$w_3 = \frac{\beta_a{}^2}{9(U_{\mathrm{fd}} - 4D\mathrm{q})} - \frac{\beta_a{}^2}{9(U_{\mathrm{fd}} - J_{\mathrm{fd}} - 4D\mathrm{q})}$$

Then, applying eq 7, we find

$$J_{\|} = \frac{\beta_a{}^2 - 2\beta_e{}^2}{9(U_{\mathrm{fd}} - 4D\mathrm{q})} - \frac{\beta_a{}^2 - 2\beta_e{}^2}{9(U_{\mathrm{fd}} - J_{\mathrm{fd}} - 4D\mathrm{q})} - \frac{2\beta'^2_e}{9(U_{\mathrm{fd}} + 6D\mathrm{q})} + \frac{2\beta'^2_e}{9(U_{\mathrm{fd}} - J_{\mathrm{fd}} + 6D\mathrm{q})}$$

$$J_{\perp} = -\frac{\beta_a{}^2}{9(U_{\mathrm{fd}} - 4D\mathrm{q})} + \frac{\beta_a{}^2}{9(U_{\mathrm{fd}} - J_{\mathrm{fd}} - 4D\mathrm{q})} \quad (14)$$

Because U_{fd} significantly exceeds J_{fd}, one can write approximately

$$J_{\|} \approx -\frac{(\beta_a{}^2 - 2\beta_e{}^2)J_{\mathrm{fd}}}{9(U_{\mathrm{fd}} - 4D\mathrm{q})^2} + \frac{2\beta'^2_e J_{\mathrm{fd}}}{9(U_{\mathrm{fd}} + 6D\mathrm{q})^2},$$

$$J_{\perp} \approx \frac{\beta_a{}^2 J_{\mathrm{fd}}}{9(U_{\mathrm{fd}} - 4D\mathrm{q})^2} \quad (15)$$

Table 1. Wave Functions of CT States Relevant to the 4f → 5d Kinetic Exchange Mechanism and the Corresponding Excitation Energies[a]

spin multiplicity	wave functions of CT states $\lvert i,a_m x_n,sm_s\rangle$ and $\lvert i,a_m u_k,sm_s\rangle$ ($m = 0, \pm1$, $n = 0, \pm1$, $k = \pm1$, i = A, B)	excitation energy
singlet	$\lvert i,a_m x_n, 00\rangle \equiv (1/\sqrt{2})(\lvert f^i_{a_m}\,\bar{d}^i_{x_n}\rvert - \lvert\bar{f}^i_{a_m}\,d^i_{x_n}\rvert)$	$U_{\mathrm{fd}} - 4D\mathrm{q}$
	$\lvert i,a_m u_k, 00\rangle \equiv (1/\sqrt{2})(\lvert f^i_{a_m}\,\bar{d}^i_{u_k}\rvert - \lvert\bar{f}^i_{a_m}\,d^i_{u_k}\rvert)$	$U_{\mathrm{fd}} + 6D\mathrm{q}$
triplet	$\lvert i,a_m x_n, 11\rangle \equiv \lvert f^i_{a_m}\,d^i_{x_n}\rvert$	$U_{\mathrm{fd}} - J_{\mathrm{fd}} - 4D\mathrm{q}$
	$\lvert i,a_m u_k, 11\rangle \equiv \lvert f^i_{a_m}\,d^i_{u_\pm}\rvert$	$U_{\mathrm{fd}} - J_{\mathrm{fd}} + 6D\mathrm{q}$

[a] Only the triplet states with maximum spin projection are shown.

Therefore, as distinguished from the 4f ↔ 4f mechanism, the exchange interaction due to electron jumps of 4f ↔ 5d type proves to be anisotropic.

6. Discussion

Before proceeding to an analysis of the results, some general remarks concerning the origin of the anisotropy are to be made. It is worthwhile to distinguish two physical reasons for the magnetic anisotropy in an exchange-coupled system. The first comes from the one-center interactions (low-symmetry crystal field combined with the spin−orbit interaction) and can be referred to as a single-ion (or local) anisotropy. This anisotropy manifests itself in the mononuclear magnetic moiety as well as in the entire exchange-coupled system. The second kind of anisotropy arises from the orbitally dependent exchange interaction and appears even when the mononuclear fragments involved in the orbitally dependent exchange are magnetically isotropic. This division has, however, true sense when we are dealing with the full terms of the interacting ions ($s\Gamma$ terms of transition metals or sj multiplets of rare earths). When the exchange, even isotropic, is projected onto the restricted space of the low-lying Kramers doublets of the interacting ions, the single-ion anisotropy (the anisotropy of the g factor) manifests itself in the effective pseudo-spin-$^1/_2$ Hamiltonian acting within the Kramers doublet space.[8,9,26−31]

