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Indirect Exchange Interaction in the Rare-Earth Metals*

FREDERICK SPECHT†
Rice University, Houston, Texas

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With a free-electron model for the conduction band, the isotropic and first-order nonisotropic terms of the indirect exchange interaction in the rare-earth metals have been calculated exactly (in second-order perturbation). The results are compared with previous treatments of the problem, all of which utilize some type of approximation, and specifically with the calculation of Kaplan and Lyons (KL), who assume that the exchange integral $\mathcal{J}(\mathbf{k},\mathbf{k}')$ depends only on $\mathbf{k}-\mathbf{k}'$. It is found that the exact calculation leads to results in disagreement with the approximate treatments: The nonisotropic term is about 4 times larger than that of KL, and the radial dependence of the interaction is significantly different. The resulting Hamiltonian predicts a ferromagnetic ordering pattern for gadolinium at 0°K, while the approximate theories predict a screw structure. However, the predicted ordering pattern for Gd is extremely sensitive to changes in the Fermi wave vector k_F. (A 5% increase in k_F stabilizes a screw structure with a turn angle of 20°.) An estimate is given of the relative contribution of the anisotropic term (relative to the isotropic) for the ferromagnetic ordering pattern. For the two-ion asymptotic interaction, this effect is found to be quite large, ranging from 35 to 200% among the heavy rare earths and over the values of k_F considered. After being summed over the lattice, the contribution is cut down by roughly an order of magnitude.

I. INTRODUCTION

THE indirect exchange interaction via the conduction electrons is chiefly responsible for the interatomic spin-spin coupling in the rare-earth metals. Following Zener's original suggestion[1] concerning this coupling mechanism in the transition metals, Ruderman and Kittel,[2] Kasuya,[3] and Yosida[4] developed a theory for such an interaction in the rare-earth metals. These authors showed that under certain conditions one obtains an effective isotropic interaction, the radial dependence of which is given by the RKKY function $[(x\cos x-\sin x)/x^4]$, where $x=2k_FR$ (k_F=Fermi wave number, R=distance between ions). These conditions are (a) the conduction electrons are treated as a free Fermi gas and (b) the $4f$ shell radius is sufficiently small relative to the Fermi wavelength that the exchange integral $\mathcal{J}(\mathbf{k},\mathbf{k}')$ between a $4f$ shell and a conduction electron may be taken independent of $\mathbf{k}$ and $\mathbf{k}'$. The fact is that neither (a) nor (b) is a very good approximation for the rare earths. In this paper we shall say no more about condition (a); our concern is to make an estimate of the effect of the finite size of the $4f$ shell. Already Liu[5] has shown that condition (b) is invalid unless $k_Fr_0\ll 1$ (r_0=radial extent of $4f$ shell). However, for the rare earths $k_Fr_0\simeq 0.5$, and Kaplan and Lyons[6] (KL) went on to investigate the effects of a nonspherical $4f$ shell. Using a free-electron gas and assuming that $\mathcal{J}(\mathbf{k},\mathbf{k}')$ depends only on $\mathbf{k}-\mathbf{k}'$, they calculated the isotropic and first-order nonisotropic terms by means of multipole expansion of $\mathcal{J}(\mathbf{k}-\mathbf{k}')$. They found that the radial dependence of both terms differs from the RKKY function and that the contribution of the nonisotropic term (relative to the isotropic) for the interaction between nearest neighbors ranges from 10 to 80%. After summing out to 12th nearest neighbors, they found the resulting anisotropic effects to be reduced by at least an order of magnitude. They went on to conclude that the usual assumption of a dominating isotropic term is reasonable but that the anisotropic terms might contribute appreciably. Following the KL formulation, Kasuya and Lyons[7] calculated the general form of the isotropic and nonisotropic terms (to the 4th order) of the interaction. Although they did not use the KL assumption that $\mathcal{J}(\mathbf{k},\mathbf{k}')=\mathcal{J}(\mathbf{k}-\mathbf{k}')$, they evaluated the integrals which determine the radial dependence by approximate techniques. Their final results are given as expansions in terms of $k_F\langle r\rangle_{4f}$.

All previous calculations of the interaction involve some type of approximation either on the functional dependence of $\mathcal{J}(\mathbf{k},\mathbf{k}')$ or in the final evaluation of the radial dependence, leading one to the question: To what extent are these approximations valid? This uncertainty served as motivation for the present work.

Using a free-electron model we have evaluated exactly (in second-order perturbation) the isotropic and first-order nonisotropic terms [using the same multipole expansion of $\mathcal{J}(\mathbf{k},\mathbf{k}')$ as KL]. The functional dependence of the resulting interaction on the angular-momentum operators is, of course, the same as that obtained by KL. However, the coefficients determining the relative magnitude of the nonisotropic term as well as those determining the radial functions differ considerably

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† Present address: Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee. (Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U.S. Atomic Energy Commission.)

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from both RKKY and KL. (The coefficient multiplying the nonisotropic term is 4 times larger than that obtained by KL; the exchange Hamiltonian we obtain predicts ferromagnetic ordering for gadolinium at 0°K, while the previous treatments predict a screw structure.) The relative effect of anisotropy on the asymptotic two-ion interaction is found to be quite larger, varying from 35 to 200% (Table IV) among the heavy rare earths and over the values of k_F considered.

In Sec. II the effective exchange Hamiltonian is obtained (in second-order perturbation), and in Sec. III the numerical results and conclusions are given. In Appendix C a closed expression for the reduced matrix element $\beta_k(LSJ)$ [of the Wigner-Eckart theorem, $\mathcal{Y}_{kq}(\mathbf{L})\rightarrow\beta_k(LSJ)\mathcal{Y}_{kq}(\mathbf{J})$] is derived directly from the irreducible tensors for the two cases $J=|L\pm S|$, resulting in considerable algebraic simplification from methods used previously. (We are able to obtain all numerical estimates by using the effective Hamiltonian expressed in terms of **L** and **S** rather than **J**. However, we include Appendix C for completeness.)

II. THE EFFECTIVE EXCHANGE HAMILTONIAN

We adopt the usual model in describing the rare-earth metals, i.e., a lattice of trivalent ions immersed in a sea of conduction electrons. The state of the 4f shell is specified by a Russell-Saunders function $\psi_{LSJM}(1,\cdots,n)$, $M=-J,\cdots,J$, with the values of L, S, and J corresponding to the Hund ground state, i.e., S maximum, L maximum subject to S, and $J=(L-S, L+S)$ for a (less, greater) than half-filled shell.

The 4f shell functions $\psi_{JM}[=\psi_{LSJM}]$ are properly antisymmetrized functions constructed from the one-particle functions of the form

$$\psi_{lm\alpha}(x_i)=R(r_i)Y_{lm}(\hat{r}_i)\chi_\alpha(i). \tag{1}$$

χ_α denotes the Pauli spinor $(\alpha=\pm\frac{1}{2})$.

The wave functions for the conduction electrons are taken to be those of a free-electron gas:

$$\psi_{\mathbf{k}\sigma}(x_i)=\Omega^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{r}_i)\chi_\sigma(i). \tag{2}$$

The exchange interaction in which we are interested results from the Coulomb interaction between the n 4f electrons of a given ion and a conduction electron. If $|JM\rangle\rightarrow|JM'\rangle$ and $|\mathbf{k}\sigma\rangle\rightarrow|\mathbf{k}'\sigma'\rangle$ denote the transitions experienced by the 4f shell and the conduction electron, then the exchange integral is given by

$$\begin{aligned}\mathcal{J}(M'\mathbf{k}'\sigma';M\mathbf{k}\sigma)&=-e^2\sum_{i=1}^{n}\langle JM'|\langle\mathbf{k}'\sigma'|V(i,n+1)|\mathbf{k}\sigma\rangle|JM\rangle\\&=-e^2\sum_{i=1}^{n}\int dx_1dx_2\cdots dx_{n+1}\,[\psi_{JM'}{}^*(1,\cdots,n)\\&\quad\times\psi_{\mathbf{k}'\sigma'}{}^*(n+1)V(i,n+1)\psi_{JM}(1,\cdots,n)\psi_{\mathbf{k}\sigma}(n+1)],\\V(i,n+1)&=|\mathbf{r}_i-\mathbf{r}_{n+1}|^{-1}P(i,n+1),\end{aligned}$$

where $P(i,n+1)$ is the permutation operator and where $\int dx$ denotes integration over coordinates and summation over spins.

