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Direct Exchange between *d* Electrons*

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The empirical data necessary to determine all the parameters in the exchange interaction between a pair of orbitally degenerate ions do not exist for any system. Given this paucity, we have resorted to using the best available theoretical estimates of the two-center exchange integrals for *d* electrons which have been calculated for particular cases of cobalt atoms and ions. With these data we have quantitatively substantiated the recent assertions made about the importance of anisotropic and higher-degree isotropic-exchange interactions. We demonstrate that a bilinear scalar spin Hamiltonian is totally inadequate to describe exchange interactions in systems containing orbitally degenerate ions. The higher-degree isotropic terms considerably alter the positions of the centers of gravity of the energy levels of exchange-coupled pairs. We estimate that the exchange interaction accounts for 25% of the discrepancy between the spin-orbit coupling constant λ required to explain the magnon spectra of cobalt in $KCoF_3$ and the λ for free cobalt ions. For orbitally degenerate ions in magnetically inequivalent sites, it is shown that antisymmetric exchange is as large as the symmetric terms.

THERE has been considerable interest recently, both experimental[1] and theoretical,[2] in the possible forms of the Hamiltonian for an exchange interaction between two electrons on separate sites, when both electrons are orbitally degenerate. We have developed a general formalism for this problem[3] and have also shown how to transform this into a Hamiltonian which acts on states of fictitious angular momentum (determined from the multiplicities of crystal-field states) for those cases where the crystal-field interaction is much larger than the exchange interaction.[4] In the treatment given in I the nonorthogonality of the electron wave functions was neglected in deriving the coefficients $\Gamma_{k_1k_2\Lambda}$ of the two-center exchange interactions. We have made a qualitative study of the effects of nonorthogonality on the exchange Hamiltonian,[5] and the purpose of this present paper is to make a quantitative estimate of the relative sizes of anisotropic and higher-degree isotropic exchange interactions when the effects of the nonorthogonality of the electron wave functions have been included. The coefficients in the Hamiltonian representing the anisotropic and higher-degree isotropic interactions have been estimated by using the integrals for the direct exchange between *d* electrons. These integrals were calculated by Freeman and Watson,[6] who included the effects of nonorthogonality.

The following analysis shows that the anisotropic and higher-degree isotropic interactions are appreciable relative to the ordinary bilinear scalar interaction. For ions with an intra-atomic spin-orbit coupling much greater than the interatomic exchange interaction, one consequence of the additional terms is the presence of a new contribution to the constant term in the exchange Hamiltonian; this contribution changes as we go to different *j* manifolds. This introduces shifts in the centers of gravity of the manifolds for pairs of exchange-coupled ions which cause significant deviations in the energy level scheme as predicted by the Landé interval rule.[7] Another important result demonstrated here is that for ions in magnetically inequivalent sites there are antisymmetric components in the exchange interaction,[3] which are large compared with the symmetric terms in the interaction.

We have studied the above effects for a pair of ions containing single 3*d* electrons, and then extended this to a pair of interacting cobalt (Co^{2+}) ions, each of which has seven equivalent 3*d* electrons in its magnetic shell. For cobalt in $KCoF_3$ we find that the exchange interaction makes appreciable contributions to the effective spin-orbit coupling parameter.[8]

EXCHANGE INTERACTIONS BETWEEN TWO *d* ELECTRONS

If we have a pair of *d* electrons on separate sites in a strong crystal field, we can describe the exchange interactions between them in two different ways. First, we can find the crystal field eigenfunctions for each electron in terms of its orbital angular momentum ($l=2$) and

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[4] P. M. Levy, J. Appl. Phys. **40**, 1139 (1969).

[5] P. M. Levy, Chem. Phys. Letters **3**, 556 (1969).

[6] A. J. Freeman and R. E. Watson, Phys. Rev. **124**, 1439 (1961).

[7] P. M. Levy and G. M. Copland, Phys. Rev. **180**, 439 (1969).

[8] W. J. L. Buyers, R. A. Cowley, T. M. Holden, E. C. Levenson, M. T. Hutchings, D. Hukin, and R. W. H. Stevenson, in *Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, Scotland, 1968*, edited by V. F. Allen, D. M. Finlayson, and D. M. McCall (University of St. Andrews Printing Dept., St. Andrews, Scotland, 1969).

spin. Then we find the exchange interaction for electrons in specific crystal field states by using an exchange Hamiltonian written in terms of operators which act on the crystal field wave functions,[9]

$$\mathcal{H}=\sum_{k_1k_2\Lambda}\Gamma_{k_1k_2\Lambda}[\mathbf{U}^{[k_1]}(a)\times\mathbf{U}^{[k_2]}(b)\times\mathbf{C}^{[\Lambda]}]^{[0]}\times(\tfrac{1}{2}+2\mathbf{S}_a\cdot\mathbf{S}_b). \quad (1)$$

For d electrons this would lead to 22 exchange parameters of the form $\Gamma_{k_1k_2\Lambda}$ for direct exchange. However, if the electrons are confined to a particular crystal-field multiplet, there will be relationships between these parameters. The alternative approach[4] is to consider the electrons to remain within one particular crystal-field multiplet described by an effective orbital angular momentum $\mathfrak{l}$. The exchange Hamiltonian can then be expressed in terms of operators which operate on states of the effective orbital angular momentum. If we have a crystal-field triplet, $\mathfrak{l}=1$, the number of coefficients in the effective Hamiltonian is 7. In many cases an effective-Hamiltonian approach simplifies the problem and demonstrates the basic symmetry properties of the interaction more directly.[10] We shall illustrate this effective-Hamiltonian approach by considering the case of a pair of single d-state electrons in a cubic crystal field which is much stronger than the spin-orbit and exchange interactions.

Let us consider a d electron in a cubic field which splits up into a t_{2g} ground triplet and an excited e_g doublet. The field is assumed to be strong enough that we can treat the triplet as being isolated. We represent this orbital triplet as an effective orbital angular momentum $\mathfrak{l}=1$. When we express the crystal field wave functions for the d electron in terms of the true angular momentum $l=2$, as $|lm\rangle$, and the triplet functions in terms of the effective angular momentum $\mathfrak{l}=1$, as $|\mathfrak{l}\mathfrak{m}\rangle$, we can make the following equivalence:

$$|\mathfrak{l}\mathfrak{m}\rangle\equiv\sum_m b(\mathfrak{m},m)|lm\rangle,$$

$$\begin{aligned}|1,1\rangle&=|2,-1\rangle,\\|1,0\rangle&=(1/\sqrt{2})[|2,2\rangle-|2,-2\rangle],\\|1,-1\rangle&=-|2,1\rangle.\end{aligned} \quad (2)$$

For this equivalence we obtain the projection of $\mathbf{L}$ in this triplet equal to $-\mathfrak{l}$.[11]

We shall consider, initially, the exchange interactions between two electrons whose coordinate axes are parallel, with the z axes oriented along the interionic axis. The polar angles describing this axis are thus $\theta_{ab}=0°$, $\phi_{ab}=0°$. The form of the exchange interaction in fictitious angular momentum space has been discussed by Levy,[4] who shows that it may be written in the form

$$\tilde{\mathcal{H}}=\sum_{\rho_1\rho_2P}[\boldsymbol{\sigma}^{[\rho_1]}(a)\times\mathbf{A}^{[P]}\times\boldsymbol{\sigma}^{[\rho_2]}(b)]^{[0]}(\tfrac{1}{2}+2\mathbf{S}_a\cdot\mathbf{S}_b). \quad (3a)$$

