Rare-Earth-Iron Exchange Interaction in the Garnets. I. Hamiltonian for Anisotropic Exchange Interaction*†

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The salient feature of the splittings of the crystalline levels of a rare-earth ion in the iron garnets is the difference of their anisotropy from that of the g tensor for the Zeeman effect. This additional anisotropy arises from the dependence of the rare-earth-iron (RE-Fe) exchange interaction on the orbital state of the rare earth. On the assumption that the spin dependence of the RE-Fe exchange interaction is reasonably well described by the Dirac-Van Vleck effective spin Hamiltonian, we find that the Hamiltonian for this interaction is

$$\mathcal{H}_{ex} = -2 \sum_{r=1}^{2l+1} \sum_{mm'} \tilde{\beta}_r(m,m') \tilde{J}_m^{[r]}(\mathrm{RE}) S_{m'}^{[1]}(\mathrm{Fe}),$$

where the sum is over odd r and $\tilde{J}_m^{[r]}$ (RE) are the components of either the spin or the total angular momentum of the rare-earth ion, and S (Fe) is the spin of the iron sublattice. The constants $\tilde{\beta}_r$ are different for each rare-earth element; however, they do contain a set of constants, the exchange-potential parameters α_{kq} (of which there are at most *ten*), which characterize the RE-Fe exchange interaction for all rare-earth elements $(4f^n)$ in the iron garnets. The relationship of these parameters to the exchange splittings of a Kramers' doublet is established, from which an empirical determination of the parameters will be possible when sufficient data are available. The determination of the parameters for specific models will be presented in a subsequent article.

I. INTRODUCTION

IN the iron garnets $5Fe_2O_3 \cdot 3R_2O_3$, the rare-earth ion (R^{3+}) is surrounded by a cluster of oxygen (O⁻⁻) and ferric (Fe^{3+}) ions. The effect of the oxygen ions on the rare earth may be replaced by a crystalline potential; the ferric ions, which are strongly coupled by a ferrimagnetic exchange interaction, form a sublattice. It is reasonable to assume that the rare-earth-iron (RE-Fe) exchange interaction does not affect the spin of the iron sublattice.[1] This interaction may therefore be treated in the molecular field approximation, and we can think of an "exchange field" due to the resultant spin of the ferrimagnetically coupled ferric ions acting on the *spin* of the rare earth. The interaction between rare-earth ions is weak in comparison to the RE-Fe and Fe-Fe interactions, and thus may be neglected.

From the g-tensor values for the Zeeman effect one can calculate the splittings of a crystalline energy level by an exchange field. For an isotropic exchange field, the splittings exhibit the same symmetry as for the Zeeman effect. However, from the recent spectroscopic studies of Wickersheim and White[2-5] on the lowest doublets of the $^2F_{5/2}$ and $^2F_{7/2}$ states of Yb^{3+}, we see

that (1) the anisotropy in the exchange splittings in YbIG exceeds that due to the anisotropy of the g tensor for the Zeeman effect, as inferred from Yb^{3+} in YbGaG, and (2) for the lowest doublet of the $^2F_{5/2}$ state, the ordering of the principal values of the exchange tensor differs from that of the g tensor. Since the splittings of the $^2F_{5/2}$ and $^2F_{7/2}$ doublets produced by the exchange interaction have the same angular dependence as those produced by a magnetic field, the exchange field has a first-rank tensorial behavior, and therefore arises from S-state ions, i.e., the Fe^{3+} ions.

The g tensor for the Zeeman effect is a measure of the ease with which the magnetic electrons in a crystalline field may be reoriented by a magnetic field. An anisotropic g tensor thus infers that the magnitude of the reorientation of the orbital state of the magnetic ion depends on the direction of the magnetic field with respect to the g-tensor axes. The difference between the exchange splittings arrived at by assuming an isotropic exchange field and those observed is due to the effect of the *reorientation* on the *magnitude* of the exchange interaction. We are therefore led to the conclusion that the RE-Fe exchange interaction depends on the orbital state of the rare earth. This was anticipated by Wolf, who reasoned that the interaction should be anisotropic solely on the basis of the spiked nature of the rare earth's $4f$ orbital wave function.

We develop in this paper a Hamiltonian for the RE-Fe $(4f-3d^5)$ exchange interaction on the assumptions (1) that the spin dependence of the superexchange interaction between a rare-earth electron and the ferric ions is well described by the Dirac-Van Vleck effective spin Hamiltonian $s(4f) \cdot S(Fe)$, and (2) that the de-

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[1] W. P. Wolf and J. H. Van Vleck, Phys. Rev. **118**, 1490 (1960).

[2] K. A. Wickersheim, Phys. Rev. **122**, 1376 (1961).

[3] K. A. Wickersheim (private communication).

[4] K. A. Wickersheim and R. L. White, Phys. Rev. Letters **4**, 123 (1960).

[5] K. A. Wickersheim and R. L. White, Phys. Rev. Letters **8**, 483 (1962).

pendence of this interaction on the orbital state of the rare earth is accounted for by an exchange potential. This exchange potential is expanded in a set of irreducible tensors (similar to spherical harmonics). The orbital and spin variables of the rare earth are coupled together and the final Hamiltonian is expressed in terms of either the total angular momentum $\mathbf{J}(RE)$, or the spin $\mathbf{S}(RE)$. The extension to $4f^n$ electrons is made under the assumption that each electron experiences the same exchange potential.