In fact, the interaction between effective spins proves to be of the form[31]

$$H_{\mathrm{eff}} = -2J_x s^{\mathrm{A}}_x\, s^{\mathrm{B}}_x - 2J_y s^{\mathrm{A}}_y\, s^{\mathrm{B}}_y - 2J_z s^{\mathrm{A}}_z\, s^{\mathrm{B}}_z \quad (16)$$

The effective exchange parameters in eq 16 are given by

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$$J_\alpha = -\frac{1}{2}(g_\alpha/g_j)^2(g_j - 1)^2\, J, \quad \alpha = x, y, z \qquad (17)$$

where g_j is a Lande factor for the state with the total angular momentum j and J is the exchange integral describing the isotropic interaction between true spins. Therefore, given the anisotropy of g factor, we arrive at the anisotropic effective pseudo-spin-$^1/_2$ Hamiltonian.

At the same time, in most cases involving ions with unquenched orbital angular momenta, the interaction between the true spins is highly anisotropic and should be described by a Hamiltonian that includes both spin and orbital operators.[1−7] This anisotropy also manifests itself in the effective pseudo-spin-$^1/_2$ Hamiltonian, but as distinguished from the single-ion anisotropy, it comes directly from the interaction between the magnetic ions. For this reason, this kind of anisotropy can be referred to as genuine exchange anisotropy. Note that this anisotropy remains even when the rare-earth ions occupy perfect octahedral sites, in which case no anisotropy coming from the single ions can exist. One can expect that, in general, the two kinds of anisotropy coexist and their interplay results in the highly anisotropic interaction between the ions in the ground Kramers doublet states.

Proceeding from this general consideration to an analysis of the data for $Cs_3Yb_2Cl_9$ and $Cs_3Yb_2Br_9$ crystals, one can say that the local anisotropy in these systems is not very pronounced in the ground Kramers doublets. In fact, the principal values of the g tensor for the Kramers doublet state calculated from crystal field wave functions are $g_{||} = 2.63$ and $g_\perp = 2.70$.[16] These values are quite close to the value $g = 2.66$ calculated for Γ_6 in O_h, so that, according to eq 17, the local factors cannot significantly contribute to the overall anisotropy of the pseudo-spin-$^1/_2$ Hamiltonian. Despite this fact, the isotropic form of the pseudo-spin-$^1/_2$ Hamiltonian discovered in ref 16 was still very surprising because a significant exchange anisotropy arising from the orbital degeneracy was found in numerous systems including the isostructural compounds $Cs_3Ho_2Br_9$[15] and $YbCrBr_9$.[12] To elucidate the reason the genuine exchange anisotropy also vanishes in $Cs_3Yb_2Cl_9$ and $Cs_3Yb_2Br_9$, we have expressed in this work the parameters of the effective Hamiltonian operating within the ground $(\Gamma_6)_A \otimes (\Gamma_6)_B$ manifold through the microscopic parameters involved in the orbitally dependent kinetic superexchange (the set of nonzero transfer integrals). We have considered two main mechanisms for kinetic exchange. The first mechanism is related to intercenter hole transfer between the 4f orbitals, and the other involves transfer of the hole from the 5d orbital of one magnetic ion to the 4f orbital of the second ion. The results obtained can be summarized as follows:

1. The calculation of the effective exchange parameters within the 4f ↔ 4f mechanism demonstrated that, regardless of the relative values of the two nonvanishing transfer integrals t_a and t_e, the exchange interaction in the Kramers doublet pair is isotropic and at the same time antiferromagnetic, eqs 15. This result is compatible with main experimental observations,[16] namely, the isotropy of the exchange and its antiferromagnetic character.

To determine the extent to which this result is related to the trigonal symmetry of the Yb^{3+} pair, we have performed a model calculation for a corner-shared Yb^{3+} dimer of D_{4h} symmetry. In this case, the following two transfer parameters t'_a and t'_e connecting the t_1 orbitals are allowed by the symmetry of the pair

$$t'_a = \langle f^{A}_{T_1\gamma}|h|f^{B}_{T_1\gamma}\rangle, \quad t'_e = \langle f^{A}_{T_1\alpha}|h|f^{B}_{T_1\alpha}\rangle = \langle f^{A}_{T_1\beta}|h|f^{B}_{T_1\beta}\rangle \qquad (18)$$