The operators $\sigma_\pi{}^{[\rho]}$ transform like spherical harmonics[12] and act on a space of dimensionality 3. The reduced matrix elements of $\boldsymbol{\sigma}^{[\rho]}$ are defined here as

$$(l\|\boldsymbol{\sigma}^{[\rho]}\|l)\equiv(-1)^{\frac{1}{2}\rho}[\rho]^{1/2}.$$

For the case of direct exchange, which is the only form of exchange considered here, the angular dependence of the term $A_Q{}^{[P]}(\rho_1\rho_2)$ can be factored out to give $A_{\rho_1\rho_2P}C_{-Q}{}^{[P]}(\Omega_{ab})$. Then Eq. (3a) can be rewritten as

$$\tilde{\mathcal{H}}=\sum_{\rho_1\rho_2P}A_{\rho_1\rho_2P}[\boldsymbol{\sigma}^{[\rho_1]}(a)\times\boldsymbol{\sigma}^{[\rho_2]}(b)\times\mathbf{C}^{[P]}(\Omega_{ab})]^{[0]}\times(\tfrac{1}{2}+2\mathbf{S}_a\cdot\mathbf{S}_b). \quad (3b)$$

For a triplet with $\mathfrak{l}=1$, the ranks ρ_i can take the values 0, 1, 2 and $\rho_1+\rho_2$ must be even.[3] We expand the invariant in the above equation and write the operators in component form using the definitions of Ref. 12. For convenience we transform the operators $\sigma_\pi{}^{[\rho]}$ into effective orbital operators $\mathfrak{l}_\pi{}^{[\rho]}$ whose reduced matrix elements are defined in Edmonds.[13] This gives an effective Hamiltonian $\tilde{\mathcal{H}}$ for $\Omega_{ab}=0°$, as:

$$\begin{aligned}\tilde{\mathcal{H}}=\{&\tfrac{1}{3}A_{000}+(1/2\sqrt{3})A_{110}(\mathfrak{l}_a\cdot\mathfrak{l}_b)\\&+[1/2(30^{1/2})]A_{112}(\mathfrak{l}_a\cdot\mathfrak{l}_b-3\mathfrak{l}_a{}^z\mathfrak{l}_b{}^z)\\&+[1/3(10^{1/2})]A_{202}(4-3(\mathfrak{l}_a{}^z)^2-3(\mathfrak{l}_b{}^z)^2)\\&+\text{higher terms}\}(\tfrac{1}{2}+2\mathbf{S}_a\cdot\mathbf{S}_b).\end{aligned} \quad (4)$$

The total number of parameters $A_{\rho_1\rho_2P}$ for $\mathfrak{l}=1$ for direct exchange is 7, whereas had we worked with the full $l=2$ configuration there would be 22 parameters. Special note should be taken of the single-ion terms in the expansion of the orbital part of the exchange Hamiltonian.

Thus far we have ignored the effects of spin-orbit coupling. For a d electron with spin $S=\frac{1}{2}$, this interaction splits the ground orbital triplet into a quartet and a doublet with *effective* total angular momentum $\mathfrak{j}=\frac{3}{2}$ and $\frac{1}{2}$, respectively.[14] The effect of this spin-orbit interaction on the exchange Hamiltonian can be accounted for by coupling the spin and effective orbital operators to form effective total angular momentum operators. The case for $l=1$, $S=\frac{1}{2}$ has already been discussed in some detail,[7] and we shall merely quote the

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[9] See Eq. (15) of Ref. 3. We have omitted the negative sign in that equation throughout this work. The restrictions on the summation ranges in Eq. (15) of Ref. 3 give k_1, k_2 as having integer values from 0 to 4.

[10] However, like all effective Hamiltonian treatments, it suffers from the restriction that we are neglecting the presence of higher orbital states at this level of calculation.

[11] J. Kanamori, Progr. Theoret. Phys. (Kyoto) **17**, 177 (1957).

[12] D. Smith and J. H. M. Thornley, Proc. Phys. Soc. (London) **89**, 779 (1966).

[13] We use the definitions for the reduced matrix elements from Eqs. (5.4.2) and (5.5.5) in A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N. J., 1957).

[14] We define the effective total angular momentum as $\mathfrak{j}=\mathfrak{l}+\mathbf{s}$. This differs from the projection on the t_{2g} triplet of the total angular momentum $\langle\mathbf{j}\rangle=\langle\mathbf{l}\rangle+\mathbf{s}=-\mathfrak{l}+\mathbf{s}$.

TABLE I. Coefficients $\alpha_{\rho_1\rho_2P}'$ entering Eq. (5) for various j manifolds. $A_{110}'=3^{-1/2}A_{110}$, $A_{220}'=5^{-1/2}A_{220}$, $A_{202}'=(10)^{-1/2}A_{202}$, $\alpha_{110}'=3^{-1/2}\alpha_{110}$, and $\alpha_{112}'=(30)^{-1/2}\alpha_{112}$.

$\mathfrak{j}_a$	$\mathfrak{j}_b$	α_{000}	α_{110}'	α_{112}'
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{6}(A_{000}+2A_{110}')$	$(2/27)(A_{000}+6A_{110}'+20A_{220}')$	$(4/9)[-A_{110}'-(5/3)A_{220}'+\frac{2}{3}A_{202}']$
$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{6}(A_{000}-A_{110}')$	$(-2/27)(A_{000}-3A_{110}'+2A_{220}')$	$(2/9)[-A_{110}'+\frac{1}{3}A_{220}'-(11/15)A_{202}']$
$\frac{3}{2}$	$\frac{3}{2}$	$\frac{1}{6}(A_{000}+\frac{1}{2}A_{110}')$	$(2/27)(A_{000}+\frac{3}{2}A_{110}'+\frac{1}{5}A_{220}')$	$\frac{1}{9}[-A_{110}'-(1/15)A_{220}'+(4/15)A_{202}']$

leading terms of the resulting Hamiltonians.[15]

$$\mathfrak{H}=[\alpha_{000}+\alpha_{110}'\mathfrak{j}_a\cdot\mathfrak{j}_b+\alpha_{112}'(\mathfrak{j}_a\cdot\mathfrak{j}_b-3\mathfrak{j}_a^z\mathfrak{j}_b^z)+\cdots]\ \mathrm{cm}^{-1},\quad(5)$$

where the coefficients $\alpha_{\rho_1\rho_2P}'$ are given in Table I. This form of effective Hamiltonian for a superexchange interaction between two d electrons has been calculated by Hartmann-Boutron.[16]

It will be seen from Table I that the constant term in the Hamiltonian for each combination of interacting ions is different. This term gives the position of the center of gravity of each manifold; therefore the exchange interaction shifts the centers of gravity of the manifolds by different amounts. This center-of-gravity shift will appear to produce deviations from the Landé interval rule for pairs of exchange-coupled ions; the magnitude of the shifts is proportional to the coefficient A_{110}'. The over-all center of gravity of the complete set of manifolds within a Russell-Saunders term (L,S) is shifted *only* by the "constant" term A_{000}.