In order to relate the empirical parameters in the exchange potential to the data on the above-mentioned splittings the Hamiltonian is evaluated in a Kramers' doublet. At the present time the six observed splittings[5] are insufficient to determine the ten parameters α_{kq}; thus, to determine the parameters relationships between them must be derived on the basis of models of the RE-Fe^{3+} exchange interaction. Specific models from which these relationships are derived will be discussed in a subsequent paper.

II. THE RARE-EARTH-IRON EXCHANGE INTER-ACTION FOR ONE $4f$ ELECTRON

The exchange between the $4f$ rare-earth electrons and the $3d$ iron electrons is probably not direct, but takes place by some indirect mechanism via the oxygen ions. The Dirac-Van Vleck vector model of the exchange energy of two electrons on different ions is valid for several types of superexchange, and its validity in the case of the RE-Fe^{3+} exchange mechanism forms the basic assumption in the following analysis.

The Dirac-Van Vleck vector model leads to an effective Hamiltonian of the form[6]

$$K_{ij} - \tfrac{1}{2}[1 + 4\mathbf{s}(i) \cdot \mathbf{s}(j)]J_{ij}, \qquad (2.1)$$

where K_{ij} = Coulomb integral and J_{ij} = exchange integral.

When this Hamiltonian is applied to the electron exchange interaction between two atoms, the dependence of the exchange integral on the orbital states of the electrons is commonly neglected. If one takes into account the orbital states, Van Vleck[7] has shown that, in general, the resulting exchange Hamiltonian will be anisotropic. The particular case of exchange between two S-state ions is, however, an exception to this rule.

For two S-state ions, the appropriate form of the spin-dependent part of the Hamiltonian (2.1) is[7]

$$V_{12} = A_{12}\mathbf{S}_1 \cdot \mathbf{S}_2, \qquad (2.2)$$

where

$$\mathbf{S}_1 = \sum_i \mathbf{s}_i, \quad \mathbf{S}_2 = \sum_j \mathbf{s}_j, \quad A_{12} = -\frac{2}{n_1 n_2} \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} J_{ij},$$

and n_i = number of electrons to a half-filled shell, which is just $2l_i + 1$.

When only one of the ions is in an S state the appropriate extension of Eq. (2.2) is

$$\mathfrak{K}_{ex} = -2\sum_{i=1}^{n} A_i' \mathbf{s}(i) \cdot \mathbf{S}, \qquad (2.3)$$

where

$$A_i' \equiv \frac{1}{2l+1} \sum_{j=1}^{2l+1} J_{ij},$$

and S = total spin of a *half-filled* shell. *The third bar on an equal sign denotes a definition.* Since the magnetic shell of the ferric ion is half-filled, this form of the Hamiltonian is applicable to the RE-Fe^{3+} exchange interaction and shows that no matter how complicated the precise form of the interaction, the spin of the ferric ion always enters linearly.

Van Vleck[7] displayed the anisotropic exchange interaction between an atom with a p electron and one with and S-state electron in terms of the total angular momentum $\mathbf{j}$ of the p electron and the spin $\mathbf{s}$ of the S-state electron. This section is an extension and generalization of this example for the anisotropic exchange interaction between *one* rare-earth $4f$ electron and the half-filled shells of a cluster of ferric ions.

A. Exchange Potential for Rare-Earth-Iron Cluster Interaction

The exchange interaction between the rare-earth $4f$ electron and either one ferric ion or the entire surrounding cluster has the form[8]

$$\mathfrak{K}_{ex} = -2A_i(l,m_l,m_l')_{op}\mathbf{s}(i) \cdot \mathbf{S}(Fe), \qquad (2.4)$$

where $A_i(l,m_l,m_l')_{op}$ will be called the "generalized exchange potential operator" because it describes the dependence of the exchange interaction on the orbital state of the rare earth. The angular dependence of the generalized exchange potential is expanded in a set of irreducible tensorial operators[9] $T_q^{[k]}(i)$ which act on the orbital part of the rare-earth wave function, and are defined by their matrix elements [see Eqs. (2.6) and (2.7)],

$$A_i(l,m_l,m_l')_{op} = \sum_{k=0}^{2l} \sum_{q=-k}^{k} \alpha_{kq}T_q^{[k]}(i), \qquad (2.5)$$

where k *is even* as shown in Appendix B, and the α_{kq}'s are parameters that can be *evaluated empirically*.[10] Tensors of rank $k > 2l$ need not be considered as they do not satisfy the triangular condition implied in the

[6] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (The Clarendon Press, Oxford, 1932).

[7] J. H. Van Vleck, Revista de Matemática y Física Teórica (Tucumán, Argentina, 1962), Vol. 14, p. 189.

[8] In the garnets the iron sublattice is ferrimagnetically coupled so that the spins of the ferric ions are either parallel or antiparallel to one another. Denoting the spin of the iron sublattice by $\mathbf{S}(Fe)$, the spin of each ion $\mathbf{S}$ may be written as $\mathbf{S} = \pm$constant $\mathbf{S}(Fe)$.

[9] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959).

[10] A theoretical determination of these parameters requires *additional assumptions* about the superexchange mechanism.

matrix elements of $T_q{}^{[k]}$ within an l manifold [see Eq. (2.6)].