where the f orbitals $f_{T_1\gamma} = f_{z^3}$, $f_{T_1\alpha} = f_{x^3}$, and $f_{T_1\beta} = f_{y^3}$ form the real cubic T_1 basis (local z axes are directed along the C_4 axis of the pair). In D_{4h} symmetry $f_{T_1\gamma}$ is of A_1 type, and $f_{T_1\alpha}$, $f_{T_1\beta}$ form the E basis. Using the $|g_i\rangle$ functions defined in Appendix VI and following the same procedure as in the case of D_{3h} symmetry, we arrive at eq 10 for the exchange parameters in which t_a and t_e are substituted by t'_a and t'_e. In this way, one can conclude that the 4f ↔ 4f mechanism results in isotropic exchange in both D_{3h} and D_{4h} cases. This means that the isotropy of the exchange is related to the special structure of the ground Kramers doublet arising from the $^2F_{7/2}$ term of the Yb^{3+} ion rather than to the trigonal symmetry of the pair or the simplifying assumptions of the model. More definite conclusions about the role of the symmetry in this phenomenon can be made by considering the remaining high-symmetric case, namely, the edge-shared bioctahedral cluster of D_{2h} symmetry. This work is under way.

2. The 4f ↔ 5d mechanism was shown to result in an essentially anisotropic exchange interaction. Because $J_{||} \neq J_\perp$, the symmetry of the Hamiltonian is axial, and the degree of anisotropy depends on the relative values of the different kinds of transfer integrals. By inspecting eqs 14 and 15, one can see that the only possibility for eliminating the anisotropy within this mechanism is to set $\beta_e = \pm\beta_a$ and $\beta'_e = 0$. In this case, we obtain a Heisenberg-type Hamiltonian with the exchange parameter

$$J \approx \frac{{\beta_a}^2 J_{fd}}{9(U_{fd} - 4Dq)^2} \qquad (19)$$

This parameter is obviously positive, thus corresponding to a ferromagnetic interaction that is in contradiction to the experimental observations. Further, the condition $\beta_e = \pm\beta_a$ looks unrealistic because the transfer integral β_a corresponds to a strong direct $\sigma-\sigma$ interaction in a face-shared geometry whereas β_e describes a relatively weak superexchange. The limit $\beta_a \gg \beta_e, \beta'_e$ looks more realistic, but it leads to a highly anisotropic interaction of the special form

$$J_\perp = -J_{||} = \frac{{\beta_a}^2 J_{fd}}{9(U_{fd} - 4Dq)} \qquad (20)$$

Therefore, the 4f ↔ 5d mechanism proves to be incompatible with the experimentally observed isotropic interaction; hence, the 4f ↔ 4f mechanism should dominate in this system, and the 4f ↔ 5d mechanism should play a minor role. To support this conclusion, one can invoke the following two independent arguments that favor the 4f ↔ 4f mechanism: (1) As was clearly demonstrated in ref 32, the 4f ↔ 4f mechanism dominates in the case of short metal−metal distances between trivalent rare-earth ions, whereas the remaining mechanisms with participation of 5d, 6s, and/or 6p orbitals become more important at longer distances. (2) In trivalent rare-earth ions, the energy gap Δ_{fd} between the 4f and 5d orbitals [and hence the energy F^0(4f,5d) + Δ_{fd} of CT states] is high, so electron hopping to the 5d orbitals is constrained. In the case under consideration, the intermetallic distances are short (3.70 and 3.83, respectively[16]) as the Yb−Yb pairs are sharing a face of the octahedron, and at the same time, the 4f 5d group of states in Yb^{3+} are 13.5 eV higher in energy than the levels arising from $4f^2$ configuration.[25] It is worth noting that Δ_{fd} rapidly increases across the lanthanide series[22] (from 57812 cm^{-1} for Ce^{3+} to 109809 cm^{-1} for Ln^{3+}). That is why, among the trivalent lanthanides, Yb^{3+} provides the most unfavorable conditions for 4f ↔ 5d exchange. Of course, more comprehensive study of the relative importance of different mechanisms of superexchange should involve the calculation of the microscopic parameters (hopping integrals, charge-transfer energies, etc). The aim of this short paper was only to demonstrate how different mechanisms of exchange manifest themselves in the anisotropic properties of the system and to investigate how the surprising isotropy of the exchange in the Yb pairs could appear.