In crystals where there are ions on magnetically inequivalent sites, the possibility for antisymmetric exchange arises.[17] Such an inequivalence can arise from the crystal site symmetry axes being nonparallel as for the rare-earth sites in the garnet structure. To obtain an estimate of the relative importance of the antisymmetric exchange, we have considered a simple situation where we have two interacting d electrons as above but with the system of axes for electron 2 being rotated by $\frac{1}{2}\pi$ about the y axis to carry the z axis into the original x direction and x into $-z$. As we are still dealing with a cubic crystal field, the rotation by $\frac{1}{2}\pi$ is a symmetry operation of the crystal point group and the t_{2g} triplet remains unchanged. Thus we can still use the projected Hamiltonian developed above and apply the rotation operations to the effective angular momenta. Furthermore, if we assume that there is a small tetragonal distortion of the crystal field, this new arrangement of axes is physically distinguishable from the original parallel arrangement. When, as we will assume, the energy of the spin-orbit coupling is much greater than the energy of the crystal field distortion, we can form the effective total angular momentum operators in the original geometry and rotate these operators to the new axes. Should the distortion be much greater than the spin-orbit coupling energy, then one would have to work with the uncoupled fictitious angular momentum and spin operators separately. We also assume that the noncubic distortion is greater than the exchange interaction and thus, when doing perturbation theory, it is best to use the axes of quantization which diagonalize the distortion Hamiltonian.

If the exchange Hamiltonian in the parallel system of axes, Eq. (5), be written in the form

$$\mathfrak{H}=(\alpha_{000}+\alpha_{110}[\mathfrak{j}_a^{[1]}\times\mathfrak{j}_b^{[1]}]^{[0]}+(\alpha_{112}/5^{1/2})[\mathfrak{j}_a^{[1]}\times\mathfrak{j}_b^{[1]}]_0^{[2]}+\cdots),\quad(5')$$

the effective Hamiltonian in the new nonparallel coordinate system (rotated by $\frac{1}{2}\pi$ about the y axis) takes the form[18]

$$R^{-1}\mathfrak{H}R=(\alpha_{000}+\Gamma^{[0]}(1,1)[\mathfrak{j}_a^{[1]}\times\mathfrak{j}_b^{[1]}]^{[0]}+\sum_m\Gamma_m^{[1]}(1,1)[\mathfrak{j}_a^{[1]}\times\mathfrak{j}_b^{[1]}]_m^{[1]}+\sum_{m'}\Gamma_{m'}^{[2]}(1,1)[\mathfrak{j}_a^{[1]}\times\mathfrak{j}_b^{[1]}]_{m'}^{[2]}+\cdots),\quad(6)$$

where

$$\begin{aligned}&\Gamma^{[0]}(1,1)=(1/\sqrt{3})(\alpha_{110}'+\alpha_{112}'),\\&\Gamma_1^{[1]}(1,1)=\Gamma_{-1}^{[1]}(1,1)=-\alpha_{110}'+\tfrac{1}{2}\alpha_{112}',\\&\Gamma_0^{[1]}(1,1)=0,\\&\Gamma_2^{[2]}(1,1)=\Gamma_{-2}^{[2]}(1,1)=\tfrac{1}{2}(\alpha_{110}'+\alpha_{112}'),\\&\Gamma_1^{[2]}(1,1)=-\Gamma_{-1}^{[2]}(1,1)=-\tfrac{3}{2}\alpha_{112}',\\&\Gamma_0^{[2]}(1,1)=6^{-1/2}(\alpha_{110}'+\alpha_{112}').\end{aligned}\quad(7)$$

The values of α for the possible combination of $\mathfrak{j}_a$ and $\mathfrak{j}_b$ are tabulated in Table I. By writing out the operators in the rotated Hamiltonian in terms of their Cartesian components, we find

$$\begin{aligned}\mathfrak{H}'=(\alpha_{000}&+(1/\sqrt{3})\Gamma^{[0]}(1,1)\mathfrak{j}_a\cdot\mathfrak{j}_b\\&+\Gamma_1^{[1]}(1,1)(\mathfrak{j}_a^x\mathfrak{j}_b^z-\mathfrak{j}_a^z\mathfrak{j}_b^x)\\&+\Gamma_0^{[2]}(1,1)(1/6^{1/2})(\mathfrak{j}_a\cdot\mathfrak{j}_b-3\mathfrak{j}_a^z\mathfrak{j}_b^z)\\&+\Gamma_1^{[2]}(1,1)(\mathfrak{j}_a^z\mathfrak{j}_b^x+\mathfrak{j}_a^x\mathfrak{j}_b^z)\\&+\Gamma_2^{[2]}(1,1)(\mathfrak{j}_a^y\mathfrak{j}_b^y-\mathfrak{j}_a^x\mathfrak{j}_b^x)+\cdots).\end{aligned}\quad(6')$$

The third term of this equation could equally well be written in the form $\mathbf{D}\cdot\mathfrak{j}_a\times\mathfrak{j}_b$ with $D_x=D_z=0$, and $D_y=-\Gamma_1^{[1]}(1,1)$. This has the form of a Dzyaloshinsky-Moriya antisymmetric[19] exchange interaction. This

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[15] The reduced matrix elements are defined in this paper as $\langle l\|\boldsymbol{\sigma}^{[\rho]}\|l\rangle=(-1)^{\frac{1}{2}\rho}[\rho]^{1/2}$. This changes the coefficients in Eq. (5) from those expected from Eqs. (7) and (8) of Ref. 7.

[16] F. Hartmann-Boutron, J. Phys. **29**, 212 (1968).

[17] P. M. Levy, Phys. Rev. Letters **20**, 1366 (1968); R. M. White and R. L. White, *ibid.* **20**, 62 (1968).

[18] See Eqs. (18) and (18′) of I.

[19] I. Dzyaloshinsky, J. Phys. Chem. Solids **4**, 241 (1958); T. Moriya, Phys. Rev. **120**, 91 (1960).

antisymmetric term arises because we have considered the exchange interaction to be a perturbation on the crystal field interaction where the ions are on inequivalent sites.

NUMERICAL ESTIMATES OF TERMS IN HAMILTONIAN

Frequently the anisotropy of exchange interactions is described in terms of exchange "integrals" which are functions of the components of the orbital angular momentum of the ions involved. The exchange interaction is represented by a Hamiltonian of the form

$$\mathcal{H}=J_{\mathrm{op}}(\tfrac{1}{2}+2\mathbf{S}_a\cdot\mathbf{S}_b)$$

and the exchange integrals are defined as the matrix elements of the operator J_{op} between orbital states of the electrons:

$$J(m_a'm_b';m_am_b)\equiv\langle l_am_a',l_bm_b'|J_{\mathrm{op}}|l_am_a,l_bm_b\rangle\,.$$

Freeman and Watson[6] have calculated integrals of this sort for the direct-exchange interaction between d electrons including nonorthogonality under various conditions. However, they only considered those integrals arising from diagonal terms of the exchange operator. Ideally we would like also the integrals from off-diagonal terms to complete the calculation. As the Freeman and Watson integrals appear to be the best available, we shall use them and write them as

$$J(m_a,m_b)=J(m_a'm_b';m_am_b)\delta_{m_a'm_a}\delta_{m_b'm_b}\,.$$

When calculating the full d-d electron exchange, the coefficients $\Gamma_{k_1k_2\Lambda}$ in Eq. (1) are obtained from the exchange integrals by the relation[20]

$$\Gamma_{k_1k_2\Lambda}=[\Lambda]\sum_{m_am_b}J(m_a,m_b)\langle m_am_b|[\mathbf{U}^{[k_1]}(a)\times\mathbf{U}^{[k_2]}(b)\times\mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]}|m_am_b\rangle^*\,.\quad(8)$$