KL have shown that $\mathcal{J}$ may be reduced to the form

$$\begin{aligned}\mathcal{J}(M'\mathbf{k}'\sigma';M\mathbf{k}\sigma)&=-e^2\sum_{i=1}^{n}(JM'|\langle\chi_{\sigma'}(n+1)|(\tfrac{1}{2}+2\mathbf{s}_i\cdot\mathbf{s}_{n+1})\\&\quad\times\mathcal{P}(\mathbf{k}'\mathbf{k}\mathbf{l}_i)|\chi_\sigma(n+1)\rangle|JM).\end{aligned}\tag{3}$$

The quantities in (3) have the following meaning: $\mathbf{s}_{n+1}$ denotes the spin operator for the conduction electron, $\mathbf{l}_i$ and $\mathbf{s}_i$ are the orbital and spin operators for the individual 4f shell electrons, and $\mathcal{P}$ is given by

$$\begin{aligned}\mathcal{P}(\mathbf{k}'\mathbf{k}\mathbf{l})&=(4\pi)^2\sum_{\lambda}\sum_{pq}\sum_{p'q'}[(-)^{p'}i^{p+p'}/(2\lambda+1)]\\&\quad\times I(pp'\lambda;kk')Y_{pq}{}^*(\hat{k})Y_{p'q'}{}^*(\hat{k}')Q(pq;p'q';\lambda l\mathbf{l}),\end{aligned}$$

where

$$\begin{aligned}I(pp'\lambda;kk')&=\int_0^\infty r_1^2dr_1\int_0^\infty r_2^2dr_2\\&\quad\times R(r_1)R(r_2)j_p(kr_1)j_{p'}(k'r_2)(r_<{}^\lambda/r_>{}^{\lambda+1})\end{aligned}\tag{4}$$

[$j_p(x)$ are the spherical Bessel functions], and where Q is defined by

$$\begin{aligned}4\pi\sum_{\mu}&(Y_{lm'},Y_{pq}Y_{\lambda\mu},Y_{p'q'}Y_{lm'})\\&=(Y_{lm'},Q(pq;p'q';\lambda l\mathbf{l})Y_{lm}).\end{aligned}$$

$|JM)$ denotes the spin and angular portion of the 4f shell wave function.

The leading term of $\mathcal{P}$ with $(p=p'=0)$ is a constant and leads to an effective isotropic interaction. All remaining terms of $\mathcal{P}$ contain irreducible tensor operators $\mathcal{Y}_{kq}(\mathbf{l})$ of higher order $(k>0)$ and give rise to nonisotropic corrections to the isotropic term. The first set of nonzero terms beyond $(p=p'=0)$ are those for which $p+p'=2$, and from this set the terms satisfying $(q=q'=0)$ dominate. [When second-order perturbation is performed, only those nonisotropic terms with $(q=q'=0)$ for one of the ions will combine with the isotropic term of the other ion.] We refer to these terms $(p+p'=2,\ q=q'=0)$ as the first-order nonisotropic terms.

In Table I are given the operators Q corresponding to the isotropic and first-order nonisotropic terms (with $l=3$ for the rare earths), and evaluating $\mathcal{P}$ to this

TABLE I. Orbital angular-momentum operators Q. [$T_{20}(\mathbf{l})$ is given in Table V.]

p	q	p'	q'	λ	l	$Q(pqp'q'\lambda l\mathbf{l})$
0	0	0	0	3	3	1
1	0	1	0	2	3	$-(3/35)[T_{20}(\mathbf{l})-5]$
1	0	1	0	4	3	$-(1/21)[T_{20}(\mathbf{l})-12]$
0	0	2	0	3	3	$-(5/15)^{1/2}T_{20}(\mathbf{l})$
2	0	0	0	3	3	$-(5/15)^{1/2}T_{20}(\mathbf{l})$

approximation, we have

$$\begin{aligned}\mathcal{P}(\mathbf{k}'\mathbf{k}\mathbf{l}) = {} & (4\pi/7)I(003;kk') \\ & -(36\pi/175)I(112;kk')\cos k_\theta \cos k_\theta'[T_{20}(\mathbf{l})-5] \\ & -(4\pi/63)I(114;kk')\cos k_\theta \cos k_\theta'[T_{20}(\mathbf{l})-12] \\ & +(2\pi/7)[I(203;kk')(\cos^2 k_\theta-\tfrac{1}{3}) \\ & +I(023;kk')(\cos^2 k_\theta'-\tfrac{1}{3})]T_{20}(\mathbf{l}). \qquad (5)\end{aligned}$$

In second-order perturbation theory, the indirect exchange energy between two ions located at the positions $\mathbf{R}_a$ and $\mathbf{R}_b$ is given by

$$\begin{aligned}E_{ab} = {} & \sum_{\mathbf{kk}'}\sum_{\sigma\sigma'}\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ab}]}{E(k)-E(k')} \\ & \times[1+P(a,b)]\mathcal{J}_a(M_a'\mathbf{k}'\sigma';M_a\mathbf{k}\sigma) \\ & \times\mathcal{J}_b(M_b'\mathbf{k}\sigma;M_b\mathbf{k}'\sigma'),\end{aligned}$$

where $\mathbf{k}$ and $\mathbf{k}'$ are, respectively, summed over the occupied and unoccupied states of the conduction band and where $|JM_a\rangle\rightarrow|JM_a'\rangle$ and $|JM_b\rangle\rightarrow|JM_b'\rangle$ represent the transitions experienced by the two ions. Performing the summations over σ and σ' and using (3), we have

$$E_{ab}=(JM_a'\,|\,(JM_b'\,|\,H_{ab}\,|\,JM_a)\,|\,JM_b),$$

where

$$\begin{aligned}H_{ab} = {} & \frac{e^4}{\Omega^2}\sum_{\mathbf{kk}'}\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ab}]}{E(k)-E(k')} \\ & \times\sum_{ij}[\tfrac{1}{2}+2\mathbf{s}_{ai}\cdot\mathbf{s}_{bj}][1+P(a,b)]\mathcal{P}(\mathbf{k}'\mathbf{k};\mathbf{l}_{ai})\mathcal{P}(\mathbf{k}\mathbf{k}';\mathbf{l}_{bj}).\end{aligned}$$

Using the relation $E(k)=\hbar^2k^2/2m$ for a free electron and the fact that the effective operator is already symmetric in a and b, we obtain

$$H_{ab}=G\sum_{ij}[\tfrac{1}{2}+2\mathbf{s}_{ai}\cdot\mathbf{s}_{bj}]\mathcal{J}_{\mathbf{kk}'}\mathcal{P}(\mathbf{k}'\mathbf{k};l_{ai})\mathcal{P}(\mathbf{kk}';l_{bj}), \qquad (6)$$

where

$$G=4me^4/\hbar^2(2\pi)^6$$

and where $\mathcal{J}_{\mathbf{kk}}'$ denotes the integral operator

$$\int_0^{k_F}d\mathbf{k}\int_{\mathbf{k}_F}^{\infty}d\mathbf{k}'\,\frac{\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ab}]}{k^2-k'^2}. \qquad (7)$$

Substituting (5) into (6) and neglecting those terms which contain greater than zero-order contributions from both ions, we have

$$\begin{aligned}H_{ab} = {} & \pi^2G\sum_{ij}[\tfrac{1}{2}+2\mathbf{s}_{ai}\cdot\mathbf{s}_{bj}]\mathcal{J}_{\mathbf{kk}'}\{(16/49)I^2(003;kk') \\ & -(144/1225)I(003;kk')I(112;kk')\cos k_\theta \\ & \times\cos k_\theta'[T_{20}(\mathbf{l}_{ai})+T_{20}(\mathbf{l}_{bj})-10] \\ & -(16/49)I(003;kk')I(114;kk') \\ & \times\cos k_\theta\cos k_\theta'[T_{20}(\mathbf{l}_{ai})+T_{20}(\mathbf{l}_{bj})-24] \\ & +(8/49)I(003;kk')[I(203;kk')(\cos^2k_\theta-\tfrac{1}{3}) \\ & +I(023;kk')(\cos^2k_\theta'-\tfrac{1}{3})][T_{20}(\mathbf{l}_{ai})+T_{20}(\mathbf{l}_{bj})]\}. \qquad (8)\end{aligned}$$

TABLE II. $I(lmn;k_F)$ and $k_F\partial/\partial k_F I(lmn;k_F)$.

l	m	n	k_F (Å^{-1})	I (10^{-1} Å^2)	$k_F(\partial/\partial k_F)I$ (10^{-1} Å^2)
0	0	3	1.33	0.857	−0.445
			1.40	0.834	−0.473
			1.47	0.809	−0.501
1	1	2	1.33	0.0997	0.104
			1.40	0.107	0.109
			1.47	0.114	0.114
1	1	4	1.33	0.0630	0.0899
			1.40	0.0675	0.0927
			1.47	0.0722	0.0946
2	0	3	1.33	0.0465	0.0622
			1.40	0.0498	0.0630
			1.47	0.0529	0.0633