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Appendix I. Trigonal One-Electron 4f Basis of T_1 Type

Because of the trigonal symmetry of the system, a convenient choice of basis is that in which C_3 is a quantization axis. We use here the definition of ref 18 for the trigonal coordinate frame. This definition assumes that the trigonal coordinates (X, Y, Z) and the cubic ones (x, y, z) are related as

$$\begin{aligned} x &= -\frac{1}{\sqrt{6}}X + \frac{1}{\sqrt{2}}Y + \frac{1}{\sqrt{3}}Z \\ y &= -\frac{1}{\sqrt{6}}X - \frac{1}{\sqrt{2}}Y + \frac{1}{\sqrt{3}}Z \\ z &= \frac{2}{\sqrt{6}}X + \frac{1}{\sqrt{3}}Z \end{aligned} \tag{I.1}$$

To satisfy this definition, the local trigonal coordinate systems associated with sites A and B should be rotated with respect to each other by the angle π around the C_3 axis as shown in Figure 1. Under the above definition of the local trigonal coordinates, the expressions for the one-electron 4f basis of T_1 type are given by

$$\begin{aligned} f_{T_1a} &= \frac{5}{6\sqrt{2}}f_{X^3} - \frac{2}{3}f_{Z^3} + \frac{\sqrt{5}}{2\sqrt{6}}f_{X(Y^2-Z^2)} \\ f_{T_1\theta} &= -\frac{1}{4}f_{X^3} + \frac{\sqrt{5}}{4\sqrt{3}}f_{X(Y^2-Z^2)} - \frac{\sqrt{5}}{\sqrt{6}}f_{Z(X^2-Y^2)} \\ f_{T_1\epsilon} &= -\frac{1}{4}f_{Y^3} - \frac{\sqrt{5}}{4\sqrt{3}}f_{Y(Z^2-X^2)} + \frac{\sqrt{5}}{\sqrt{6}}f_{XYZ} \end{aligned} \tag{I.2}$$

In eq I.2, the conventional short notation for the 4f functions is used. For the sake of simplicity, the label of the center (A, B) is omitted. One can easily show that the second two functions in eq I.2 are transformed as the θ and ϵ components of E representation ($\theta \propto X$, $\epsilon \propto Y$) when the symmetry is lowered to the C_{3v} site symmetry of each metal site. In the same way, the function f_{T_1a} is of A_2 symmetry in the C_{3v} group. Along with the real trigonal basis defined by eq I.2, we will use the complex trigonal basis that is related to the real one as follows

$$f_{T_1a_o} = f_{T_1a}, \quad f_{T_1a_{\pm1}} = \mp\frac{1}{\sqrt{2}}(f_{T_1\theta} \pm if_{T_1\epsilon}) \tag{I.3}$$

Within the concept of $T-P$ isomorphism, the states $f_{T_1a_o}$, $f_{T_1a_{+1}}$, and $f_{T_1a_{-1}}$ correspond to the states $|l = 1, m_l = 0\rangle$, $|l = 1, m_l = 1\rangle$, and $|l = 1, m_l = -1\rangle$, respectively ($l = 1$ is a fictious orbital angular momentum).

Appendix II. Nonzero Matrix Elements Connecting the Ground Manifold with the CT States of $(4f^2)_A$ Configuration

The set of CT states comprises all Slater determinants describing the $(t_1^2)_A$ and $(t_1^2)_B$ configurations. At the same time, only a few of these Slater determinants are connected with the ground state by one-hole transfer, being thus relevant to the kinetic exchange. The 10 nonzero matrix elements connecting the ground manifold with the excited states of $(t_1^2)_A$ type are given by

$$\begin{aligned} &\langle g_1|h|f^A_{a_o}\,\bar{f}^A_{a_+}|\rangle = \frac{\sqrt{2}}{3}(t_a - t_e) && \langle g_4|h||\bar{f}^A_{a_o}\,f^A_{a_-}|\rangle = \frac{\sqrt{2}}{3}(t_a - t_e) \\ &\langle g_2|h||\bar{f}^A_{a_+}\,f^A_{a_-}|\rangle = \frac{2}{3}t_e && \langle g_2|h||f^A_{a_o}\,\bar{f}^A_{a_o}|\rangle = \frac{1}{3}t_a \\ &\langle g_2|h||\bar{f}^A_{a_o}\,\bar{f}^A_{a_+}|\rangle = \frac{\sqrt{2}}{3}t_a && \langle g_2|h||f^A_{a_o}\,f^A_{a_-}|\rangle = -\frac{\sqrt{2}}{3}t_e \\ &\langle g_3|h||\bar{f}^A_{a_+}\,f^A_{a_-}|\rangle = -\frac{2}{3}t_e && \langle g_3|h||f^A_{a_o}\,\bar{f}^A_{a_o}|\rangle = -\frac{1}{3}t_a \\ &\langle g_3|h||\bar{f}^A_{a_o}\,\bar{f}^A_{a_+}|\rangle = -\frac{\sqrt{2}}{3}t_e && \langle g_3|h||f^A_{a_o}\,f^A_{a_-}|\rangle = \frac{\sqrt{2}}{3}t_a \end{aligned}$$

The CT states of $(t_1^2)_B$ type give the same contribution to the kinetic exchange splitting.