From the geometrical arrangement considered by Freeman and Watson, $\Omega_{ab}=0°$, and from the fact that we have integrals only for diagonal matrix elements of the exchange interaction, we conclude that the only possible components of the orbital operators are $U_0^{[k_i]}$. By using the exchange integrals given by Freeman and Watson for two d electrons in Co^{2+} ions separated by 4.75 a.u., we find the exchange Hamiltonian is written as

$$\begin{aligned}\mathcal{H}=\{\tfrac{1}{5}\Gamma_{000}&+(1/3^{1/2})\Gamma_{110}\mathbf{l}_a\cdot\mathbf{l}_b\\&+(1/5^{1/2})\Gamma_{112}(\mathbf{l}_a\cdot\mathbf{l}_b-3l_a^zl_b^z)+\cdots\\&+\Gamma_{448}[\mathbf{l}^{[4]}\times\mathbf{l}^{[4]}]_0^{[8]}\}(\tfrac{1}{2}+2\mathbf{S}_a\cdot\mathbf{S}_b)\,,\end{aligned}\quad(9)$$

where the coefficients $\Gamma_{k_1k_2\Lambda}$ are given in Table II. Although the coefficients of the terms representing the orbital anisotropy of the interaction seem small, it should be realized that their effect is quite appreciable since the magnitude of the orbital angular momentum is 2. An immediate conclusion we make by looking at Eq. (9) is that the Hamiltonian is far from the form given by Heisenberg, Dirac, and Van Vleck for S electrons. Higher-degree isotropic and anisotropic terms make very appreciable contributions to the exchange interaction.

TABLE II. Coefficients $\Gamma_{k_1k_2\Lambda}$ for the exchange interaction between two d electrons on Co^{2+} ions 4.75 a.u. apart given in cm^{-1}. The coefficients have been calculated using the exchange integrals of Freeman and Watson (Ref. 6) (Tables II and III). Whereas it is necessary, in general, to describe the d-d direct-exchange interaction by 22 independent coefficients, we have only 9 coefficients. This is a consequence of only considering the diagonal elements of the exchange integral $J(m_a'm_b',m_am_b)$.

$$\Gamma_{k_1k_2\Lambda'}=\frac{[\Lambda']}{[\Lambda]}\left\{\begin{pmatrix}k_1k_2\Lambda'\\0\,0\,0\end{pmatrix}\Big/\begin{pmatrix}k_1k_2\Lambda\\0\,0\,0\end{pmatrix}\right\}\Gamma_{k_1k_2\Lambda}$$

$\Gamma_{000}=445$	$\Gamma_{202}=17.0$
$\Gamma_{110}=5.3$	$\Gamma_{132}=8.0$
$\Gamma_{220}=6.6$	$\Gamma_{242}=7.3$
$\Gamma_{330}=1.4$	$\Gamma_{404}=65.5$
$\Gamma_{440}=2.0$	

To obtain the parameters $A_{\rho_1\rho_2P}$ for the effective Hamiltonian, Eq. (3b), we have to form the appropriate linear combinations of the exchange integrals $J(m_a,m_b)$. Since we are using integrals diagonal in m_α, and because of the simple correspondence between the real and fictitious crystal-field eigenfunctions, Eq. (2), the effective exchange integrals take the form

$$\mathfrak{J}(\mathfrak{m}_a,\mathfrak{m}_b)=\mathfrak{J}(\mathfrak{m}_a'\mathfrak{m}_b';\mathfrak{m}_a\mathfrak{m}_b)\delta(\mathfrak{m}_a',\mathfrak{m}_a)\delta(\mathfrak{m}_b',\mathfrak{m}_b)\,,$$

where for typographical reasons we have used $\delta(p,q)\equiv\delta_{pq}$. By using the relations Eq. (2) between $\mathfrak{m}_\alpha$ and m_α, we find the following relations between $\mathfrak{J}$ and J:

$$\begin{aligned}\mathfrak{J}(0,0)&=\tfrac{1}{2}[J(2,2)+J(2,-2)]\,,\\\mathfrak{J}(1,0)&=\tfrac{1}{2}[J(-1,2)+J(-1,-2)]\,,\\\mathfrak{J}(1,-1)&=J(-1,1)\,,\\\mathfrak{J}(1,1)&=J(-1,-1)\,.\end{aligned}\quad(10)$$

We now have all the distinct exchange integrals in the fictitious $\mathfrak{l}=1$ space, and we relate these to the coefficients $A_{\rho_1\rho_2P}$ in the effective Hamiltonian by using the relationship analogous to Eq. (8)

$$A_{\rho_1\rho_2P}=[P]\sum_{\mathfrak{m}_a\mathfrak{m}_b}\mathfrak{J}(\mathfrak{m}_a,\mathfrak{m}_b)\langle\mathfrak{m}_a,\mathfrak{m}_b|[\mathfrak{l}^{[\rho_1]}\times\mathfrak{l}^{[\rho_2]}\times\mathbf{C}^{[P]}(\Omega_{ab})]^{[0]}|\mathfrak{m}_a\mathfrak{m}_b\rangle^*\,.\quad(11)$$

Once again $\Omega_{ab}=0°$, and we derive the following set of parameters $A_{\rho_1\rho_2P}$:

$$\begin{aligned}A_{000}&=\tfrac{1}{3}[\mathfrak{J}(0,0)+4\mathfrak{J}(0,1)+2\mathfrak{J}(1,1)+2\mathfrak{J}(1,-1)]\,,\\A_{110}&=\tfrac{1}{3}\sqrt{3}[\mathfrak{J}(1,1)-\mathfrak{J}(1,-1)]\,,\\A_{220}&=(5^{1/2}/15)[2\mathfrak{J}(0,0)-4\mathfrak{J}(0,1)+\mathfrak{J}(1,1)+\mathfrak{J}(1,-1)]\,,\\A_{202}&=\tfrac{1}{3}(10^{1/2})[\mathfrak{J}(0,0)+\mathfrak{J}(0,1)-\mathfrak{J}(1,1)-\mathfrak{J}(1,-1)]\,.\end{aligned}\quad(12)$$

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[20] From Eq. (26) of I. The reduced matrix elements of the orbital operators are defined in the present paper as $\langle l\|\mathbf{U}^{[k]}\|l\rangle=(-1)^{k/2}[k]^{1/2}$. This accounts for the factors $[k_i]$ not being present in Eq. (8) above.

By using the set of equations (10) we now have the basic parameters for the effective exchange Hamiltonian between two single d electrons in triplet t_{2g} states expressed in terms of the exchange integrals of Freeman and Watson.[6] If we take the set of integrals calculated in Ref. 6 for two $3d$ orbitals in Co^{2+} ions separated by 4.75 a.u., we find the numerical values for the parameters $A_{\rho_1\rho_2P}$ given in Table III. The coefficients of the various effective exchange Hamiltonians are shown in Table IV.

By inspection of the exchange Hamiltonians [see Eqs. (5), (6′), (9) and Table IV] we note three important points:

(1) The exchange interactions are described by a biharmonic series of orbital operators in which *all* harmonics are important. It would be a rather gross oversimplification to neglect all harmonics other than $(k_1=k_2=\Lambda=0)$ and assume the interaction is described by interaction $\Gamma_{000}(\frac{1}{2}+2\mathbf{S}_a\cdot\mathbf{S}_b)$.

(2) For $\mathfrak{j}$ manifolds, the constant term varies, changing the interval between centers of gravity of different $\mathfrak{j}$ manifolds.