The integrals over $\mathbf{k}$ and $\mathbf{k}'$ are evaluated in Appendix A with the results expressed in an asymptotic expansion in terms of $(2k_FR_{ab})^{-1}$. Substituting Eqs. (A8) through (A11) into (8) and remembering that in these equations the z axis coincides with $\mathbf{R}_{ab}$, we have

$$\begin{aligned}H_{ab} = {} & \eta\pi^2G\sum_{ij}\{\tfrac{1}{2}+2\mathbf{s}_{ai}\cdot\mathbf{s}_{bj}\}A\{f_1(x)+Cf_2(x) \\ & \times[(\mathbf{l}_{ai}\cdot\mathbf{n}_{ab})^2+(\mathbf{l}_{bj}\cdot\mathbf{n}_{ab})^2-\tfrac{2}{3}l(l+1)]\}, \qquad (9)\end{aligned}$$

where

$$\mathbf{n}_{ab}=\mathbf{R}_{ab}/R_{ab},$$

$$x=2k_FR_{ab},$$

$$f_1(x)=(x\cos x+B\sin x)/x^4,$$

$$f_2(x)=(x\cos x+D\sin x)/x^4,$$

and where

$$B=b/A, \qquad C=c/A, \qquad D=d/c,$$

$$\begin{aligned}A= {} & K_1[(16/49)K_1-(1440/1225)K_2-(384/441)K_3], \\ b= {} & -(16/49)[K_1^2+2K_1K_1']+(1440/1225) \\ & \times[5K_1K_2+(K_1K_2)']+(384/441)[5K_1K_3+(K_1K_3)'], \\ c= {} & K_1[(144/1225)K_2+(16/441)K_3+(32/147)K_4], \\ d= {} & -(144/1225)[5K_1K_2+(K_1K_2)'] \\ & -(16/441)[5K_1K_3+(K_1K_3)']-(224/147)K_1K_4 \\ & -(32/147)(K_1K_4)', \qquad (10)\end{aligned}$$

with $K_1=I(003;\,k_F)$, $K_2=I(112;\,k_F)$, $K_3=I(114;\,k_F)$, $K_4=I(203;\,k_F)$, and $(K)'=k_F\partial/\partial k_F(K)$.

The operator equivalent of H_{ab} in terms of the total $4f$ shell operator is easily obtained following Appendix B. Using (B1), we have

$$\begin{aligned}H_{ab}= {} & \tfrac{1}{4}\xi\{n^2f_1(x)+\alpha_{20}Cf_2(x)[(\mathbf{L}_a\cdot\mathbf{n}_{ab})^2+(\mathbf{L}_b\cdot\mathbf{n}_{ab})^2 \\ & -\tfrac{2}{3}L(L+1)]\}+\xi(\mathbf{S}_a\cdot\mathbf{S}_b)\{f_1(x)+\alpha_{21}Cf_2(x)[(\mathbf{L}_a\cdot\mathbf{n}_{ab})^2 \\ & +(\mathbf{L}_b\cdot\mathbf{n}_{ab})^2-\tfrac{2}{3}L(L+1)]\}, \qquad (11)\end{aligned}$$

where

$$\xi=2\eta\pi^2GA.$$

And finally, to obtain the operator equivalent in terms

TABLE III. Coefficients in radial functions.

k_F (Å^{-1})	A (10^{-3} Å^4)	B	C	D
1.33	0.925	9.11	0.223	−6.52
1.40	0.729	12.2	0.296	−6.43
1.47	0.545	17.0	0.409	−6.33

of the total angular-momentum operators $\mathbf{J}_a$ and $\mathbf{J}_b$, we use Eqs. (B2), (B3), and (B8). We obtain

$$\begin{aligned}H_{ab}=&\tfrac{1}{4}\xi[n^2f_1(x)+\alpha_{20}\beta_2f_2(x)(U_{20}{}^a+U_{20}{}^b)]\\&+\xi\gamma_1{}^2f_1(x)(\mathbf{J}_a\cdot\mathbf{J}_b)+\xi\alpha_{21}Cf_2(x)\{\tfrac{1}{2}\zeta(\mathbf{J}_a\cdot\mathbf{J}_b)(U_{20}{}^a+U_{20}{}^b)\\&+\tfrac{1}{2}\zeta(U_{20}{}^a+U_{20}{}^b)(\mathbf{J}_a\cdot\mathbf{J}_b)+\lambda[(\mathbf{J}_a\cdot\mathbf{n}_{ab})(\mathbf{J}_b\cdot\mathbf{n}_{ab})\\&-\tfrac{1}{3}(\mathbf{J}_a\cdot\mathbf{J}_b)]\},\end{aligned}\qquad(12)$$

where

$$\zeta=\gamma_1(\beta_2-\beta_3),$$

$$\lambda=\tfrac{1}{5}\gamma_1[\beta_3(4\mathbf{J}^2-3)-\beta_1(4\mathbf{L}^2-3)],$$

$$U_{20}{}^i=(\mathbf{J}_i\cdot\mathbf{n}_{ab})^2-\tfrac{1}{3}\mathbf{J}^2.$$

The form of H_{ab} is most easily seen in Eq. (11), where it consists of four terms. The first term is a constant, independent of magnetic ordering. The second represents single-ion anisotropy, i.e., its contribution (after being summed over the crystal) depends only on the orientation of each moment relative to its crystalline environment. The third and fourth terms are, respectively, isotropic and nonisotropic exchange. One can readily see that the fourth term depends not only on the angle between moments a and b but also on the angle that each makes with the line connecting ions a and b.

III. NUMERICAL ESTIMATES AND CONCLUSION

In this section we confine our attention to the heavy rare-earth metals, Gd through Tm.

For a free-electron gas the Fermi wave vector is given by

$$k_F{}^3=3\pi^2(N/V),$$

where (N/V) is the density of conduction electrons. For the heavy metals $N=3$ and $V=a^2c\sqrt{3}/4$ (hcp). Using the lattice constants $a=3.6$ Å and $c=5.65$ Å, we obtain $k_F=1.4$ Å^{-1}. However, since the Fermi surface is not spherical, we should not feel bound to this value of k_F. Therefore, in addition to $k_F=1.4$ Å^{-1}, let us also consider, say, a ±5% variation from this estimate.

To evaluate $I(lmn;k_F)$ we require a choice for the radial function $R(r)$. For this choice we use the Hartree-Fock $4f$ shell function for gadolinium[8] given by Freeman and Watson.[9] By numerical integration we obtain the values of $I(lmn;k_F)$ and $k_F\partial/\partial k_F I(lmn;k_f)$ given in Table II, which with Eq. (10) yield the values of the coefficients A through D in Table III.

We first observe that the value of B (the coefficient of $\sin x/x^4$ in the isotropic radial function) in Table III is larger than that obtained by both RKKY and KL. [KL obtained the values[10] $(B, C, D)=(3.2, 0.07, -4.1)$.] The effect of this variation in B is most easily seen in the case of gadolinium. Since $L=0$, the exchange energy of the crystal from Eq. (11) may be put into the form

$$H=\sum_{ab}{}'(\mathbf{S}_a\cdot\mathbf{S}_b)(x\cos x+B\sin x)/x^4.$$

Assuming a spiral ordering pattern (where the moments in each hexagonal plane are parallel and lying in the plane but are rotated by an angle ω from plane to plane), one finds[11] that the turn angle depends sensitively on both B and k_F. With a hcp lattice ($a=3.6$ Å, $c=5.65$ Å) and with $k_F=1.4$ Å^{-1}, H is minimized with a turn angle which decreases from ~50° to ~45° as B increases from (-1) to $(+6)$. For $B>6$, $\omega=0$ minimizes H. Both the KL function $B=3.2$ and the RKKY function $(B=-1)$ predict a screw structure for Gd at 0°K with $\omega\simeq45°$ to 50°, while with the appropriate value from Table III $(B=12.2)$ one obtains ferromagnetic ordering in agreement with experimental observation.[12] With $k_F=1.33$ Å^{-1} and $B=9.11$, one again obtains ferromagnetic ordering; however, with $k_F=1.47$ Å^{-1} and $B=17.0$, H is minimized with a turn angle of 20°. The predicted ordering pattern for Gd appears to be too sensitive on the value of k_F to allow one to reach a definite conclusion with a free-electron model.

We next consider the anisotropic term; we note that the coefficient C (which gives the relative magnitude of the anisotropic term) is about 4 times larger than that obtained by KL. Of course, one cannot conclude that the anisotropic contribution will be 4 times greater, since the coefficients B and D are also different. Due to anisotropy the two-ion exchange energy E_{ab} for a ferromagnetic arrangement will depend on the angle between each moment and the vector $\hat{n}_{ab}$. In general, E_{ab} is obtained by taking the expected value of (12). However, for the heavy rare earths, this calculation can be greatly simplified by using (11) instead. Since $J=L+S$, the state of maximum M_J is given by $|J,J\rangle=|L,L\rangle|S,S\rangle$, so that E_{ab} can be obtained by choosing the z axis in the direction of the moments and taking the expected value of (11) between $|L,L\rangle|S,S\rangle$ for each of the two ions. Retaining only the two-ion interaction terms of (11), we obtain

$$\begin{aligned}E_{ab}=&\xi S^2\{f_1(x)+\alpha_{21}Cf_2(x)[2L^2(n_{ab}{}^z)^2\\&+L((n_{ab}{}^x)^2+(n_{ab}{}^y)^2)-\tfrac{2}{3}L(L+1)]\}.\end{aligned}\qquad(13)$$

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[8] Doubtless the variation in $R(r)$ through the rare-earth series affects the interaction. However, owing to the crudeness of our band functions, taking $R(r)$ for Gd as representative does not appear a bad approximation.