From the Wigner-Eckart theorem[9] the matrix element of the generalized exchange potential, i.e., the generalized exchange constant, is

$$A_i(l,m_l,m_l') \equiv (lm_l | A_i(l,m_l,m_l')_{op} | lm_l')$$

$$= (-1)^{l-m_l} \sum_{\substack{k=0 \\ k \text{ even}}}^{2l} \sum_{q=-k}^{k} \alpha_{kq}(l\|\mathbf{T}^{[k]}\|l)$$

$$\times \bar{V}(llk; -m_l m_l' q). \quad (2.6)$$

The Fano and Racah $\bar{V}$ symbol is the same as Wigner's $3\text{-}j$ coefficient except for a phase factor. For convenience in later applications the $T_q{}^{[k]}$ are defined by setting

$$(l\|\mathbf{T}^{[k]}\|l) \equiv 1 \quad l \neq 0. \quad (2.7)$$

This definition is arbitrary only to the extent that defining the reduced matrix element as being real does not alter the intrinsic time-reversal symmetry of the Hamiltonian Eq. (2.4). This point will be discussed in Appendix B.

The largest possible number of different exchange constants, $A(l,m_l,m_l')$, is $(2l+1)(l+1)$; the number of adjustable parameters α_{kq} equals the number of exchange constants (2.6). The expansion is therefore consistent and unique, and thus can be inverted to find the parameters α_{kq} in terms of the matrix elements; the result is

$$\alpha_{kq} = (2k+1) \sum_{m_l=-l}^{l} (-1)^{l-m_l} A(l,m_l,q)$$

$$\times \bar{V}(llk; -m_l, m_l-q, q), \quad (2.8)$$

where $q \equiv m_l - m_l'$ and condition (2.7) has been used. The sum[11]

$$\sum_{m_l} \sum_{m_l'} \bar{V}(llk; -m_l m_l' q) \bar{V}(llk'; -m_l m_l' q')$$

$$= \frac{\delta_{kk'} \delta_{qq'} \delta(l,l,k)}{(2k+1)}, \quad (2.9)$$

where $\delta(l,l,k)$ is zero unless k is an integer and $0 \leqslant k \leqslant 2l$, was used to derive (2.8) and expresses the orthogonality of the operators used as the basis of the expansion (2.5). The advantage of using irreducible tensor operators in defining the exchange potential is apparent; they simplify the transformation (2.8) as the $T_q{}^{[k]}$'s are a complete set of orthogonal operators [rather,

$$(lm_l | T_q{}^{[k]} | lm_l') = (-1)^{l-m_l} \bar{V}(llk; -m_l m_l' q)$$

is the orthogonal set]. If nonorthogonal operators were used to find the parameters the solution would lead to a set of m simultaneous equations, where m is equal to the number of the independent parameters.

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[11] See Ref. 9, p. 51, Eq. (10.17).

B. The Hamiltonian for the Exchange Interaction

With the Hamiltonian (2.4) and the exchange potential operator (2.5), one finds

$$\mathcal{H}_{ex} = -2 \sum_{k=0}^{2l} \sum_{q=-k}^{k} \alpha_{kq} T_q{}^{[k]}(i) \mathbf{s}(i) \cdot \mathbf{S}(Fe). \quad (2.10)$$

To find the matrix elements of this Hamiltonian in a coupled representation of the rare earth, i.e., $|jm_j\rangle$, one can either uncouple the rare-earth wave functions into their orbital and spin states,[12] or couple the operators $T_q{}^{[k]}(i)\mathbf{s}(i)$ and express the irreducible products as operator equivalents $J_m{}^{[p]}$ which act on total angular-momentum wave functions. The first approach, although feasible for electrons with low orbital quantum numbers, i.e., for $l=s$ or p, becomes too unwieldy for a $4f^n$ configuration; the second approach has therefore been adopted.

The transformation of the Hamiltonian (2.10) to the coupled form (2.20) is readily accomplished by using Racah's algebra, and it may be divided into three steps:

(1) The direct products in Eq. (2.10) are coupled into irreducible products. By definition of an irreducible product[13]

$$a_{m_1}{}^{[j_1]} b_{m_2}{}^{[j_2]} = \sum_{jm} (m_1 m_2 | jm)[\mathbf{A}^{[j_1]} \times \mathbf{B}^{[j_2]}]_m{}^{[j]}, \quad (2.11)$$

where

$$(jm | m_1 m_2) = (m_1 m_2 | jm) \equiv (j_1 m_1, j_2 m_2 | j_1 j_2, jm)$$

is a Clebsch-Gordan coefficient and $a_{m_1}{}^{[j_1]}$, $b_{m_2}{}^{[j_2]}$ are the components of the tensorial sets $\mathbf{A}^{[j_1]}$, $\mathbf{B}^{[j_2]}$.

With the components of the first-rank tensorial set defined by Fano and Racah,[14] i.e.,

$$S_1{}^{[1]} = (-iS_x + S_y)/\sqrt{2}, \quad S_0{}^{[1]} = iS_z,$$

$$S_{-1}{}^{[1]} = (iS_x + S_y)/\sqrt{2}, \quad (2.12)$$

one finds that

$$T_q{}^{[k]}(i)\mathbf{s}(i) \cdot \mathbf{S}(Fe)$$

$$= \sqrt{3}[\mathbf{T}^{[k]}(i) \times [\mathbf{S}^{[1]}(i) \times \mathbf{S}^{[1]}(Fe)]^{[0]}]_q{}^{[k]}. \quad (2.13)$$

(2) The operators acting on the rare-earth electron may be written in terms of the total angular momentum or spin by recoupling the irreducible products, as (2.13), so that operators referring to the rare-earth electron are together. The triple product of irreducible tensors