(3) For magnetically inequivalent sites, antisymmetric exchange is large when the spin-orbit coupling is larger than other perturbations.

The parameters calculated for the effective Hamiltonian (5) (see Table IV) lead to an interaction which is nearly Ising in form. This arises from the use of only diagonal elements of the exchange operator. Similarly, the dominance of the antisymmetric terms over the isotropic in the Hamiltonian referred to nonparallel axes Eq. (6′) (see Table IV) arises for the same reason. However it is reasonable to assume that the inclusion of off-diagonal elements of the exchange operator will not change the above conclusions drawn from this work.

CENTER-OF-GRAVITY SHIFTS

The constant terms in the different $\mathfrak{j}$ manifolds in Table IV lead to shifts in the relative positions of the centers of gravity of the manifolds for each ion. This has been discussed in detail by Levy and Copland.[7] The part of the exchange interaction [see Eq. (9) and Eq. (4)] which causes the shifts is

$$(2/\sqrt{3})\Gamma_{110}(\mathbf{l}_a\cdot\mathbf{l}_b)(\mathbf{S}_a\cdot\mathbf{S}_b)$$
$$=(2/\sqrt{3})\Gamma_{110}(\mathbf{l}_a\cdot\mathbf{S}_a)(\mathbf{l}_b\cdot\mathbf{S}_b)+\text{nonscalar terms.}$$

TABLE III. Values for $A_{\rho_1\rho_2P}$ for exchange between two d electrons in t_{2g} triplet states on Co^{2+} ions separated by 4.75 a.u., expressed in cm^{-1}.

$$A_{kk\Lambda}=(-1)^k[\Lambda][k]^{1/2}\begin{pmatrix} k & k & \Lambda \\ 0 & 0 & 0 \end{pmatrix}A_{kk0}$$

$A_{000}=$ 280
$A_{110}=$ 242
$A_{220}=$ 63.8
$A_{202}=-436$

TABLE IV. Hamiltonians describing the exchange interaction between two d electrons on Co^{2+} ions 4.75 a.u. apart in t_{2g} triplet states. Without spin-orbit coupling [See Eq. (4)]

$$\tilde{\mathcal{H}}=[93+70\mathfrak{l}_a\cdot\mathfrak{l}_b-70(\mathfrak{l}_a\cdot\mathfrak{l}_b-3\mathfrak{l}_a{}^z\mathfrak{l}_b{}^z)$$
$$-46[4-3(\mathfrak{l}_a{}^z)^2-3(\mathfrak{l}_b{}^z)^2]+\cdots](\tfrac{1}{2}+2\mathbf{S}_a\cdot\mathbf{S}_b)\ \text{cm}^{-1}.$$

With spin-orbit coupling $\mathcal{H}_{so}=-\lambda\mathfrak{l}\cdot\mathbf{s}$ [see Eq. (5) and Table I]

$\mathfrak{j}_a$	$\mathfrak{j}_b$	α_{000}	α_{110}'	α_{112}'
$\frac{1}{2}$	$\frac{1}{2}$	93	125	-124
$\frac{1}{2}$	$\frac{3}{2}$	23	6.2	-6.6
$\frac{3}{2}$	$\frac{3}{2}$	58	37	-20

With nonparallel axes and $\mathcal{H}_{so}>\mathcal{H}_{\text{distortion}}>\tilde{\mathcal{H}}$ [see Eq. (6′)]

$\mathfrak{j}_a$	$\mathfrak{j}_b$	α_{000}	$\Gamma^{[0]}$	$\Gamma_1{}^{[1]}$	$\Gamma_0{}^{[2]}$	$\Gamma_1{}^{[2]}$	$\Gamma_2{}^{[2]}$
$\frac{1}{2}$	$\frac{1}{2}$	93	~0	188	~0	-186	~0
$\frac{1}{2}$	$\frac{3}{2}$	23	~0	9.5	~0	-9.9	~0
$\frac{3}{2}$	$\frac{3}{2}$	58	5.6	47	3	-30	8.4

Within a j manifold the scalar product $\mathbf{l}_\alpha\cdot\mathbf{S}_\alpha$ has a unique value and thereby shifts all levels in the manifold equally. By using the value of α_{000} in Table IV, it is seen that for one d electron held in a $\mathfrak{j}=\frac{1}{2}$ manifold, the exchange interaction causes the separation of the centers of gravity for the $\mathfrak{j}=\frac{1}{2}$ and $\mathfrak{j}=\frac{3}{2}$ manifolds for the second d electron to change by 70 cm^{-1}. If the first electron is held in the $\mathfrak{j}=\frac{3}{2}$ state, the change in separation is 35 cm^{-1}. The spin-orbit coupling parameter for a $3d$ electron is typically $\sim$200 cm^{-1}, and thus shifts in the relative positions of the manifolds for each ion of the size indicated above have a distinct measurable effect on the relative separations of the manifolds. For exchange interactions of this magnitude it is clear that we cannot treat $\tilde{\mathcal{H}}$ as a perturbation on the spin-orbit interaction, and thus for a correct treatment the two interactions (spin-orbit coupling and exchange) should be simultaneously diagonalized.

One further interesting point arising from the Hamiltonian, Eq. (4), concerns the effect of the constant term A_{000}. This term will shift all levels of each single-ion triplet equally from the position determined by the crystal field. If we also generate the effective Hamiltonians for the exchange interactions between electron a in the t_{2g} state and electron b in the e_g doublet and for both electrons in the e_g doublet states, we can define the parameters

$$(A_{000})_{t-t}=\tfrac{1}{9}\sum_{\mathfrak{m}_a\mathfrak{m}_b}\mathfrak{J}_{tt}(\mathfrak{m}_a,\mathfrak{m}_b)\,,$$

$$(A_{000})_{t-e}=\tfrac{1}{6}\sum_{\mathfrak{m}_a\mathfrak{m}_b}\mathfrak{J}_{te}(\mathfrak{m}_a,\mathfrak{m}_b)\,,$$

$$(A_{000})_{e-e}=\tfrac{1}{4}\sum_{\mathfrak{m}_a\mathfrak{m}_b}\mathfrak{J}_{ee}(\mathfrak{m}_a,\mathfrak{m}_b)\,.$$

Here $\mathfrak{J}_{ij}$ is an exchange integral for the effective Hamiltonian with electron a in crystal field multiplet i and electron b in multiplet j. The effect of the exchange interactions is to shift the single-ion crystal-field levels

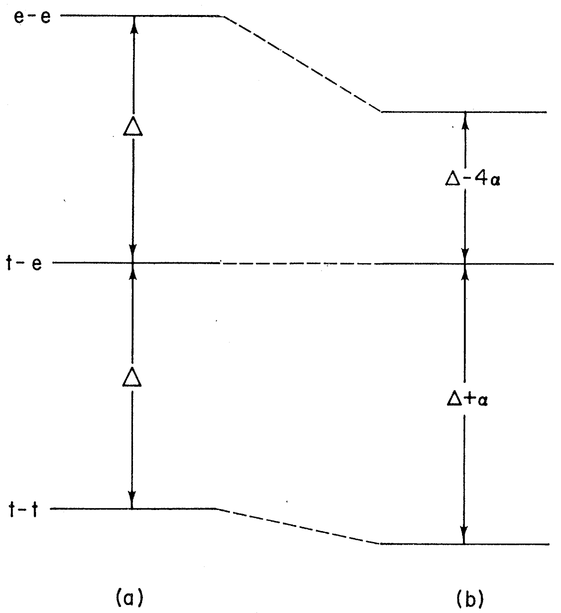

FIG. 1. Pair spectrum of two d electrons in cubic crystalline field (a) without exchange, (b) with exchange coupling, Δ = crystal-field splitting of the doublet e from the triplet t for each electron, and $\alpha=(A_{000})_{d-d}$.