[9] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[10] Although KL used hydrogenic functions for $R(r)$, it is doubtful that this could produce the large discrepancies in the coefficients.

[11] All hcp lattice summations evaluated for this paper were taken over all lattice points inside a cylinder centered at the origin, with axis parallel to the c axis and with radius and half-height equal to 50 nearest-neighbor spacings (=50×3.6 Å).

[12] W. C. Koehler, J. Appl. Phys. **36**, 1078 (1965).

TABLE IV. Exchange energy for nearest-neighbor and asymptotic two-ion interaction and exchange energy (per ion) of crystal.

		Nearest-neighbor two-ion energy			Asymptotic two-ion energy			Ferromagnetic energy (per ion) of crystal		
$\langle k_F \rangle$ (Å^{-1})	Rare earth	$E_{NN}(0)$ (k_B°K)	$E_{NN}(\pi/2)$ (k_B°K)	χ_{NN}	$E_\infty(0)$ (10 k_B°K)	$E_\infty(\pi/2)$ (10 k_B°K)	χ_∞	$E_{\mathrm{crys}}(0)$ (k_B°K)	$E_{\mathrm{crys}}(\pi/2)$ (k_B°K)	χ_{crys}
1.33	Tb	−4.79	−7.73	47	329	621	61	−78.8	−79.6	1.0
	Dy	−3.05	−5.50	57	202	445	75	−54.6	−55.3	1.3
	Ho	−2.48	−3.26	27	181	259	35	−35.1	−35.3	0.6
	Er	−2.08	−1.49	33	169	111	42	−19.9	−19.7	1.0
	Tm	−1.40	−0.42	108	123	26	130	− 9.0	− 8.7	3.4
1.40	Tb	−6.59	−8.06	20	257	632	84	−77.7	−79.5	2.3
	Dy	−4.44	−5.67	24	144	456	104	−53.8	−55.3	2.8
	Ho	−3.10	−3.50	12	159	259	48	−34.8	−35.2	1.7
	Er	−2.09	−1.79	15	177	102	54	−20.0	−19.6	2.0
	Tm	−1.17	−0.68	53	140	15	162	− 9.2	− 8.6	6.7
1.47	Tb	−7.66	−7.07	8.0	147	617	123	−72.2	−75.8	4.9
	Dy	−5.38	−4.89	9.5	58	451	154	−49.8	−52.8	5.9
	Ho	−3.34	−3.18	4.9	121	247	68	−32.5	−33.5	3.0
	Er	−1.74	−1.86	6.7	178	84	72	−19.1	−18.4	3.7
	Tm	−0.68	−0.87	24.5	156	− 1.1	202	− 9.1	− 7.9	14.1

With θ denoting the angle between $\mathbf{n}_{ab}$ and $\hat{z}$, this becomes

$$E_{ab}(\theta)=\xi S^2[f_1(x)+\alpha_{21}Cf_2(x)L(2L-1)(\cos^2\theta-\tfrac{1}{3})].$$

A good estimate of the anisotropic strength can be obtained by comparing the values of $E_{ab}(0)$ and $E_{ab}(\pi/2)$. For nearest neighbors ($R_{ab}=3.6$ Å) these values are given in Table IV, along with the value of χ_{NN},

$$\chi=200\,|\,E(0)-E(\pi/2)\,|\,|\,E(0)+E(\pi/2)\,|^{-1},$$

which gives the percentage contribution of the anisotropy.

Since the anisotropic strength clearly depends on $R_{ab}[f_1(x)\neq f_2(x)]$, it is instructive to consider the asymptotic behavior of the anisotropy. As $R_{ab}\rightarrow\infty$, both $f_1(x)$ and $f_2(x)$ approach $\cos x/x^3$. In Table IV the values of $E_\infty(0)$, $E_\infty(\pi/2)$, and χ_∞ are tabulated, where $E_\infty(\theta)$ is obtained from $E_{ab}(\theta)$ by setting $f_1(x)=f_2(x)=1$.

To estimate the effect of anisotropy on the exchange energy of the crystal, we again consider the ferromagnetic case. Using (13) and the symmetry of a hcp lattice, we obtain

$$E_{\mathrm{crys}}(\alpha)=\xi S^2\sum_b{}'\,[f_1(x)+\tfrac{3}{2}\alpha_{21}Cf_2(x)L(2L-1)(\cos^2\theta_{ab}-\tfrac{1}{3})(\cos^2\alpha-\tfrac{1}{3})]$$

as the exchange energy per ion for a ferromagnetic ordering pattern. Here θ_{ab} is the angle between $\mathbf{n}_{ab}$ and the c axis, and α is the angle made with the c axis by each moment. The summations over b were performed[11] for the two cases in which the moments are along the c axis $E_{\mathrm{crys}}(0)$ and in the hexagonal plane $E_{\mathrm{crys}}(\pi/2)$. The values of $E_{\mathrm{crys}}(0)$, $E_{\mathrm{crys}}(\pi/2)$, and χ_{crys} are given in Table IV.

We note from the values of E_{crys} that for each rare earth the energy favors the experimentally observed ordering pattern (concerning the ordering relative to the c axis) and has the correct order of magnitude with respect to the observed ordering temperature. From the values of χ_{NN} and χ_∞ it can be seen that the anisotropic contribution for two-ion interaction is significant. After being summed over the lattice, however, the contribution χ_{crys} is reduced to about 5% of χ_∞. (This reduction occurs as a result of cancellation due to the symmetry of the hcp lattice.) Further, it is seen that the anisotropic contribution depends sensitively on k_F. (A 5% variation in k_F alters the anisotropy by about a factor of 2.) With $k_F=1.33$ Å^{-1}, χ_{crys} is negligible, while with $k_F=1.47$ Å^{-1} the anisotropy could possibly be of significance in the case of Tb, Dy, and Tm. The fact that χ_{NN} is reduced with increasing k_F while χ_{crys} is increased indicates that the nearest-neighbor interaction does not give a good measure of the two-ion anisotropic behavior. Since χ_∞ and χ_{crys} have roughly the same dependence on k_F, the value of χ_∞ appears to be more indicative of the anisotropic behavior for the two-ion interaction. Because of the strong dependence on k_F and the small value of $\chi_{\mathrm{crys}}/\chi_\infty$, it also appears that the exchange energy per ion for a ferromagnetic ordering pattern, although physically significant, does not represent a good test of the exchange anisotropy for the crystal. Although χ_∞ is equally sensitive to k_F, its value remains quite large over the region $1.33\leq k_F$ Å≤ 1.47, and one would expect to find effects in which such a large two-body interaction would be manifested. One such possibility is the spin-wave dispersion curve, and calculations concerning this are in progress.

Recent band calculations of Dimmock, Freeman, and Watson[13] suggest that near the Fermi surface the bands

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[13] A. J. Freeman, J. O. Dimmock, and R. E. Watson, Phys. Rev. Letters **16**, 94 (1966).

are not at all like those of free electrons. In view of these calculations, any specific physical conclusions drawn from our results would appear somewhat questionable. However, the purpose of this work is not to question the validity of the free-electron model, but to extend the calculation along the lines of previous authors. With this in mind the present results are significant: The mathematical approximations used previously lead to results significantly different from our calculation; the predicted ordering pattern for Gd is too sensitive to k_F to allow a definite conclusion with a free-electron model; the anisotropic contribution which we have evaluated strengthens the conclusions of KL, i.e., that the anisotropic correction to the standard calculations of Liu and previous workers can be expected to be physically significant. Further, the present results suggest that the corrections to the RKKY R dependence of the interaction are considerably larger than those found by KL and will probably be physically important.