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[12] Wickersheim and White (see Ref. 5) have chosen to uncouple the rare-earth's wave functions $^2F_{5/2}$ and $^2F_{7/2}$. The relationship between their notation and that adopted here is

$$\alpha_{00} = -(\tfrac{1}{3}7^{1/2})g\beta H_e,$$
$$\alpha_{20} = -3(3 \times 5 \times 7)^{1/2} g\beta H_e G_2{}^0,$$
$$\alpha_{22} = -3(2 \times 5 \times 7)^{1/2} g\beta H_e G_2{}^2.$$

[13] See Ref. 9, p. 36, Eq. (7.10).
[14] See Ref. 9, p. 24, Eq. (5.15).

is recoupled with the aid of the Racah coefficient,[15] i.e.,

$$[[\mathbf{A}^{[j_1]} \times \mathbf{B}^{[j_2]}]^{[j_{12}]} \times \mathbf{C}^{[j_3]}]_m{}^{[j]}$$

$$= \sum_{j_{23}} (-)^{j_1+j_2+j_3+j}[(2j_{12}+1)(2j_{23}+1)]^{1/2}$$

$$\times \bar{W}(j_1 j_2 j_{12}/j_3 j j_{23})$$

$$\times [\mathbf{A}^{[j_1]} \times [\mathbf{B}^{[j_2]} \times \mathbf{C}^{[j_3]}]^{[j_{23}]}]_m{}^{[j]}. \quad (2.14)$$

The Racah coefficient with one zero element is

$$\bar{W}(j_1 j_2 j_{12}/j_3 k 0) = \frac{(-1)^{j_1+j_2+j_{12}} \delta_{j_1 k} \delta_{j_2 j_3}}{[(2k+1)(2j_2+1)]^{1/2}}$$

$$\times \delta(j_1, j_2, j_{12}), \quad (2.15)$$

where $\delta(j_1, j_2, j_{12}) = 1$ if the following conditions are satisfied:

$$j_1 + j_2 + j_{12} = \text{integer},$$
$$j_1 + j_2 \geqslant j_{12} \geqslant |j_1 - j_2|; \quad (2.16)$$

if these conditions are not satisfied

$$\delta(j_1, j_2, j_{12}) = 0.$$

The inequality in Eq. (2.16) is known as the triangular condition. By using the Racah coefficient (2.15) ($j_1 = k$, $j_2 = j_3 = 1$, $j_{12} = p$) in Eq. (2.14), one finds

$$T_q{}^{[k]}(i)\mathbf{s}(i)\cdot\mathbf{S}(\text{Fe}) = (-1)^{k+1}\sum_{p=|k-1|}^{k+1}(-1)^p\left[\frac{2p+1}{2k+1}\right]^{1/2}$$

$$\times [[\mathbf{T}^{[k]}(i) \times \mathbf{S}^{[1]}(i)]^{[p]} \times \mathbf{S}^{[1]}(\text{Fe})]_q{}^{[k]}. \quad (2.17)$$

(3) With the aid of the Wigner-Eckart theorem, one finds

$$[\mathbf{T}^{[k]}(i) \times \mathbf{S}^{[1]}(i)]_m{}^{[p]}$$

$$\doteq \frac{(j\|[\mathbf{T}^{[k]} \times \mathbf{S}^{[1]}]^{[p]}\|j')}{(j\|\tilde{\mathbf{J}}^{[p]}\|j')}\tilde{J}_m{}^{[p]}, \quad (2.18)$$

where

$$\tilde{J}_m{}^{[p]} \equiv J_m{}^{[p]} \quad \text{for} \quad j = j',$$
$$\equiv S_m{}^{[p]} \quad \text{for} \quad j \neq j',$$

and $J_m{}^{[p]}$ and $S_m{}^{[p]}$ are irreducible tensorial operators defined by the reduced matrix elements (2.24), (2.25). *The dot over the equal sign signifies that the equality is restricted to states within j and j'.*

Placing the operator equivalents (2.18) in Eq. (2.17) and forming the irreducible product of $\tilde{J}_m{}^{[p]}$ and $S_{m'}{}^{[1]}$,

one finds

$$T_q{}^{[k]}(i)\mathbf{s}(i)\cdot\mathbf{S}(\text{Fe})$$

$$\doteq (-1)^{k+1}\sum_{p=|k-1|}^{k+1}(-1)^p\left[\frac{2p+1}{2k+1}\right]^{1/2}$$

$$\times \frac{(j\|[\mathbf{T}^{[k]} \times \mathbf{S}^{[1]}]^{[p]}\|j')}{(j\|\tilde{\mathbf{J}}^{[p]}\|j')}$$

$$\times [\tilde{\mathbf{J}}^{[p]}(i) \times \mathbf{S}^{[1]}(\text{Fe})]_q{}^{[k]}. \quad (2.19)$$

Using this result in the exchange Hamiltonian (2.10) one finds

$$\mathcal{H}_{\text{ex}} \doteq 2\sum_{k=0}^{2l}\sum_{q=-k}^{k}\sum_{p=|k-1|}^{k+1}\gamma_{kqr}$$

$$\times [\tilde{\mathbf{J}}^{[p]}(i) \times \mathbf{S}^{[1]}(\text{Fe})]_q{}^{[k]}, \quad (2.20)$$

where

$$\gamma_{kqr} \equiv (-1)^{p+k}\alpha_{kq}\left[\frac{2p+1}{2k+1}\right]^{1/2}\frac{(j\|[\mathbf{T}^{[k]} \times \mathbf{S}^{[1]}]^{[p]}\|j')}{(j\|\tilde{\mathbf{J}}^{[p]}\|j')}.$$