from the positions given by the crystal-field interaction only. The exchange interaction for the d electron in no crystal field will cause a shift of the over-all configuration by a quantity $(A_{000})_{d-d}$ which is just one-fifth of the coefficient Γ_{000} in Eq. (1). The shifts of the individual multiplets within this configuration are related to $(A_{000})_{d-d}$ as follows:

$$(A_{000})_{t-t}\cong(A_{000})_{d-d}\,,\quad (A_{000})_{t-e}\cong 0\,,$$
$$(A_{000})_{e-e}\cong 4(A_{000})_{d-d}\,.$$

The effect of these terms on the crystal-field levels of a pair of exchange-coupled ions is shown in Fig. 1. The Freeman and Watson integrals used above give $(A_{000})_{d-d}=89$ cm^{-1}. It can be seen, then, that these effects on the single-ion crystal-field spectrum can be significant in altering the effective splittings between the crystal-field multiplets.

EXCHANGE INTERACTION BETWEEN COBALT IONS

To obtain some idea of the form of the exchange Hamiltonian when there is more than one d electron per ion, we now consider the exchange interactions between Co^{2+} ions in a cubic crystal field. The single-ion problem is treated in a weak-field approximation which is a reasonable approximation to the situation found in many divalent cobalt complexes with the high-spin configuartion ($S=\frac{3}{2}$).[21] The free-ion ground-state configuration of Co^{2+} is ^4F, and under a cubic crystal field with the z axis defined as a fourfold rotation axis the orbital degeneracy is decomposed into two triplets and a singlet. In an octahedral cubic crystal field the T_1 triplet is the lowest state for Co^{2+}, and its wave functions,[11] in terms of $|M_L\rangle$, where $L=3$, are $\Lambda_1=(\frac{3}{8})^{1/2}|1\rangle+(\frac{5}{8})^{1/2}|-3\rangle$, $\Lambda_0=-|0\rangle$, $\Lambda_{-1}=(\frac{3}{8})^{1/2}|-1\rangle+(\frac{5}{8})^{1/2}|3\rangle$. This triplet can be represented by an effective angular momentum $\mathfrak{l}=1$, such that the projection of orbital angular momentum on the triplet is $\langle\mathbf{L}\rangle=-\frac{3}{2}\mathfrak{l}$.[11] The effect of spin-orbit coupling on this triplet ($S=\frac{3}{2}$) is to form, in order of increasing energy, a doublet $\mathfrak{j}=\frac{1}{2}$, a quartet $\mathfrak{j}=\frac{3}{2}$, and a sextet $\mathfrak{j}=\frac{5}{2}$. We shall confine ourselves to a discussion of the exchange interactions between Co^{2+} ions in the ground ($\mathfrak{j}=\frac{1}{2}$) and first excited ($\mathfrak{j}=\frac{3}{2}$) states.

The principal difference between this situation and that discussed above for one d electron, is that we are dealing with seven equivalent d electrons coupled to give the ^4F state. We use the exchange integrals of Freeman and Watson again as a starting point, but now we have to consider the effect of the coupling together of the electrons. This is treated in a straightforward manner by using the fractional-parentage technique. By using this technique the orbital part of the exchange integral may be written as

$$\begin{aligned}
&\langle L_aM_a'L_bM_b'|J_{\mathrm{op}}|L_aM_aL_bM_b\rangle\\
&\quad\equiv\bar{J}^{(0)}(M_a'M_b';M_aM_b)\\
&\quad=n_an_b(-1)^{M_a+M_b+M_a'+M_b'}[L_a][L_b]\sum_{\bar{\pi}_a\bar{\pi}_b}|(\pi_a\rrbracket\bar{\pi}_a)|^2\\
&\qquad\times|(\pi_b\rrbracket\bar{\pi}_b)|^2\sum_{\bar{M}_am_am_a'}\;\sum_{\bar{M}_bm_bm_b'}\begin{pmatrix}\bar{L}_a & l & L_a\\ \bar{M}_a & m_a & -M_a\end{pmatrix}\\
&\qquad\times\begin{pmatrix}\bar{L}_a & l & L_a\\ \bar{M}_a & m_a' & -M_a'\end{pmatrix}\begin{pmatrix}\bar{L}_b & l & L_b\\ \bar{M}_b & m_b & -M_b\end{pmatrix}\\
&\qquad\qquad\times\begin{pmatrix}\bar{L}_b & l & L_b\\ \bar{M}_b & m_b' & -M_b'\end{pmatrix}J(m_a'm_b';m_am_b)\,,\quad(13)
\end{aligned}$$

where $(\pi_i\rrbracket\bar{\pi}_i)$ represents the fractional-parentage coefficient coupling the state L_i to the parent state $\bar{L}_i$ and $J(m_a'm_b';m_am_b)$ is an exchange integral between two d electrons. The remaining terms are Wigner $3j$ symbols. For Co^{2+} $n_a=n_b=7$, $L=3$, $l=2$, and we have more than a half-filled shell of d electrons. The exchange integrals $\bar{J}^{(0)}(M_a'M_b';M_aM_b)$ may be evaluated using the above equation directly, with the appropriate coefficients and parent states for the configuration d^7. However, a simpler approach is to use the relations between matrix elements of configurations of n electrons and those of $(4l+2-n)$ electrons derived by Racah.[22] One must remember that the operator J_{op} actually involves irreducible tensor operators of ranks running from 0 to $2l$ as seen from the explicit form for these operators derived in I. The n to $(4l+2-n)$ correspondence given by Racah does not hold for operators of rank zero, and these must be considered separately. We use the

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[21] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Co., New York, 1962).

[22] G. Racah, Phys. Rev. **63**, 367 (1943).

techniques described in I for writing the one-electron $J(m_a'm_b';m_am_b)$ integrals as matrix elements of the Hamiltonian, Eq. (1), using Eq. (8). We now define operators acting on the full d^7 configuration[23] and transform back to coupled exchange operators, $\bar{J}^{(K)}$.[24] We find that the full exchange Hamiltonian for the case of Co^{2+} ions in the ^4F configuration may be written as

$$\mathcal{H}=(\tfrac{1}{2}\bar{J}^{(0)}+2\bar{J}^{(1)}\mathbf{S}_1\cdot\mathbf{S}_2)\,, \qquad (14)$$

where S operates on the total spin $\frac{3}{2}$ of the configuration.[25] It must be stressed that the operators $\bar{J}^{(K)}(K=0,1)$ are different and not simply related. The matrix elements of these operators are

$$\begin{aligned}\bar{J}^{(K)}(M_a'M_b';M_aM_b)=\Big[4\sum_{m_am_b}\sum_{m_a'm_b'}&J(m_a'm_b';m_am_b)\\ -(42/5)\sum_{m_am_b}J(m_a'm_b';m_am_b)&(f(a)+f(b))\Big]\delta_{K0}\\ +(49/25)(9\delta_{K0}+\delta_{K1})\sum_{m_am_b}&f(a)f(b)\\ &\times J(m_a'm_b';m_am_b)\,, \qquad (15)\end{aligned}$$

where

$$\begin{aligned}f(i)=&\begin{pmatrix}3 & 2 & 1\\ M_i' & -m_i' & m_i'-M_i'\end{pmatrix}\begin{pmatrix}3 & 2 & 1\\ M_i & -m_i & m_i-M_i\end{pmatrix}\\ &+4\begin{pmatrix}3 & 2 & 3\\ M_i' & -m_i' & m_i'-M_i'\end{pmatrix}\begin{pmatrix}3 & 2 & 3\\ M_i & -m_i & m_i-M_i\end{pmatrix}.\end{aligned}$$