APPENDIX A: RADIAL DEPENDENCE

The technique for evaluating the integrals over $\mathbf{k}$ and $\mathbf{k}'$ is best illustrated by an example. Let us consider

$$I=\mathcal{J}_{\mathbf{kk}'}\{I(003;kk')[I(203;kk')\cos^2k_\theta+I(023;kk')\cos^2k_\theta']\},\quad\text{(A1)}$$

where $\mathcal{J}_{\mathbf{kk}'}$ and $I(lmn;kk')$ are defined in (7) and (4). To simplify the notation we introduce the integral operator

$$\mathcal{J}_{r_1r_2}{}^n=\int_0^\infty r_1^2dr_1\int_0^\infty r_2^2dr_2\,R(r_1)R(r_2)\,(r_<{}^n/r_>{}^{n+1}).\quad\text{(A2)}$$

Then from (4) we have

$$I(lmn;kk')=\mathcal{J}_{r_1r_2}{}^n j_l(kr_1)j_m(k'r_2)\quad\text{(A3)}$$

and (A1) becomes

$$I=\mathcal{J}_{kk'}\mathcal{J}_{r_1r_2}{}^3\mathcal{J}_{r_3r_4}{}^3 j_0(kr_1)j_0(k'r_2)[j_2(kr_3)j_0(k'r_4)\cos^2k_\theta+j_0(kr_3)j_2(k'r_4)\cos^2k_\theta'].$$

Introducing the Taylor expansion for the spherical Bessel functions,

$$j_l(x)=\sum_{n=0}^\infty f_l(n)x^{2n+l},\quad\text{(A4)}$$

and making use of the symmetry in $\mathbf{k}$ and $\mathbf{k}'$, we have

$$\begin{aligned}I=\frac{1}{2}\sum_{abcd}&\mathcal{J}_{\mathbf{kk}'}\mathcal{J}_{r_1r_2}{}^3\mathcal{J}_{r_3r_4}{}^3f_0(a)f_0(b)\\&\times\{f_2(c)f_0(d)r_3{}^2[k^{2(a+c+1)}k'^{2(b+d)}\cos^2k_\theta\\&+k^{2(b+d)}k'^{2(a+c+1)}\cos^2k_\theta']\\&+f_0(c)f_2(d)r_4{}^2[k^{2(a+c)}k'^{2(b+d+1)}\cos^2k_\theta'\\&+k^{2(b+d+1)}k'^{2(a+c)}\cos^2k_\theta'][r_1{}^{2a}r_2{}^{2b}r_3{}^{2c}r_4{}^{2d}]\}.\quad\text{(A5)}\end{aligned}$$

To evaluate I we first perform the integrations over $\mathbf{k}$ and $\mathbf{k}'$, integrating term by term in (A5). Evaluating I in this manner requires the inclusion of a convergence factor in the integrand, for otherwise each term of the expansion would be undefined (in the sense that $\int_0^\infty x^n\sin x dx$ is undefined).

After introducing the factor $\exp[-\alpha(k+k')]$, we see that each term of (A5) contains integrals of the form

$$\begin{aligned}I'=\lim_{\alpha\to0}\int_0^{k_F}d\mathbf{k}\int_{k_F}^\infty d\mathbf{k}'\exp[-\alpha(k+k')]&\\\times\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}][k^mk'^n\cos^2k_\theta+k^nk'^m\cos^2k_\theta']&\\\times[k^2-k'^2]^{-1},&\quad\text{(A6)}\end{aligned}$$

where $m=2,4,6,\cdots$ and $n=0,2,4,\cdots$.

Since the integrand of (A6) is antisymmetric in $\mathbf{k}$ and $\mathbf{k}'$, the lower limit on $\int d\mathbf{k}'$ may be extended to zero.[14] Further, there is no loss of generality in taking $\mathbf{R}$ along the z axis. Making use of these simplifications and integrating over the angular variables k_θ, k_ϕ, k_θ' and k_ϕ', we have

$$\begin{aligned}I'=\lim_{\beta\to0}\left(\frac{-16\pi^2}{R^{m+n+4}}\right)\int_0^{k_FR}dx\int_0^\infty dy\frac{\exp[-\beta(x+y)]}{y^2-x^2}&\\\times\{(x^{m+1}\sin x+2x^m\cos x-2x^{m-1}\sin x)(y^{n+1}\sin y)&\\+(x^{n+1}\sin x)(y^{m+1}\sin y+2y^m\cos y-2y^{m-1}\sin y)\},&\end{aligned}$$

where $\beta R=\alpha$. Using the relations

$$\lim_{\beta\to0}\int_0^\infty\exp(-\beta y)\frac{y^p\sin y}{y^2-x^2}dy=\tfrac{1}{2}\pi x^{p-1}\cos x$$

(p odd) and

$$\lim_{\beta\to0}\int_0^\infty\exp(-\beta y)\frac{y^p\cos y}{y^2-x^2}dy=-\tfrac{1}{2}\pi x^{p-1}\sin x$$

(p even), we obtain[15]

$$\begin{aligned}I'=\frac{8\pi^3}{R^{m+n+4}}\int_0^{k_FR}dx\,[(2x^{m+n-1}-x^{m+n+1})\sin(2x)&\\-2x^{m+n}\cos(2x)]=2\eta[\mathcal{C}-\mathcal{S}(5+m+n)+\cdots]k_F{}^{m+n}&\\=2\eta[\mathcal{C}-\mathcal{S}(5+k_F\partial/\partial k_F)+\cdots]k_F{}^{m+n},&\quad\text{(A7)}\end{aligned}$$

where $\mathcal{C}=\cos(2k_FR)/(2k_FR)^3$, $\mathcal{S}=\sin(2k_FR)/(2k_FR)^4$, $\eta=16\pi^3k_F{}^4$, and where we have neglected any terms containing $(2k_FR)^{-p}$ with $p\geq5$.

Substituting (A7) into (A5), we have

$$\begin{aligned}I=\eta[\mathcal{C}-\mathcal{S}(5+k_F\partial/\partial k_F)+\cdots]\mathcal{J}_{r_1r_2}{}^3\mathcal{J}_{r_3r_4}{}^3&\\\times\sum_{abcd}(k_Fr_1)^{2a}(k_Fr_2)^{2b}(k_Fr_3)^{2c}(k_Fr_4)^{2d}&\\\times f_0(a)f_0(b)[f_2(c)f_0(d)(k_Fr_3)^2+f_0(c)f_2(d)(k_Fr_4)^2].&\end{aligned}$$

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[14] The factor $\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}]$ in the integrand is effectively symmetric in $\mathbf{k}$ and $\mathbf{k}'$. Evaluating the integrals of $\mathbf{k}$ and $\mathbf{k}'$ by this procedure amounts to taking the principal part of the integral.

[15] The form of the R dependence in (A7) looks like a special case of the recent results of Roth *et al.* [Phys. Rev. **149**, 519 (1966)].

Using (A4) and the fact that $\mathcal{G}_{r_3r_4}{}^3=\mathcal{G}_{r_4r_3}{}^3$, we obtain

$$I=2\eta[\mathcal{C}-\mathcal{S}(5+k_F\partial/\partial k_F)+\cdots]$$
$$\times[\mathcal{G}_{r_1r_2}{}^3 j_0(k_Fr_1)j_0(k_Fr_2)][\mathcal{G}_{r_3r_4}{}^3 j_2(k_Fr_3)j_0(k_Fr_4)],$$

and with (A3) I becomes

$$I=2\eta[\mathcal{C}-\mathcal{S}(5+k_F\partial/\partial k_F)+\cdots]I(003;k_F)I(203;k_F). \tag{A8}$$

Following this procedure, one can also verify

$$\mathcal{G}_{\mathbf{kk}'}I^2(003;kk')=\eta[\mathcal{C}-\mathcal{S}(1+k_F\partial/\partial k_F)+\cdots]$$
$$\times I^2(003;k_F), \tag{A9}$$

$$\mathcal{G}_{\mathbf{kk}'}I(003;kk')I(11\lambda;kk')\cos k_\theta \cos k_\theta'$$
$$=-\eta[\mathcal{C}-\mathcal{S}(5+k_F\partial/\partial k_F)+\cdots]I(003;k_F)I(11\lambda;k_F), \tag{A10}$$

$$\mathcal{G}_{\mathbf{kk}'}I(003;kk')[I(203;kk')+I(023;kk')]$$
$$=2\eta[\mathcal{C}-\mathcal{S}(1+k_F\partial/\partial k_F)+\cdots]I(003;k_F)I(203;k_F). \tag{A11}$$

It is of interest to note how (A9), the radial dependence of the leading term, differs from the RKKY function. In fact, if we had set $I(003;kk')=I(003;k_F)$ before doing the integration, we would have obtained the RKKY function instead, i.e.,

$$\mathcal{G}_{\mathbf{kk}'}I^2(003;k_F)=\eta[\mathcal{C}-\mathcal{S}]I^2(003;k_F).$$

APPENDIX B: OPERATOR EQUIVALENTS

In the Russell-Sunders coupling scheme the individual $\mathbf{l}_i$ and $\mathbf{s}_i$ are first coupled to form the total operators $\mathbf{L}$ and $\mathbf{S}$, and these are then coupled to form the total angular-momentum operator $\mathbf{J}$. It is therefore expedient to obtain the operator equivalent of (9) first in terms of $\mathbf{L}$ and $\mathbf{S}$ and then in terms of $\mathbf{J}$.

We observe that each term of (9) (after being expressed in terms of irreducible tensors) contains operators of the form

$$\sum_i \mathcal{Y}_{kq}(\mathbf{l}_i)\mathcal{Y}_{k'q'}(\mathbf{s}_i).$$

Using the Wigner-Eckart theorem and the fact that $\mathbf{L}$ and $\mathbf{S}$ are defined in disjoint spaces, we have

$$\sum_i \mathcal{Y}_{kq}(\mathbf{l}_i)\mathcal{Y}_{k'q'}(\mathbf{s}_i)\rightarrow\alpha_{kk'}(lsLS)\mathcal{Y}_{kq}(\mathbf{L})\mathcal{Y}_{k'q'}(\mathbf{S}) \tag{B1}$$

as the operator equivalent in terms of $\mathbf{L}$ and $\mathbf{S}$. Here $\alpha_{kk'}(lsLS)$ is the reduced matrix element and is independent of q and q'. The application of (B1) to (9) is given by (11).