The reduced matrix element of the irreducible product (2.18) is [16]

$$(ls_i j\|[\mathbf{T}^{[k]}(i) \times \mathbf{S}^{[1]}(i)]^{[p]}\|ls_i j')$$

$$= [(2j+1)(2j'+1)(2p+1)]^{1/2}$$

$$\times (s_i\|\mathbf{S}^{[1]}\|s_i)X(llk/s_i s_i 1/jj'p), \quad (2.21)$$

where $(l\|\mathbf{T}^{[k]}\|l) = 1$, and $X(llk/s_i s_i 1/jj'p)$ is a 9-j symbol.[17] The index i is retained on the s so as not to confuse the spin of the rare-earth electron with that of the ferric ion or iron sublattice. The off-diagonal element of the reduced matrix of $\tilde{\mathbf{J}}^{[p]}$, i.e., of $\mathbf{S}^{[p]}$ is[18]

$$(ls_i j\|\mathbf{J}^{[p]}\|ls_i j')$$

$$= (-1)^{l+s_1+j+p}[(2j+1)(2j'+1)]^{1/2}$$

$$\times (s_i\|\mathbf{S}^{[p]}\|s_i)\bar{W}(jj'p/s_i s_i l), \quad (2.22a)$$

where as the diagonal element of the reduced matrix of $\tilde{J}^{[p]}$ is

$$(ls_i j\|\tilde{\mathbf{J}}^{[p]}\|ls_i j) = (j\|\mathbf{J}^{[p]}\|j). \quad (2.22b)$$

The reduced matrix elements of the a pth-rank irreducible tensorial operator for angular momentum may be derived by repeatedly applying the relation for tensorial operators which act on the *same* system[19]

$$(j\|[\mathbf{A}^{[k_1]} \times \mathbf{B}^{[k_2]}]^{[k]}\|j')$$

$$= (-)^{j+j'+k}[2k+1]^{1/2}\sum_{j''}(j\|\mathbf{A}^{[k_1]}\|j'')$$

$$\times (j''\|\mathbf{B}^{[k_2]}\|j)\bar{W}(jj'k/k_2 k_1 j'') \quad (2.23)$$

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[15] The recoupling of irreducible tensors is independent of the component of the product and depends only on its rank j; the component m has been added for completeness.

[16] See Ref. 9, p. 84, Eq. (15.4).
[17] See Ref. 9, Sec. 12.
[18] See Ref. 9, p. 85, Eq. (15.7').
[19] See Ref. 9, p. 86, Eq. (15.15).

to the expressions

$$(j\|\mathbf{J}^{[0]}\|j')=[(2j+1)/3]^{1/2}j(j+1)\delta_{jj'},$$

$$(j\|\mathbf{J}^{[1]}\|j')=i[j(j+1)(2j+1)]^{1/2}\delta_{jj'},$$

$$(j\|\mathbf{J}^{[2]}\|j') \tag{2.24}$$

$$=-\left[\frac{(2j+3)(2j+2)(2j+1)2j(2j-1)}{24}\right]^{1/2}$$

$$\times\delta_{jj'}.$$

For $p=2n=$ even, $(p\geqslant 4)$, one finds

$$(j\|\mathbf{J}^{[2n]}\|j')=(-1)^{2j(n-1)}$$

$$\times(j\|\mathbf{J}^{[2]}\|j)^{n}\prod_{\epsilon=0}^{n-2}(4n-4\epsilon+1)^{1/2}$$

$$\times\bar{W}(j,j,2(n-\epsilon)/2,2(n-\epsilon-1),j)\delta_{jj'}, \tag{2.25a}$$

and for odd p, $(p\geqslant 3)$, the result is

$$(j\|\mathbf{J}^{[p]}\|j')=i\left[\frac{p(2j+p+1)(2j-p+1)}{4(2p-1)}\right]^{1/2}$$

$$\times(j\|\mathbf{J}^{[p-1]}\|j)\delta_{jj'}. \tag{2.25b}$$

The irreducible products in the Hamiltonian (2.20) can be written explicitly in terms of the conventional angular momentum operators, i.e., J_x, J_y, J_z and S_x, S_y, S_z, but this course will not been followed here, as the Hamiltonian that results would be unwieldy.

When evaluating the matrix elements of the Hamiltonian (2.20) with wave functions of the rare-earth ion, it is necessary to uncouple the irreducible products $[\mathbf{J}^{[p]}\times\mathbf{S}^{[1]}]_q^{[k]}$. From the definition of an irreducible product (2.11) one can rewrite the exchange Hamiltonian (2.20) as

$$\mathfrak{IC}_{\mathrm{ex}}\doteq 2\sum_{r=0}^{2l+1}\sum_{mm'}\tilde{\beta}_r(mm')\tilde{J}_m{}^{[r]}(\mathrm{RE})S_{m'}{}^{[1]}(\mathrm{Fe}), \tag{2.26}$$

where

$$\tilde{\beta}_r(mm')\equiv\frac{(-1)^r(2r+1)^{1/2}}{(j\|\tilde{\mathbf{J}}^{[r]}\|j')}$$

$$\times\sum_{k=|r-1|}^{r+1}(j\|[\mathbf{T}^{[k]}\times\mathbf{S}^{[1]}]^{[r]}\|j')$$

$$\times\sum_{q=-k}^{k}(-1)^q\,\alpha_{kq}\bar{V}(r1k\,;mm'-q). \tag{2.27}$$

The reduced matrix elements in the coefficient (2.27) are given by Eqs. (2.21) and (2.22).