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Appendix III. Trigonal One-Electron 5d Bases of T_2 and E Types

The real trigonal forms of 5d orbitals are given by

$$d_{\mathrm{T}_2a} = d_{Z^2},\ d_{\mathrm{T}_2\theta} = \frac{1}{\sqrt{3}}(\sqrt{2}d_{X^2-Y^2} - d_{XZ}),$$
$$d_{\mathrm{T}_2\epsilon} = -\frac{1}{\sqrt{3}}(\sqrt{2}d_{XY} + d_{YZ}), \quad \text{(III.1)}$$
$$d_{\mathrm{E}\theta} = \frac{1}{\sqrt{3}}(d_{X^2-Y^2} + \sqrt{2}d_{XZ}), \quad d_{\mathrm{E}\epsilon} = -\frac{1}{\sqrt{3}}(d_{XY} - \sqrt{2}d_{YZ})$$

The complex trigonal 5d orbitals are related to the real ones, eq III.1, as follows

$$d_{\mathrm{T}_2x_\mathrm{o}} \equiv d_{x_\mathrm{o}} = d_{\mathrm{T}_2a}, \quad d_{\mathrm{T}_2x_\pm} \equiv d_{x_\pm} = \mp\frac{1}{\sqrt{2}}(d_{\mathrm{T}_2\theta} \pm i d_{\mathrm{T}_2\epsilon}),$$
$$d_{\mathrm{E}u\pm} \equiv d_{u_\pm} = \mp\frac{1}{\sqrt{2}}(d_{\mathrm{E}\theta} \pm i d_{\mathrm{E}\epsilon}) \quad \text{(III.2)}$$

Appendix IV. Hole Formalism for the $4f^{13}$ Configuration

One can introduce the hole formalism and consider one hole in the 4f shell and the 5d shell fully occupied by holes. Then, the wave functions of the ground state are given by

$$|g_1\rangle = \frac{2}{3}|\bar{f}^\mathrm{A}_{a_+}\ \bar{f}^\mathrm{B}_{a_+}D^\mathrm{A}D^\mathrm{B}| + \frac{1}{3}|f^\mathrm{A}_{a_\mathrm{o}}\ f^\mathrm{B}_{a_\mathrm{o}}D^\mathrm{A}D^\mathrm{B}| - \frac{\sqrt{2}}{3}(|\bar{f}^\mathrm{A}_{a_+}\ f^\mathrm{B}_{a_\mathrm{o}}D^\mathrm{A}D^\mathrm{B}| + |f^\mathrm{A}_{a_\mathrm{o}}\ \bar{f}^\mathrm{B}_{a_+}D^\mathrm{A}D^\mathrm{B}|)$$
$$|g_2\rangle = \frac{2}{3}|\bar{f}^\mathrm{A}_{a_+}\ f^\mathrm{B}_{a_-}D^\mathrm{A}D^\mathrm{B}| + \frac{1}{3}|f^\mathrm{A}_{a_\mathrm{o}}\ \bar{f}^\mathrm{B}_{a_\mathrm{o}}D^\mathrm{A}D^\mathrm{B}| - \frac{\sqrt{2}}{3}(|\bar{f}^\mathrm{A}_{a_+}\ \bar{f}^\mathrm{B}_{a_\mathrm{o}}D^\mathrm{A}D^\mathrm{B}| + |f^\mathrm{A}_{a_\mathrm{o}}\ f^\mathrm{B}_{a_-}D^\mathrm{A}D^\mathrm{B}|)$$
$$|g_3\rangle = \frac{2}{3}|f^\mathrm{A}_{a_-}\ \bar{f}^\mathrm{B}_{a_+}D^\mathrm{A}D^\mathrm{B}| + \frac{1}{3}|\bar{f}^\mathrm{A}_{a_\mathrm{o}}\ f^\mathrm{B}_{a_\mathrm{o}}D^\mathrm{A}D^\mathrm{B}| - \frac{\sqrt{2}}{3}(|f^\mathrm{A}_{a_-}\ f^\mathrm{B}_{a_\mathrm{o}}D^\mathrm{A}D^\mathrm{B}| + |\bar{f}^\mathrm{A}_{a_\mathrm{o}}\ \bar{f}^\mathrm{B}_{a_+}D^\mathrm{A}D^\mathrm{B}|) \quad \text{(IV.1)}$$
$$|g_4\rangle = \frac{2}{3}|f^\mathrm{A}_{a_-}\ f^\mathrm{B}_{a_-}D^\mathrm{A}D^\mathrm{B}| + \frac{1}{3}|\bar{f}^\mathrm{A}_{a_\mathrm{o}}\ \bar{f}^\mathrm{B}_{a_\mathrm{o}}D^\mathrm{A}D^\mathrm{B}| - \frac{\sqrt{2}}{3}(|f^\mathrm{A}_{a_-}\ \bar{f}^\mathrm{B}_{a_\mathrm{o}}D^\mathrm{A}D^\mathrm{B}| + |\bar{f}^\mathrm{A}_{a_\mathrm{o}}\ \bar{f}^\mathrm{B}_{a_-}D^\mathrm{A}D^\mathrm{B}|)$$