Finally, to obtain the operator equivalent in terms of $\mathbf{J}$, we use the fact that $\mathbf{L}$ and $\mathbf{S}$ are coupled to form $\mathbf{J}$, and another application of the Wigner-Eckart theorem immediately yields

$$\mathcal{Y}_{kq}(\mathbf{L})\rightarrow\beta_k(LSJ)\mathcal{Y}_{kq}(\mathbf{J}), \tag{B2}$$

$$\mathcal{Y}_{kq}(\mathbf{S})\rightarrow\gamma_k(LSJ)\mathcal{Y}_{kq}(\mathbf{J}). \tag{B3}$$

TABLE V. Irreducible tensor operators $\mathcal{Y}_{kq}(\mathbf{J})$, where $\mathcal{Y}_{kq}(\mathbf{J})=D_{kq}T_{kq}(\mathbf{J})$.

k	q	D_{kq}	$T_{kq}(\mathbf{J})$
1,	0	1	J_z
1,	±1	$\mp\sqrt{2}/2$	$(J_x\pm iJ_y)$
2,	0	$(\sqrt{6})/2$	$J_z^2-\frac{1}{3}\mathbf{J}^2$
2,	±1	$\mp1/2$	$(J_x\pm iJ_y)J_z+J_z(J_x\pm iJ_y)$
2,	±2	$1/2$	$(J_x\pm iJ_y)^2$
3,	0	$(\sqrt{10})/2$	$J_z^3-\frac{1}{5}(3\mathbf{J}^2-1)J_z$
3,	±1	$\mp(\sqrt{30})/8$	$(J_x\pm iJ_y)J_z^2+J_z^2(J_x\pm iJ_y)$ $-\frac{1}{5}(2\mathbf{J}^2+1)(J_x\pm iJ_y)$
3,	±2	$\sqrt{3}/4$	$(J_x\pm iJ_y)^2J_z+J_z(J_x\pm iJ_y)^2$
3,	±3	$\mp\sqrt{2}/4$	$(J_x\pm iJ_y)^3$

Equation (11) contains four terms with $(kk')=(00)$, (01), (20), and (21). The application of (B2) and (B3) to the first three terms here is trivial. The fourth term contains the operator

$$I=(\mathbf{S}_a\cdot\mathbf{S}_b)[T_{20}(\mathbf{L}_a)+T_{20}(\mathbf{L}_b)]=[1+P(a,b)]Q, \tag{B4}$$

where

$$Q=(\mathbf{S}_a\cdot\mathbf{S}_b)T_{20}(\mathbf{L}_a)=\tfrac{1}{2}[(\mathbf{S}_a\cdot\mathbf{S}_b)T_{20}(\mathbf{L}_a)$$
$$+T_{20}(\mathbf{L}_a)(\mathbf{S}_a\cdot\mathbf{S}_b)].$$

To obtain the operator equivalent of Q we use Table V and the relation $\mathbf{S}_a=\mathbf{J}_a-\mathbf{L}_a$. We have

$$Q=Q_1-Q_2+Q_3,$$

where

$$Q_1=\tfrac{1}{2}[(\mathbf{J}_a\cdot\mathbf{S}_b)T_{20}(\mathbf{L}_a)+T_{20}(\mathbf{L}_a)(\mathbf{J}_a\cdot\mathbf{S}_b)],$$
$$Q_2=\tfrac{1}{2}[(\mathbf{L}_a\cdot\mathbf{S}_b)(L_a{}^z)^2+(L_a{}^z)^2(\mathbf{L}_a\cdot\mathbf{S}_b)],$$
$$Q_3=\tfrac{1}{3}\mathbf{L}^2(\mathbf{L}_a\cdot\mathbf{S}_b).$$

Using (B2) and (B3), we have

$$Q_1\rightarrow\tfrac{1}{2}\gamma_1\beta_2[(\mathbf{J}_a\cdot\mathbf{J}_b)T_{20}(\mathbf{J}_a)+T_{20}(\mathbf{J}_a)(\mathbf{J}_a\cdot\mathbf{J}_b)], \tag{B5}$$

$$Q_3\rightarrow\tfrac{1}{3}\gamma_1\beta_1\mathbf{L}^2(\mathbf{J}_a\cdot\mathbf{J}_b). \tag{B6}$$

The quantity Q_2 may be treated by expressing it explicitly in terms of irreducible tensors. Noting Table V, we write

$$Q_2=S_b{}^zT_{30}(\mathbf{L}_a)+\tfrac{1}{4}S_b{}^-T_{31}(\mathbf{L}_a)+\tfrac{1}{4}S_b{}^+T_{3,-1}(\mathbf{L}_a)$$
$$+\tfrac{1}{10}(2\mathbf{L}^2+1)(\mathbf{L}_a\cdot\mathbf{S}_b)+\tfrac{1}{10}(4\mathbf{L}^2-3)(L_a{}^zS_b{}^z).$$

Using (B2) and (B3), we have

$$Q_2\rightarrow\tfrac{1}{2}\gamma_1\beta_3[(\mathbf{J}_a\cdot\mathbf{J}_b)(J_a{}^z)^2+(J_a{}^z)^2(\mathbf{J}_a\cdot\mathbf{J}_b)]$$
$$+\tfrac{1}{10}\gamma_1[\beta_1(2\mathbf{L}^2+1)-\beta_3(2\mathbf{J}^2+1)](\mathbf{J}_a\cdot\mathbf{J}_b)$$
$$+\tfrac{1}{10}\gamma_1[\beta_1(4\mathbf{L}^2-3)-\beta_3(4\mathbf{J}^2-3)](J_a{}^zJ_b{}^z). \tag{B7}$$

Substituting (A5), (A6), and (A7) into (A4), we obtain

$$
\begin{aligned}
&(\mathbf{S}_a\cdot\mathbf{S}_b)[T_{20}(\mathbf{L}_a)+T_{20}(\mathbf{L}_b)] \\
&\quad\to\tfrac{1}{2}\gamma_1(\beta_2-\beta_3)\{(\mathbf{J}_a\cdot\mathbf{J}_b)[T_{20}(\mathbf{J}_a)+T_{20}(\mathbf{J}_b)] \\
&\quad+[T_{20}(\mathbf{J}_a)+T_{20}(\mathbf{J}_b)](\mathbf{J}_a\cdot\mathbf{J}_b)\}+\tfrac{1}{5}\gamma_1[\beta_3(4\mathbf{J}^2-3) \\
&\quad-\beta_1(4\mathbf{L}^2-3)][\mathbf{J}_a{}^z\mathbf{J}_b{}^z-\tfrac{1}{3}\mathbf{J}_a\cdot\mathbf{J}_b]. \qquad \text{(B8)}
\end{aligned}
$$

The operator equivalent of H_{ab} in terms of $\mathbf{J}$ is given in Eq. (12).

APPENDIX C: REDUCED MATRIX ELEMENTS

A. Evaluation of $\alpha_{kk'}$

To evaluate the reduced matrix elements $\alpha_{kk'}$ [defined in (B1)], we must first consider the explicit form of the $4f$ shell functions ψ_{JM}. These functions are constructed from the one-particle functions, Eq. (1), according to Hund's rule and the Pauli exclusion principle, and are given by

$$
\begin{aligned}
&\psi_{JM}(1,\cdots,n)=[R(r_1)\cdots R(r_n)]\phi_{JM}(1,\cdots,n), \\
&\phi_{JM}(1,\cdots,n) \\
&\quad=\sum_{mm'}[C(LSJ\mid mm'M)\phi_{Lm;Sm'}(1,\cdots,n)], \qquad \text{(C1)}
\end{aligned}
$$

where $\phi_{Lm;Sm'}$ is totally antisymmetric.

For a less than half-filled shell ($n<2l+1$), $\phi_{Lm;Sm'}$ can be expressed as the product of an antisymmetric orbital function $\phi_{Lm}(1,\cdots,n)$ and a symmetric spin function $\phi_{Sm'}(1,\cdots,n)$. For $m=L$ and $m'=S$, these functions have the particularly simple form

$$\phi_{LL}(1,\cdots,n)=\mathcal{A}[Y_{ll}(1)Y_{ll-1}(2)\cdots Y_{ll-n+1}(n)], \qquad \text{(C2)}$$

$$\phi_{SS}(1,\cdots,n)=[\chi_{1/2}(1)\chi_{1/2}(2)\cdots\chi_{1/2}(n)], \qquad \text{(C3)}$$

where $\mathcal{A}$ is the normalized antisymmetrizer.