To summarize, the transformation of the Hamiltonian (2.10) to the coupled form (2.20) may be divided into three steps:

(1) The components in the Hamiltonian (2.10) are coupled into irreducible products (2.13).

(2) These products are recoupled (2.17), so that the operators that act on the same electron are coupled together.

(3) The portion of the irreducible product that refers to the rare-earth electron (2.18) is expressed in terms of an operator equivalent $\tilde{J}_m{}^{[p]}(\mathrm{RE})$.

III. THE N-ELECTRON HAMILTONIAN FOR THE RARE-EARTH-ION EXCHANGE INTERACTION

The one-electron Hamiltonian (2.4) will now be used to derive the rare-earth-iron exchange Hamiltonian for *n equivalent* electrons. In this derivation the one-electron approximation is made, i.e., each equivalent electron is assumed to experience the same exchange potential. The population of the orbital and spin states available to the n equivalent electrons is governed by the requirement that the wave functions satisfy Pauli's exclusion principle.

A. The Derivation of the n-Electron Hamiltonian

The n-electron Hamiltonian for rare-earth-iron exchange interactions is the sum of one-electron Hamiltonians (2.4, 2.5). If one makes the one-electron approximation, the exchange-potential parameters α_{kq} are assumed independent of the particular electron referred to, and the n-electron Hamiltonian may be written as

$$\mathfrak{IC}_{\mathrm{ex}}=-2\sum_{k=0}^{2l}\sum_{q=-k}^{k}\alpha_{kq}\sum_{i=1}^{n}T_q{}^{[k]}(i)\mathbf{s}(i)\cdot\mathbf{S}(\mathrm{Fe}), \tag{3.1}$$

where $\mathbf{S}(\mathrm{Fe})$ refers to one ferric ion or a cluster of ferric ions.

With the same procedure as in Sec. II B, one finds

$$\mathfrak{IC}_{\mathrm{ex}}\doteq 2\sum_{k=0}^{2l}\sum_{q=-k}^{k}\sum_{r=|k-1|}^{k+1}\gamma_{kqr}[\tilde{\mathbf{J}}^{[r]}(i)\times\mathbf{S}^{[1]}(\mathrm{Fe})]_q{}^{[k]}, \tag{3.2}$$

where *now*

$$\gamma_{kqr}\equiv(-1)^{r+k}\alpha_{kq}\left[\frac{2r+1}{2k+1}\right]^{1/2}$$

$$\frac{(J\|\sum_{i=1}^{n}[\mathbf{T}^{[k]}(i)\times\mathbf{S}^{[1]}(i)]^{[r]}\|J')}{\times\frac{}{(J\|\tilde{\mathbf{J}}^{[r]}\|J')}}.$$

and

$$\mathfrak{IC}_{\mathrm{ex}}\doteq 2\sum_{r=0}^{2l+1}\sum_{mm'}\tilde{\beta}_r(mm')\tilde{J}_m{}^{[r]}(\mathrm{RE})S_{m'}{}^{[1]}(\mathrm{Fe}), \tag{3.3}$$

$$\tilde{\beta}_r(mm')\equiv\frac{(-1)^r(2r+1)^{1/2}}{(J\|\tilde{\mathbf{J}}^{[r]}\|J')}$$

$$\times\sum_{k=|r-1|}^{r+1}(J\|\sum_{i=1}^{n}[\mathbf{T}^{[k]}(i)\times\mathbf{S}^{[1]}(i)]^{[r]}\|J')$$

$$\times\sum_{q=-k}^{k}(-1)^q\,\alpha_{kq}\bar{V}(r1k\,;mm'-q),$$

where the reduced matrix elements $(J\|\mathbf{J}^{[r]}\|J')$ are given by Eqs. (2.25), and $\mathbf{J}^{[r]}(i)$ refers to the total angular momentum of the rare-earth ion, and *not* of one electron.

The only terms in the exchange Hamiltonian dependent on the configuration are the reduced matrix elements

$$(J\|\sum_{i=1}^{n} [\mathbf{T}^{[k]}(i)\times\mathbf{S}^{[1]}(i)]^{[r]}\|J'). \qquad (3.4)$$

It remains to evaluate these for $4f^n$ configurations either by the general Racah approach using fractional parentage techniques,[9,20,21] or by applying a technique which is feasible only for a state of maximum multiplicity, i.e., $S=S_{max}$, which is the case for the ground state of a rare-earth ion.

B. The Evaluation of the Reduced Matrix Elements Using Coefficients of Fractional Parentage

The reduced matrix element (3.4) may be generalized by replacing the first rank tensor $S^{[1]}$ by a tensor of rank κ and f^n by l^n. Consider *one* L, S multiplet, i.e., $L=L'$ and $S=S'$; similarly, to Eq. (2.21) one writes

$$(l^n LSJ\|\sum_{i=1}^{n} [\mathbf{T}^{[k]}(i)\times\mathbf{S}^{[\kappa]}(i)]^{[r]}\|l^n LSJ')$$

$$= [(2J+1)(2J'+1)(2r+1)]^{1/2}$$

$$\times (l^n LS\|\sum_{i=1}^{n} \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i)\|l^n LS)$$

$$\times X(LLk/SS\kappa/JJ'r). \qquad (3.5)$$

$\mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i)$ is called a double tensor. This relation is not a direct extension of Eq. (2.21). The exclusion principle requires a multielectron wave function to be antisymmetric with respect to the interchange of equivalent electrons. Due to the construction of the antisymmetrized wave function $|l^n LM'_L SM_S\rangle$, L and S are still partially coupled in Eq. (3.5) although $\mathbf{T}^{[k]}$ and $\mathbf{S}^{[\kappa]}$ have been uncoupled as regards their irreducible tensorial product.