where the short notation $D^i = d^i_{x_\mathrm{o}}\ \bar{d}^i_{x_\mathrm{o}}\ d^i_{x_+}\ \bar{d}^i_{x_+}\ d^i_{x_-}\ \bar{d}^i_{x_-}\ d^i_{u_+}\ \bar{d}^i_{u_+}\ d^i_{u_-}\ \bar{d}^i_{u_-}$ (i = A, B) is used.

Let us calculate, for example, the exchange parameter using the relation $J_\perp = -w_3 = -\langle g_2 \| g_3\rangle$. Because both A → B and A ← B contribute equally, it is enough to consider the CT states in which one hole is transferred from the fully occupied 5d shell of the ion A to the 4f shell of the ion B. In this case, one hole in the 5d shell of A remains unpaired. This hole interacts by the intra-atomic exchange with the 4f hole, forming the triplet ($s_\mathrm{A} = 1$) and singlet ($s_\mathrm{A} = 0$). At the same time, in the adopted model, the exchange interaction between 4f electrons is neglected, so the singlet and triplet states arising from the $4f^2$ configuration of the ion B have the same energy. This allows us to choose the wave functions of these CT states in such a way that they are characterized by spin s_A and spin-projection m^B_s. The only CT state with $s_\mathrm{A} = 0$ that is connected to both $|g_2\rangle$ and $|g_3\rangle$ by the transfer is

$$|(a_\mathrm{o}x_\mathrm{o})^\mathrm{A}, s_\mathrm{A} = 0; (a_\mathrm{o}a_\mathrm{o})^\mathrm{B}, m^\mathrm{B}_\mathrm{s} = 0\rangle = \frac{1}{\sqrt{2}}(|f^\mathrm{A}_{a_\mathrm{o}}\ \bar{d}^\mathrm{A}_{x_\mathrm{o}}\ f^\mathrm{B}_{a_\mathrm{o}}\ \bar{f}^\mathrm{B}_{a_\mathrm{o}}\ D^\mathrm{A}_{x_\mathrm{o}}D^\mathrm{B}| - |\bar{f}^\mathrm{A}_{a_\mathrm{o}}\ d^\mathrm{A}_{x_\mathrm{o}}\ f^\mathrm{B}_{a_\mathrm{o}}\ \bar{f}^\mathrm{B}_{a_\mathrm{o}}\ D^\mathrm{A}_{x_\mathrm{o}}D^\mathrm{B}|) \quad \text{(IV.2)}$$

where $D^i[k]$ denotes D^i in which a pair of the orbitals $d^i_k\ \bar{d}^i_k$ is extracted, for example, $D^i_{x_\mathrm{o}} = d^i_{x_+}\ \bar{d}^i_{x_+}\ d^i_{x_-}\ \bar{d}^i_{x_-}\ d^i_{u_+}\ \bar{d}^i_{u_+}\ d^i_{u_-}\ \bar{d}^i_{u_-}$, $D^i_{x_+} = d^i_{x_\mathrm{o}}\ \bar{d}^i_{x_\mathrm{o}}\ d^i_{x_-}\ \bar{d}^i_{x_-}\ d^i_{u_+}\ \bar{d}^i_{u_+}\ d^i_{u_-}\ \bar{d}^i_{u_-}$, etc.