For a greater than half-filled shell ($n>2l+1$), $\phi_{Lm;Sm'}$, in general, cannot be factored into this product. However, due to the fact that $J=L+S$, the function ϕ_{JJ} is given by

$$
\begin{aligned}
\phi_{rJ}(1,\cdots,n)&=\phi_{LL;SS}(1,\cdots,n) \\
&=\mathcal{A}[\langle l,\tfrac{1}{2}\mid 1\rangle\langle l-1,\tfrac{1}{2}\mid 2\rangle\cdots\langle -l,\tfrac{1}{2}\mid 2l+1\rangle \\
&\quad\times\langle l,-\tfrac{1}{2}\mid 2l+2\rangle\langle l-1,-\tfrac{1}{2}\mid 2l+3\rangle\cdots \\
&\quad\times\langle l-t+1,-\tfrac{1}{2}\mid 2l+1+t\rangle], \qquad \text{(C4)}
\end{aligned}
$$

where

$$t=n-(2l+1)$$

and

$$\langle m,\alpha\mid p\rangle=Y_{lm}(p)\chi_a(p).$$

For this case it is convenient to deal with the number of holes p defined by

$$p=4l+2-n=2l+1-t. \qquad \text{(C5)}$$

According to Hund's rule, the values of L and S are given by

$$L=nl-\tfrac{1}{2}n(n-1),$$

$$S=\tfrac{1}{2}n, \qquad \text{(C6)}$$

for $n\leq 2l+1$, and $L=pl-\tfrac{1}{2}p(p-1)$,

$$S=\tfrac{1}{2}p \qquad \text{(C7)}$$

for $n\geq 2l+1$.

In Eq. (11) appear the reduced matrix elements α_{20} and α_{21}. These are most easily obtained by setting $q=q'=0$ in (B1) and taking the expected value between $\phi_{LL;SS}$. We have

$$\alpha_{kk'}=\langle\Sigma T_{k0}(\mathbf{l}_i)T_{k'0}(\mathbf{s}_i)\rangle/\langle T_{k0}(\mathbf{L})T_{k'0}(\mathbf{S})\rangle. \qquad \text{(C8)}$$

Using (C2), (C3), and Table V, we obtain for $n<2l+1$

$$
\begin{aligned}
\langle\Sigma T_{20}(\mathbf{l}_i)\rangle&=\sum_{j=1}^{n}(l-j+1)^2-\tfrac{1}{3}nl(l+1) \\
&=\tfrac{1}{6}n(2l-n+1)(2l-2n+1), \qquad \text{(C9)}
\end{aligned}
$$

$$\langle\Sigma T_{20}(\mathbf{l}_i)T_{10}(\mathbf{s}_i)\rangle=\tfrac{1}{12}n(2l-n+1)(2l-2n+1), \qquad \text{(C10)}$$

and using (C6), we have

$$\langle T_{20}(\mathbf{L})\rangle=\tfrac{1}{3}L(2L-1)=\tfrac{1}{6}n(2l-n+1)(2nl-n^2+n-1), \qquad \text{(C11)}$$

$$\langle T_{20}(\mathbf{L})T_{10}(\mathbf{S})\rangle=\tfrac{1}{12}n^2(2l-n+1)(2nl-n^2+n-1). \qquad \text{(C12)}$$

Substituting (C9) and (C11) into (C8), we have

$$\alpha_{20}=(2l-2n+1)/(2nl-n^2+n-1), \qquad \text{(C13)}$$

and substituting (C10) and (C12) into (C8), we obtain

$$\alpha_{21}=(2l-2n+1)/[n(2nl-n^2+n-1)] \qquad \text{(C14)}$$

for $n<2l+1$.

For a greater than half-filled shell, we use (C4), and we have

$$
\begin{aligned}
\langle\Sigma T_{20}(\mathbf{l}_i)\rangle&=4\sum_{j=1}^{l}j^2-\sum_{j=1}^{p}(l-j+1)^2-\tfrac{1}{3}nl(l+1) \\
&=-\sum_{j=1}^{p}(l-j+1)^2+\tfrac{1}{3}pl(l+1) \\
&=-\tfrac{1}{6}p(2l-p+1)(2l-2p+1), \qquad \text{(C15)}
\end{aligned}
$$

$$
\begin{aligned}
\langle\Sigma T_{20}(\mathbf{l}_i)T_{10}(\mathbf{s}_i)\rangle&=\tfrac{1}{2}\sum_{j=1}^{p}(l-j+1)^2-\tfrac{1}{6}pl(l+1) \\
&=\tfrac{1}{12}p(2l-p+1)(2l-2p+1), \qquad \text{(C16)}
\end{aligned}
$$

and using (C7), we have

$$\langle T_{20}(\mathbf{L})\rangle=\tfrac{1}{6}p(2l-p+1)(2pl-p^2+p-1), \qquad \text{(C17)}$$

$$\langle T_{20}(\mathbf{L})T_{10}(\mathbf{S})\rangle=\tfrac{1}{12}p^2(2l-p+1)(2pl-p^2+p-1). \qquad \text{(C18)}$$

TABLE VI. Eigenvalues and reduced matrix elements for rare earths.

Rare earth	L	S	J	α_{20}	α_{21}	β_1	β_2	β_3	γ_1
Ce	3	1/2	5/2	1	1	8/7	9/7	10/7	−1/7
Pr	5	2/2	4	1/3	1/6	6/5	78/55	91/55	−1/5
Nd	6	3/2	9/2	1/11	1/33	14/11	35/22	280/143	−3/11
Pm	6	4/2	4	−1/11	−1/44	7/5	21/11	28/11	−2/5
Sm	5	5/2	5/2	−1/3	−1/15	12/7	39/14	13/3	−5/7
Eu	3	6/2	0	−1	−1/6	0	0	0	0
Gd	0	7/2	7/2	0	0	0	0	0	1
Tb	3	6/2	6	1	−1/6	1/2	5/22	1/11	1/2
Dy	5	5/2	15/2	1/3	−1/15	2/3	3/7	24/91	1/3
Ho	6	4/2	8	1/11	−1/44	3/4	11/20	11/28	1/4
Er	6	3/2	15/2	−1/11	1/33	4/5	22/35	44/91	1/5
Tm	5	2/2	6	−1/3	1/6	5/6	15/22	6/11	1/6
Yb	3	1/2	7/2	−1	1	6/7	5/7	4/7	1/7

Substituting (C15) and (C17) into (C8), we obtain

$$\alpha_{20}=-(2l-2p+1)/(2pl-p^2+p-1), \tag{C19}$$

and substituting (C16) and (C18) into (C8), we have

$$\alpha_{21}=(2l-2p+1)/[p(2pl-p^2+p-1)]. \tag{C20}$$

The values of α_{20} and α_{21} for each rare earth ($l=3$) are tabulated from Eqs. (C13), (C14), (C19), and (C20) in Table VI.

B. Evaluation of β_k and γ_k

We observe that the reduced matrix elements β_k and γ_k [defined in (B2) and (B3)] may be obtained from each other by simply interchanging **L** and **S**, so that it is sufficient to evaluate only one of them. Let us consider β_k.

From Eq. (B2) two expressions for β_k may be obtained. The first, which is valid for all values of J from $L+S$ to $L-S$, is obtained by multiplying both sides by $\mathcal{Y}_{kq}{}^\dagger(\mathbf{J})$, summing over q, and taking the expected value between $|J, M\rangle$. One obtains

$$\beta_k=\frac{\langle JM\,|\,C_k(\mathbf{J},\mathbf{L})\,|\,JM\rangle}{\langle JM\,|\,C_k(\mathbf{J},\mathbf{J})\,|\,JM\rangle}=\frac{\langle C_k(\mathbf{J},\mathbf{L})\rangle_M}{\langle C_k(\mathbf{J},\mathbf{J})\rangle_M}, \tag{C21}$$

where

$$\begin{aligned}C_k(\mathbf{J},\mathbf{L})&=\sum_q \mathcal{Y}_{kq}{}^\dagger(\mathbf{J})\mathcal{Y}_{kq}(\mathbf{L})\\&=\sum_q(-)^q\mathcal{Y}_{k,-q}(\mathbf{J})\mathcal{Y}_{kq}(\mathbf{L})\end{aligned} \tag{C22}$$

is the contraction. The second expression, which is valid for $J=L+S$ only, follows from the fact that for this case $|J, J\rangle$ is given by $|J, J\rangle=|L, L\rangle\,|S, S\rangle$. Setting $q=0$ in (B2) and taking the expected value between $|J, J\rangle$, one has

$$\beta_k=\langle L, L\,|\,\mathcal{Y}_{k0}(\mathbf{L})\,|\,L, L\rangle/\langle J, J\,|\,\mathcal{Y}_{k0}(\mathbf{J})\,|\,J, J\rangle, \tag{C23}$$

$(J=L+S)$.