The reduced matrix element of the double tensor in Eq. (3.5) was evaluated by a method analogous to the one used by Elliott, Judd, and Runciman[22] for the spin-orbit interaction. Their procedure removes one electron from the n-electron wave function and allows the single-particle operators $\mathbf{T}^{[k]}(i)$ and $\mathbf{S}^{[\kappa]}(i)$ to act on this fractionated state. The result one obtains after using

[20] G. Racah, Phys. Rev. **63**, 367 (1943).
[21] G. Racah, Phys. Rev. **76**, 1352 (1949).
[22] J. P. Elliott, B. R. Judd, and W. A. Runciman, Proc. Roy. Soc. (London) **A240**, 509 (1957).

the relation (3.5) is

$$(l^n LSJ\|\sum_i [\mathbf{T}^{[k]}(i)\times\mathbf{S}^{[\kappa]}(i)]^{[r]}\|l^n LSJ')$$

$$= (-1)^{L+S+l+s+k+\kappa} n(2L+1)(2S+1)$$

$$\times [(2J+1)(2J'+1)(2r+1)]^{1/2}$$

$$\times (s\|\mathbf{S}^{[\kappa]}\|s) X(LLk/SS\kappa/JJ'r)$$

$$\times \sum_{L'S'} (-1)^{L'+S'} |(l^n LS\{|l^{n-1}(L'S'),lLS)|^2$$

$$\times \bar{W}(LLk/llL')\bar{W}(SS\kappa/ssS'), \qquad (3.6)$$

where $(l^n LS\{|l^{n-1}(L'S'),lLS)$ is a coefficient of fractional parentage,[9] and $L'S'$ is a parent state, i.e., when $L'S'$ are coupled to l, s one obtains L, S. In applying this formula to the exchange Hamiltonian's reduced matrix elements (3.4) note that $s=\frac{1}{2}$ and $S=$ total spin of rare-earth ion, *not* the spin of the ferric ion.

Two special cases of the reduced matrix element (3.6) must be separately considered. $n=1$: Eq. (3.6) is inapplicable and the proper specialization is Eq. (2.21). $n=2$: Eq. (3.6) applies if one uses $l^{n-1}=l$, $L'=l$, $S'=s$ and $(l^2 LS\{|l(l,s),lLS)=1$.

The coefficients of fractional parentage have been evaluated for the $4f^n$ ground states with methods given by Racah.[21] The v, w, and u numbers for these states were taken from Elliott, Runciman, and Judd.[22] In Table I are the coefficients of fractional parentage for the ground multiplets of the rare-earth ions from Pr^{3+} to Gd^{3+}, i.e., $n=2$ to 7.

The reduced matrix elements (3.5) from Tb^{3+} to Yb^{3+}, i.e., $n=8$ to 14, may be obtained from those with $n \leq 7$ by using the following relation derived by Racah.[23] For $k+\kappa \neq 0$

$$(S''L''\|\sum_{i=1}^{4l+2-n} \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i)\|S'L')$$

$$= (-1)^{k+\kappa+1}(S'L'\|\sum_{i=1}^{n} \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i)\|S''L''), \qquad (3.7a)$$

and for $k=\kappa=0$

$$(SL\|\sum_{i=1}^{4l+2-n} \mathbf{T}^{[0]}(i)\mathbf{S}^{[0]}(i)\|SL)=n(l\|\mathbf{T}^{[0]}\|l), \qquad (3.7b)$$

$$(SL\|\sum_{i=1}^{n} \mathbf{T}^{[0]}(i)\mathbf{S}^{[0]}(i)\|SL)= (4l+2-n)$$

$$\times (l\|\mathbf{T}^{[0]}\|l).$$

These relations are valid for states in the ground and excited multiplets.

In states of maximum spin multiplicity, i.e., ground states of ions obeying Hund's Rule, the reduced matrix elements are related for configurations in different quarters of an electron shell, e.g., $4f^1$ is related to $4f^6$,

[23] G. Racah, Phys. Rev. **62**, 438 (1942).

TABLE I. The coefficients of fractional parentage for the ground L, S multiplets of the rare-earth ions in the first half of the $4f$ shell.

n	L, S	L', S'	$(f^n LS \{\mid f^{n-1}(L'S'), fLS)$
2	^3H	^2F	1
3	^4I	^3F	$-(2/9)^{1/2}$
		^3H	$(7/9)^{1/2}$
4	^5I	^4F	$-(1/8)^{1/2}$
		^4G	$(21/88)^{1/2}$
		^4I	$(7/11)^{1/2}$
5	^6H	^5F	$-(1/10)^{1/2}$
		^5D	$-(2/21)^{1/2}$
		^5G	$-(3\times 13/2\times 77)^{1/2}$
		^5I	$(91/5\times 33)^{1/2}$
6	^7F	^6F	$(1/3)^{1/2}$
		^6P	$(1/7)^{1/2}$
		^6H	$(11/21)^{1/2}$
7	^8S	^7F	1

$4f^9$ to $4f^{12}$; this was pointed out by Van Vleck[24] and Judd.[25] In Appendix A the reduced matrix elements of a double tensor are related for configurations in different quarters of the electron shell by using unsymmetrized products of single-electron wave functions. Eqs. (A7) and (A8) relate the $(4l+2)$ reduced matrix elements of a double tensor to $(l+1)$ independent ones; for the rare-earth series there are only four independent elements and the first one, $4f^0$, is trivial.