One finds

$$\langle g_2|h|(a_\mathrm{o}x_\mathrm{o})^\mathrm{A}, s_\mathrm{A} = 0; (a_\mathrm{o}a_\mathrm{o})^\mathrm{B}, m^\mathrm{B}_\mathrm{s} = 0\rangle = -\frac{1}{3\sqrt{2}}\beta_a$$
$$\langle (a_\mathrm{o}x_\mathrm{o})^\mathrm{A}, s_\mathrm{A} = 0; (a_\mathrm{o}a_\mathrm{o})^\mathrm{B}, m^\mathrm{B}_\mathrm{s} = 0|h|g_2\rangle = \frac{1}{3\sqrt{2}}\beta_a \quad \text{(IV.3)}$$

so the contribution of states with $s_\mathrm{A} = 0$ to the $J_\perp$ is $-\beta_a{}^2/[9(U_\mathrm{fd} - 4D\mathrm{q})]$. Considering the states with $s_\mathrm{A} = 1$, one can show that they result in the term $\beta_a{}^2/[9(U_\mathrm{fd} - J_\mathrm{fd} - 4D\mathrm{q})]$ in $J_\perp$. Combining these two contributions, we find

$$J_\perp = -\frac{\beta_a{}^2}{9(U_\mathrm{fd} - 4D\mathrm{q})} + \frac{\beta_a{}^2}{9(U_\mathrm{fd} - J_\mathrm{fd} - 4D\mathrm{q})} \quad \text{(IV.4)}$$

This result coincides with that given by eq 14. Therefore ,we obtained the same expression for $J_\perp$ as in the case of one electron. The same identity can be derived for the parameter $J_\|$.

Appendix V. Nonzero Matrix Elements Connecting the Ground Manifold with the CT States of $(4f^1 5d^1)_\mathrm{A}$ Configuration

(Note that the symbol A is omitted in the notation of the wave functions of CT states).

$$\langle g_1||a_+x_0, 00\rangle = \frac{1}{3}\beta_a, \qquad \langle g_2||a_0x_0, 00\rangle = \frac{1}{3\sqrt{2}}\beta_a$$
$$\langle g_1||a_0x_0, 11\rangle = \frac{1}{3}\beta_a, \qquad \langle g_2||a_0x_0, 10\rangle = \frac{1}{3\sqrt{2}}\beta_a$$
$$\langle g_1||a_+x_0, 10\rangle = -\frac{1}{3}\beta_a, \qquad \langle g_2||a_+x_0, 1\ {-1}\rangle = -\frac{\sqrt{2}}{3}\beta_a$$
$$\langle g_1||a_0x_+, 00\rangle = -\frac{1}{3}\beta_e, \qquad \langle g_2||a_+x_-, 00\rangle = -\frac{\sqrt{2}}{3}\beta_e$$
$$\langle g_1||a_0u_+, 00\rangle = -\frac{1}{3}\beta'_e, \qquad \langle g_2||a_+u_-, 00\rangle = -\frac{\sqrt{2}}{3}\beta'_e$$
$$\langle g_1||a_+x_+, 1\ {-1}\rangle = \frac{2}{3}\beta_e, \qquad \langle g_2||a_0x_-, 11\rangle = -\frac{\sqrt{2}}{3}\beta_e$$
$$\langle g_1||a_0x_+, 10\rangle = -\frac{1}{3}\beta_e, \qquad \langle g_2||a_+x_-, 10\rangle = \frac{\sqrt{2}}{3}\beta_e$$
$$\langle g_1||a_+u_+, 1\ {-1}\rangle = \frac{2}{3}\beta'_e, \qquad \langle g_2||a_0u_-, 11\rangle = -\frac{\sqrt{2}}{3}\beta'_e$$

$$\langle g_1||a_0u_+, 10\rangle = -\frac{1}{3}\beta'_e, \qquad \langle g_2||a_+u_-, 10\rangle = \frac{\sqrt{2}}{3}\beta'_e$$

$$\langle g_3||a_0x_0, 00\rangle = -\frac{1}{3\sqrt{2}}\beta_a, \qquad \langle g_4||a_-x_0, 00\rangle = -\frac{1}{3}\beta_a$$

$$\langle g_3||a_0x_0, 10\rangle = \frac{1}{3\sqrt{2}}\beta_a, \qquad \langle g_4||a_0x_0, 1\ -1\rangle = \frac{1}{3}\beta_a$$

$$\langle g_3||a_-x_0, 11\rangle = -\frac{\sqrt{2}}{3}\beta_a, \qquad \langle g_4||a_-\ x_0, 10\rangle = -\frac{1}{3}\beta_a$$

$$\langle g_3||a_-x_+, 00\rangle = \frac{\sqrt{2}}{3}\beta_e, \qquad \langle g_4||a_0x_-, 00\rangle = \frac{1}{3}\beta_e$$

$$\langle g_3||a_-u_+, 00\rangle = \frac{\sqrt{2}}{3}\beta'_e, \qquad \langle g_4||a_0u_-, 00\rangle = \frac{1}{3}\beta'_e$$

$$\langle g_3||a_0x_+, 1\ -1\rangle = -\frac{\sqrt{2}}{3}\beta_e, \qquad \langle g_4||a_-x_-, 11\rangle = \frac{2}{3}\beta_e$$