To utilize (C21) and (C23), general expressions for the irreducible tensors are needed. Two such expressions may be obtained by using the definitions given by Racah.[16]

$$[J^-, \mathcal{Y}_{kq}(\mathbf{J})]=[k(k+1)-q(q-1)]^{1/2}\mathcal{Y}_{k,q-1}(\mathbf{J}), \tag{C24}$$

$$[J^+, \mathcal{Y}_{kq}(\mathbf{J})]=[k(k+1)-q(q+1)]^{1/2}\mathcal{Y}_{k,q+1}(\mathbf{J}), \tag{C25}$$

$$[J^z, \mathcal{Y}_{kq}(\mathbf{J})]=q\mathcal{Y}_{kq}(\mathbf{J}), \tag{C26}$$

and the fact that for $q=\pm k$ these tensors are given by

$$\mathcal{Y}_{kk}(\mathbf{J})=(-2^{-1/2}J^+)^k, \tag{C27}$$

$$\mathcal{Y}_{k,-k}(\mathbf{J})=(2^{-1/2}J^-)^k. \tag{C28}$$

By repeated applications of (C24) and (C25) to (C27) and (C28), respectively, one can verify

$$\mathcal{Y}_{k,k-n}(\mathbf{J})=[2^kn!F(k;n)]^{-1/2}\times\sum_{p=0}^{n}\frac{(-)^{p+k}n!}{p!(n-p)!}(J^-)^{n-p}(J^+)^k(J^-)^p, \tag{C29}$$

and

$$\mathcal{Y}_{k,n-k}(\mathbf{J})=[2^kn!F(k;n)]^{-1/2}\times\sum_{p=0}^{n}\frac{(-)^{p}n!}{p!(n-p)!}(J^+)^{n-p}(J^-)^k(J^+)^p, \tag{C30}$$

where $F(k; n)$ is defined by

$$F(k;n)=\prod_{p=0}^{n}f(k;p), \tag{C31}$$

$$\begin{aligned}&f(k;0)=1,\\&f(k;p)=2k+1-p\qquad(p>0).\end{aligned} \tag{C32}$$

Setting $n=k$ in (C30), we have

$$\langle J, J\,|\,\mathcal{Y}_{k0}(\mathbf{J})\,|\,J, J\rangle=\langle\mathcal{Y}_{k0}(\mathbf{J})\rangle_J=[2^kk!F(k;k)]^{-1/2}\times\sum_{p=0}^{k}\frac{(-)^pk!}{p!(k-p)!}\langle(J^+)^{k-p}(J^-)^k(J^+)^p\rangle_J.$$

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[16] G. Racah, Phys. Rev. 61, 186 (1942); 62, 438 (1942); 63, 367 (1943).

The only term which contributes is the one for which $p=0$.

$$\langle \mathcal{Y}_{k0}(\mathbf{J})\rangle_J=[2^k k!F(k;k)]^{-1/2}\langle (J^+)^k(J^-)^k\rangle_J$$

$$=[2^k k!F(k;k)]^{-1/2}k!F(J;k). \qquad \text{(C33)}$$

Substituting (C33) into (C23), we obtain

$$\beta_k=F(L;k)/F(J;k) \qquad \text{(C34)}$$

for $J=L+S$.

To evaluate β_k for $J=|L-S|$ we first consider the denominator of (C21). Since $C_k(\mathbf{J},\mathbf{J})$ is invariant, $\langle C_k(\mathbf{J},\mathbf{J})\rangle_M$ is independent of M, and we set $M=J$. Using (C29) and (C30), we have

$$\langle C_k(\mathbf{J},\mathbf{J})\rangle_J=\sum_{n=0}^{2k}(-)^{k-n}\langle \mathcal{Y}_{k,k-n}(\mathbf{J})\mathcal{Y}_{k,n-k}(\mathbf{J})\rangle_J$$

$$=\sum_{n=0}^{2k}\frac{(-)^{k-n}}{2^k n!F(k;n)}\sum_{p=0}^{n}\sum_{r=0}^{n}\frac{(-)^{p+k+r}(n!)^2}{p!r!(n-p)!(n-r)!}$$
$$\times\langle (J^-)^{n-p}(J^+)^k(J^-)^p(J^+)^{n-r}(J^-)^k(J^+)^r\rangle_J.$$

The only terms which contribute are those satisfying $r=0$, $p=n$, and $0\leq n\leq k$. Thus

$$\langle C_k(\mathbf{J},\mathbf{J})\rangle_J=\sum_{n=0}^{k}\frac{\langle (J^+)^k(J^-)^n(J^+)^n(J^-)^k\rangle_J}{2^k n!F(k;n)}$$

$$=k!F(J;k)H(J;k), \qquad \text{(C35)}$$

where

$$H(J;k)=\sum_{n=0}^{k}\frac{\langle (J^-)^n(J^+)^n\rangle_{J-k}}{2^k n!F(k;n)}.$$

Since $C_k(\mathbf{J},\mathbf{J})$ is invariant, it must be of the form

$$C_k(\mathbf{J},\mathbf{J})=\sum_{n=0}^{k}a_n(\mathbf{J}\cdot\mathbf{J})^n,$$

from which follows

$$\langle C_k(\mathbf{J},\mathbf{J})\rangle=\sum_{n=0}^{k}a_n[J(J+1)]^n,$$

and since $\langle C_k(\mathbf{J},\mathbf{J})\rangle$ is a polynomial of degree k, it can be factored into the form

$$\langle C_k(\mathbf{J},\mathbf{J})\rangle=\prod_{n=1}^{k}[b_nJ(J+1)+c_n]$$

$$=\prod_{n=1}^{k}[(b_n/4)(2J+1+d_n)(2J+1-d_n)], \qquad \text{(C36)}$$

where

$$d_n=[1-(4c_n/b_n)]^{1/2}.$$

From (C36) we see that the factors of $\langle C_k(\mathbf{J},\mathbf{J})\rangle$ occur in pairs, and since one member of each pair is contained in $F(J;k)$ in (C35), $H(J;k)$ must be of the form

$$H(J;k)=\xi_kG(J;k),$$

where

$$G(J;k)=\prod_{p=0}^{k}g(J;p),$$
$$g(J;0)=1,$$
$$g(J;p)=2J+1+p \qquad (p>0),$$

and where ξ_k is independent of J. Thus, we obtain

$$\langle C_k(\mathbf{J},\mathbf{J})\rangle=k!\xi_kF(J;k)G(J;k). \qquad \text{(C37)}$$

Substituting (C37) into (C21) and using (C34), we have

$$\langle C_k(\mathbf{J},\mathbf{L})\rangle=k!\xi_kF(L;k)G(J;k) \qquad \text{(C38)}$$

for $J=L+S$.

Since the relation

$$\langle C_k(\mathbf{J},\mathbf{L})\rangle_M=\beta_k\langle C_k(\mathbf{J},\mathbf{J})\rangle_M=\langle C_k(\mathbf{L},\mathbf{J})\rangle_M$$

is valid for all values of M, $C_k(\mathbf{J},\mathbf{L})$ is symmetric in $\mathbf{J}$ and $\mathbf{L}$. Furthermore, since $C_k(\mathbf{J},\mathbf{L})$ is invariant, it must consist solely of the invariant operators $(\mathbf{J}\cdot\mathbf{J})$, $(\mathbf{L}\cdot\mathbf{L})$, and $(\mathbf{J}\cdot\mathbf{L})$. For the three cases $J=L+S$, $L-S$, and $S-L$, $\langle\mathbf{J}\cdot\mathbf{L}\rangle$ has the values of $L(J+1)$, $J(L+1)$, and $-JL$, respectively. (Of course, $\langle\mathbf{J}\cdot\mathbf{J}\rangle$ and $\langle\mathbf{L}\cdot\mathbf{L}\rangle$ are the same in each case.)

From (C38) we obtain $\langle C_k(\mathbf{J},\mathbf{L})\rangle$ for $J=L-S$ and $S-L$ by constructing transformations under which the symmetry of $\langle\mathbf{J}\cdot\mathbf{J}\rangle$ and $\langle\mathbf{L}\cdot\mathbf{L}\rangle$ is maintained and under which

$$L(J+1)\rightarrow J(L+1),$$
$$L(J+1)\rightarrow -JL,$$

respectively. The transformations are

$$J\rightarrow L, \qquad L\rightarrow J \qquad \text{(C39)}$$

and

$$J\rightarrow -(L+1), \qquad L\rightarrow J, \qquad \text{(C40)}$$

respectively. Using (C38), (C39), and (C40), we have

$$\langle C_k(\mathbf{J},\mathbf{L})\rangle=k!\xi_kF(J;k)G(L;k) \qquad \text{(C41)}$$

for $J=L-S$ and

$$\langle C_k(\mathbf{J},\mathbf{L})\rangle=k!\xi_kF(J;k)G(-L-1;k) \qquad \text{(C42)}$$

for $J=S-L$. Substituting (C37), (C41), and (C42) into (C21), we obtain

$$\beta_k=[G(L;k)/G(J;k)] \qquad \text{(C43)}$$

for $J=L-S$ and

$$\beta_k=[G(-L-1;k)/G(J;k)] \qquad \text{(C44)}$$

for $J=S-L$.

To obtain γ_k one need only interchange $\mathbf{L}$ and $\mathbf{S}$ in (C34), (C43), and (C44). The values of γ_1 and $\beta_k(k=1, 2, 3)$ for each of the rare earths are tabulated in Table VI.