For a case of a purely isotropic interaction where $J(m_a'm_b';m_am_b)=J\delta_{m_a'm_a}\delta_{m_b'm_b}$, this Hamiltonian, Eq. (14), reduces to

$$\mathcal{H}_{\mathrm{iso}}=n_an_bJ(\tfrac{1}{2}+(2/n_an_b)\mathbf{S}_a\cdot\mathbf{S}_b)\,. \qquad (14')$$

The exchange integrals calculated by Freeman and Watson are diagonal in m_a and m_b, giving $J(m_a,m_b)\times\delta_{m_a,m_a'}\delta_{m_b,m_b'}$. For the d^7 configuration this leads to exchange integrals which are diagonal, i.e.,

$$\begin{aligned}\bar{J}^{(K)}&(M_a'M_b';M_aM_b)\\ &=\bar{J}^{(K)}(M_a,M_b)\delta_{M_a',M_a}\delta_{M_b',M_b}\,. \qquad (16)\end{aligned}$$

By using the one-electron integrals of Freeman and Watson and the equations above, we derived the appropriate exchange integrals for the seven electrons coupled as a ^4F term. The effective-Hamiltonian calculation for the case of Co^{2+} in a cubic field with the z axis defined as a fourfold axis of the cube is very straightforward, following exactly the method for one electron. The final Hamiltonian for exchange between two Co^{2+} ions, using an effective angular momentum $\mathfrak{l}=1$, and spin-orbit coupling to give an effective total angular momentum $\mathfrak{j}$, has the form

$$\begin{aligned}\tilde{\mathcal{H}}=\Big[\tfrac{1}{3}\bar{\Gamma}_{000}&+(1/\sqrt{3})\bar{\Gamma}_{110}\mathfrak{j}_a\cdot\mathfrak{j}_b\\ &+(1/\sqrt{30})\bar{\Gamma}_{112}C_0{}^{[2]}(\Omega_{ab})(\mathfrak{j}_a\cdot\mathfrak{j}_b-3\mathfrak{j}_a{}^z\mathfrak{j}_b{}^z)\\ &+(1/\sqrt{5})\bar{\Gamma}_{112}C_{|2|}{}^{[2]}(\Omega_{ab})(\mathfrak{j}_a{}^y\mathfrak{j}_b{}^y-\mathfrak{j}_a{}^x\mathfrak{j}_b{}^x)+\cdots\Big] \qquad (17)\end{aligned}$$

for all directions of the interatomic axes such that $C_{\pm1}{}^{[2]}(\Omega_{ab})=0$.[26] The leading terms in the interaction above can be rearranged into a more familiar form and written as

$$\begin{aligned}\tilde{\mathcal{H}}=\Big[\tfrac{1}{3}\bar{\Gamma}_{000}&+[(1/\sqrt{3})\bar{\Gamma}_{110}+(1/30)^{1/2}\bar{\Gamma}_{112}]\mathfrak{j}_a\cdot\mathfrak{j}_b\\ &-(3/10)^{1/2}\bar{\Gamma}_{112}(\mathfrak{j}_a\cdot\hat{r}_{ab})(\mathfrak{j}_b\cdot\hat{r}_{ab})+\cdots\Big], \qquad (17')\end{aligned}$$

where the unit vector $\hat{r}_{ab}$ is along the line connecting the centers of ions a and b. The values of the coefficients for both ions in their ground states, $\mathfrak{j}_a=\mathfrak{j}_b=\frac{1}{2}$, are

$$\begin{aligned}\bar{\Gamma}_{000}&=\tfrac{1}{6}[A_{000}{}^{(0)}+(25/2)A_{110}{}^{(1)\prime}],\\ \bar{\Gamma}_{110}{}'&\equiv(1/\sqrt{3})\bar{\Gamma}_{110}\\ &=\tfrac{1}{9}[(50/3)A_{000}{}^{(1)}+A_{110}{}^{(0)\prime}+(10/3)A_{220}{}^{(1)\prime}], \qquad (18)\\ \bar{\Gamma}_{112}{}'&\equiv(30)^{-1/2}\bar{\Gamma}_{112}\\ &=\tfrac{1}{9}[-A_{110}{}^{(0)\prime}+(20/3)A_{202}{}^{(1)\prime}-(5/3)A_{220}{}^{(1)\prime}].\end{aligned}$$

The parameters $A_{\rho_1\rho_2P}{}^{(K)}$ are related to the exchange integrals for the fictitious $\mathfrak{l}=1$ state, i.e., $\mathfrak{J}^{(K)}(M_a,M_b)$, through relationships identical to those given in Eq. (12) for the one-electron case. The presence of the superscript (K) does not affect these relations. The effective exchange integrals $\mathfrak{J}^{(K)}(M_a,M_b)$ are related to the integrals for d^7-d^7 exchange, i.e., $\bar{J}^{(K)}(M_a,M_b)$, by the relations

$$\begin{aligned}\mathfrak{J}^{(K)}(1,1)&=\tfrac{1}{64}[9\bar{J}^{(K)}(1,1)+30\bar{J}^{(K)}(1,-3)\\ &\qquad+25\bar{J}^{(K)}(3,3)],\\ \mathfrak{J}^{(K)}(1,0)&=\tfrac{1}{8}[3\bar{J}^{(K)}(1,0)+5\bar{J}^{(K)}(3,0)], \qquad (19)\\ \mathfrak{J}^{(K)}(1,-1)&=\tfrac{1}{64}[9\bar{J}^{(K)}(1,-1)+30\bar{J}^{(K)}(1,3)\\ &\qquad+25\bar{J}^{(K)}(3,-3)],\\ \mathfrak{J}^{(K)}(0,0)&=\bar{J}^{(K)}(0,0)\,.\end{aligned}$$

Upon substituting these equations in Eqs. (12) and the resulting $A_{\rho_1\rho_2P}{}^{(K)}$ in Eq. (18) we find the coefficients for the effective exchange Hamiltonian, Eqs. (17) and (18), for both ions in $\mathfrak{j}=\frac{1}{2}$ states. A similar set of coefficients can be derived for one Co^{2+} ion in an excited $\mathfrak{j}=\frac{3}{2}$ state interacting with the other in its ground $\mathfrak{j}=\frac{1}{2}$ state. The interesting term here is the first term in the effective Hamiltonian, Eq. (17), $\bar{\Gamma}_{000}$ which determines the center of gravity of the pair states. This has the form $\bar{\Gamma}_{000}(\frac{1}{2}-\frac{3}{2})=\frac{1}{6}(A_{000}{}^{(0)}+5A_{110}{}^{(1)\prime})$. Upon comparing this coefficient with its homolog in Eq. (18) we note that the contributions from $A_{000}{}^{(0)}$ to the shifts in the centers of gravity when $\mathfrak{j}_a=\mathfrak{j}_b=\frac{1}{2}$, and when $\mathfrak{j}_a=\frac{1}{2}$ and $\mathfrak{j}_b=\frac{3}{2}$ are the same, whereas the contributions from $A_{110}{}^{(1)}$ vary.