$$\langle g_3||a_-x_+, 10\rangle = \frac{\sqrt{2}}{3}\beta_e, \qquad \langle g_4||a_0x_-, 10\rangle = -\frac{1}{3}\beta_e$$

$$\langle g_3||a_0u_+, 1\ -1\rangle = -\frac{\sqrt{2}}{3}\beta'_e, \qquad \langle g_4||a_-u_-, 11\rangle = \frac{2}{3}\beta'_e$$

$$\langle g_3||a_-u_+, 10\rangle = \frac{\sqrt{2}}{3}\beta'_e, \qquad \langle g_4||a_0u_-, 10\rangle = -\frac{1}{3}\beta'_e$$

Appendix VI. Wave Functions of the Ground Manifold for the Corner-Shared Bioctahedral Yb^{3+} cluster of D_{4h} Symmetry

The two one-hole wave functions of the γ_6 type are given by

$$\begin{aligned} \varphi^{+}_{\Gamma_6} &\equiv [+] = \frac{1}{\sqrt{3}}(-\mathrm{i}\bar{f}_\alpha + \bar{f}_\beta - \mathrm{i}f_\gamma), \\ \varphi^{-}_{\Gamma_6} &\equiv [-] = \frac{1}{\sqrt{3}}(-\mathrm{i}f_\alpha - f_\beta + \mathrm{i}\bar{f}_\gamma) \end{aligned} \qquad \text{(VI.1)}$$

By using eq VI.1, we construct the following four states belonging to the ground $(\Gamma_6)_A \otimes (\Gamma_6)_B$ manifold of the D_{4h} pair

$$\begin{aligned} |g_1\rangle \equiv |[+]_A[+]_B\rangle = \frac{1}{3}[&-|\bar{f}^A_\alpha\ \bar{f}^B_\alpha| + |\bar{f}^A_\beta\ \bar{f}^B_\beta| - |f^A_\gamma\ f^B_\gamma| - \\ &|\bar{f}^A_\alpha\ f^B_\gamma| - |f^A_\gamma\ \bar{f}^B_\alpha| - \mathrm{i}(|\bar{f}^A_\alpha\ \bar{f}^B_\beta| + |\bar{f}^A_\beta\ \bar{f}^B_\alpha| + |\bar{f}^A_\beta\ f^B_\gamma| + \\ &|f^A_\gamma\ \bar{f}^B_\beta|)] \\ |g_2\rangle \equiv |[+]_A[-]_B\rangle = \frac{1}{3}[&-|\bar{f}^A_\alpha\ f^B_\alpha| - |\bar{f}^A_\beta\ f^B_\beta| + |f^A_\gamma\ \bar{f}^B_\gamma| + \\ &|\bar{f}^A_\alpha\ \bar{f}^B_\gamma| - |f^A_\gamma\ f^B_\alpha| + \mathrm{i}(|\bar{f}^A_\alpha\ f^B_\beta| - |\bar{f}^A_\beta\ f^B_\alpha| + |\bar{f}^A_\beta\ \bar{f}^B_\gamma| + \\ &|f^A_\gamma\ f^B_\beta|)] \\ |g_3\rangle \equiv |[-]_A[+]_B\rangle = \frac{1}{3}[&-|f^A_\alpha\ \bar{f}^B_\alpha| - |f^A_\beta\ \bar{f}^B_\beta| + |\bar{f}^A_\gamma\ f^B_\gamma| - \\ &|f^A_\alpha\ f^B_\gamma| + |\bar{f}^A_\gamma\ \bar{f}^B_\alpha| + \mathrm{i}(-|f^A_\alpha\ \bar{f}^B_\beta| + |f^A_\beta\ \bar{f}^B_\alpha| + |f^A_\beta\ f^B_\gamma| + \\ &|\bar{f}^A_\gamma\ \bar{f}^B_\beta|)] \\ |g_4\rangle \equiv |[-]_A[-]_B\rangle = \frac{1}{3}[&-|f^A_\alpha\ f^B_\alpha| + |f^A_\beta\ f^B_\beta| - |\bar{f}^A_\gamma\ \bar{f}^B_\gamma| + \\ &|f^A_\alpha\ \bar{f}^B_\gamma| + |\bar{f}^A_\gamma\ f^B_\alpha| + \mathrm{i}(|f^A_\alpha\ f^B_\beta| + |f^A_\beta\ f^B_\alpha| - |f^A_\beta\ \bar{f}^B_\gamma| - |\bar{f}^A_\gamma\ f^B_\beta|)] \end{aligned} \qquad \text{(VI.2)}$$

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