Let us now look at the eigenvalues for the effective Hamiltonian, Eq. (17). For a pair of Co^{2+} ions whose interionic axis is oriented to give $\Omega_{ab}=0°$ and for

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[23] See Eq. (40) of I.

[24] See Eq. (22) of I.

[25] $\bar{J}^{(0)}$ comes from the matrix element of $\bar{J}_{\mathrm{op}}$, and $\bar{J}^{(1)}$ from the matrix element of $\bar{J}_{\mathrm{op}}\mathbf{S}_1\cdot\mathbf{S}_2$ taken between states of the ^4F configuration.

[26] The values of the nonzero harmonics $C_m{}^{[A]}(\Omega)$ are, for the interionic axis lying along the x, y, z axes, respectively,

$(\theta_{ab},\ \phi_{ab})$		$C_0[2]$	$C_{\|2\|}{}^{[2]}$
$x=\frac{1}{2}\pi$	0	$-\frac{1}{2}$	$\sqrt{\frac{3}{8}}$
$y=\frac{1}{2}\pi$	$\frac{1}{2}\pi$	$-\frac{1}{2}$	$-\sqrt{\frac{3}{8}}$
$z=0$	0	1	0

$\mathfrak{j}_a=\mathfrak{j}_b=\frac{1}{2}$ we find a doublet at $(\bar{\Gamma}_{000}+\frac{1}{4}\bar{\Gamma}_{110}'-\frac{1}{2}\bar{\Gamma}_{112}')$, a singlet at $(\bar{\Gamma}_{000}+\frac{1}{4}\bar{\Gamma}_{110}'+\bar{\Gamma}_{112}')$, and a singlet at $(\bar{\Gamma}_{000}-\frac{3}{4}\bar{\Gamma}_{110}')$. From a typical set of exchange integrals as given by Freeman and Watson[27] for the exchange between d electrons in clothed Co atoms separated by 4.75 a.u., we find for the coefficients $\bar{\Gamma}$, Eq. (18),

$$\bar{\Gamma}_{000}=443\text{ cm}^{-1},\quad \bar{\Gamma}_{110}'=133\text{ cm}^{-1},\quad \bar{\Gamma}_{112}'=-8\text{ cm}^{-1}. \tag{20}$$

This leads to the set of eigenvalues: a doublet at $+480\text{ cm}^{-1}$, singlet at 472 cm^{-1}, and singlet at 344 cm^{-1}. The center of gravity of this manifold is shifted by $+443\text{ cm}^{-1}$, i.e., by $\bar{\Gamma}_{000}$. For the interaction where one ion is excited to its $\mathfrak{j}=\frac{3}{2}$ state while the other remains fixed in the ground state, we have a value for $\bar{\Gamma}_{000}$ of $+433\text{ cm}^{-1}$, which means that the separation of the centers of gravity of the $\mathfrak{j}=\frac{1}{2}$ and $\mathfrak{j}=\frac{3}{2}$ manifolds is decreased by 10 cm^{-1} due to the exchange interaction.

$KCoF_3$

We have derived the Hamiltonian for a pair of Co^{2+} ions coupled by an antiferromagnetic exchange interaction. Each ion is in a cubic crystal field and the pair axis is parallel to a fourfold symmetry axis of the crystal field. Such a situation arises in $KCoF_3$ where the Co^{2+} ions form a simple cubic array, and each ion is subjected to a cubic crystal field from the neighboring ions. The Hamiltonian, Eq. (17), describes the different exchange interactions between the three types of nearest-neighbor ions by choosing the polar angles Ω_{ab} appropriate to the interionic bond axes.[26] The *over-all* isotropic splittings we find by using the Freeman and Watson data, Eq. (20), $(6\times 133\text{ cm}^{-1})$, is approximately 3.3 times larger than that indicated by experiment.[8] The principal contributions to this discrepancy arise from the fact that the interionic separation for which the exchange is calculated is less than that existing physically in $KCoF_3$ and that superexchange as well as direct exchange will occur. If we make the assumption that the dependence of the exchange integrals on the separation of the ions is similar for all integrals, then we suggest that the exchange interactions should all be reduced by approximately 3.3 times. This would lead to a relative shift in the centers of gravity of the two lowest exchange-coupled manifolds of 18 cm^{-1}. The free-ion spin-orbit interaction gives a 400 cm^{-1} separation between the $\mathfrak{j}=\frac{1}{2}$ and $\mathfrak{j}=\frac{3}{2}$ states. The exchange interaction calculated above reduces this separation by about 5%, thus giving an effective spin-orbit interaction which is about 5% less than that of a single isolated ion in a similar crystal.

Such a shift should be measurable in an optical study of the spectra of pairs of ions relative to single ions in a diamagnetic crystal partially doped with Co^{2+} ions. Evidence for such a reduction of the spacing between the $\mathfrak{j}$ manifolds of exchange-coupled Co^{2+} ions has been forwarded by Buyers *et al.*[8] from a neutron scattering study of $KCoF_3$. They have deduced that the *effective* spin-orbit interaction is some 20% smaller than the free-ion value, and that the anisotropy of the exchange is less than 10% of the isotropic exchange interaction. From our Hamiltonian, Eq. (17′), the anisotropy of the exchange is represented by the term $\bar{\Gamma}_{112}$ which is about 6% of the isotropic interaction. The exchange interaction reduces the effective spin-orbit interaction by about 5%, which is a significant fraction of the 20% shift observed experimentally.

In conclusion, from the above model calculations using Freeman and Watson's exchange integrals applied to the exchange interactions in $KCoF_3$, we predict a significant change in the effective spin-orbit interaction parameter of Co^{2+} ions. The change is in the same direction as that observed experimentally, and also the anisotropy of the exchange is of the order of that observed. While we do not claim that our results explain all the observed effects, we feel that this example illustrates the importance of accounting for the orbital contributions to exchange interactions. The center-of-gravity shifts described above should be considered, with other contributions to the shifts, in order to give a satisfactory explanation of the observed effects in $KCoF_3$ and other systems with exchange-coupled ions which have ground states that are orbitally degenerate.

DISCUSSION OF RESULTS

We have used the integrals given by Freeman and Watson to demonstrate that *a bilinear scalar spin Hamiltonian does not adequately describe the two-center direct-exchange interaction between ions whose electrons are orbitally degenerate.* The higher-degree isotropic and anisotropic terms in the exchange Hamiltonian comprise a major portion of the interaction; neglecting them cannot be justified. Even though it may be quite difficult to ascertain the magnitude of these terms for a particular interaction, one must find new ways of estimating their strength by using extant data.

Whereas the integrals of Freeman and Watson were given for free d electrons, we have used them to give us the exchange integrals for d electrons in cubic fields. These derived integrals are only first-order estimates of the true exchange integrals; therefore the absolute magnitudes derived by using them must be viewed as such. However, it is only the relative size of the terms in the Hamiltonian which is central to our point. From the relative magnitude of the higher-degree isotropic term A_{110} we have unambiguously demonstrated the sizable shifts in the centers of gravity of the intra-atomic j levels for exchange-coupled ions, e.g., in $KCoF_3$. Also we have positively demonstrated the existence of large antisymmetric exchange terms for ions in magnetically inequivalent sites.

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[27] See Table V of Ref. 6.