C. The Final Hamiltonian that is Hermitian and Even Under Time Reversal

The reduced matrix elements in Sec. B complete the determination of the explicit form of the constants in the Hamiltonian for rare-earth-iron exchange. It is now possible to see what conditions must be placed on the Hamiltonians (3.2) and (3.3) so that they are Hermitian and even under time reversal. These requirements, as shown in Appendix B, restrict the rank of the irreducible tensor operator $T_q^{[k]}$ to be *even* and the rank of $J_m^{[r]}$ to be *odd*.

Restrictions on the components q (other than $-k \leqslant q \leqslant k$), can only be made when the Hamiltonian is expressed in certain coordinate systems. Furthermore the parameters α_{kq} (2.8) will be real provided they are referred to a set of axes for which the potential V is even in the variable ϕ;

$$V(r_i, \theta_i, \phi_i) = \sum_n e(r_{in})^{-1},$$

and n represents the ions active in the exchange interaction. The point symmetry of a rare-earth site is D_2 and there are three mutually perpendicular twofold axes; therefore when written in these axes, the exchange potential for the rare-earth-iron cluster interaction has only *even* components of the tensors $T_q^{[k]}$, and the exchange potential parameters α_{kq} are *real* and related

[24] J. H. Van Vleck, Phys. Rev. **41**, 208 (1932).
[25] B. R. Judd, Phys. Rev. **125**, 613 (1962).

by Eq. (B6), i.e.,

$$\alpha_{k,-q} = \alpha_{kq}. \tag{3.8}$$

From the above considerations we may conclude that when referred to the proper axes the exchange potential for a RE-Fe interaction will contain at most *ten* real parameters.

IV. THE RELATION BETWEEN THE EXCHANGE POTENTIAL PARAMETERS AND THE SPLITTINGS OF A KRAMERS' DOUBLET

The Hamiltonian for the rare-earth-iron exchange interaction has been derived in the preceding sections in terms of the unknown parameters α_{kq}. These parameters are extremely difficult to calculate for this complex interaction; the alternative is to determine them empirically. At present, experimental data are available only on the exchange splittings for a couple of Kramers' doublets. The parameters could be determined (if there were enough data) from a comparison of the splittings with theoretical expressions for them written in terms of the unknowns α_{kq}.

The form of the Hamiltonian (3.3) for the rare-earth-iron exchange interaction in a pair of Kramers' conjugate states is known[2] to be

$$\langle \mathcal{K}_{ex} \rangle = \mathbf{H}_{eff} \cdot \mathbf{A} \cdot \mathbf{J}'(RE), \tag{4.1}$$

where $\mathbf{A}$ tensor is an "exchange tensor." The purpose in this section is to relate the exchange potential parameters α_{kq} to the principal values of the exchange tensor, which in turn are related to the experimentally determined exchange splittings of a doublet.

Consider the state of a rare-earth ion represented by the wave function $|JM_J\rangle$, an eigenfunction of the total angular-momentum operators J^2 and J_z. The axis of quantization to which this wave function is referred coincides with the z axis of the crystalline field g tensor. It is a tacit assumption that the exchange potential and the crystalline field are referred to the same axes. If this were not the case, either the wave function or the exchange-potential operator would have to be rotated to the axes of the other. The matrix element of the Hamiltonian (3.3) in a $|JM_J\rangle$ representation

$$\langle JM_J | \mathcal{K}_{ex} | JM'_J \rangle \equiv E(M_J, M'_J; S_{m'}^{[1]}) \tag{4.2}$$

is still an operator with respect to states of the ferric ion.

The properties of the operator-matrix element (4.2) in the states of a Kramers' doublet are derived by manipulating the Hamiltonian (3.3), and by using the symmetry properties of the $\bar{V}$ symbols[9] and parameters α_{kq} (see Appendix B). The necessary relations for evaluating the exchange Hamiltonian in a Kramers' doublet are:

(1) $E(M'_J, M_J; S_{m'}^{[1]}) = (E(M_J, M'_J; S_{m'}^{[1]}))^\dagger. \tag{4.3}$

A dagger denotes the Hermitian adjoint of an operator.

(2) $E(-M_J, -M'_J; S_{m'}^{[1]})$
$$= (-1)^{M_J - M'_J + 1} E(M'_J, M_J; S_{m'}^{[1]}), \tag{4.4}$$

and

(3) $*\langle JM_J | \mathfrak{IC}_{\mathrm{ex}} | JM'_J \rangle^* = -\langle JM'_J | \mathfrak{IC}_{\mathrm{ex}} | JM_J \rangle.$ (4.5)

The last relation shows that the exchange Hamiltonian changes sign when evaluated in a time-reversed state of *one* system of the composite rare-earth-iron system.

Written within the subspace spanned by the Kramers' conjugate wave functions ψ and ψ^*, the exchange Hamiltonian reduces to a 2×2 matrix whose elements are operators of the iron sublattice system. As these wave functions are linear combinations of states $|JM_J\rangle$, one finds from Eq. (4.5) that the diagonal matrix elements are the negative of one another and from Eq. (4.4) that one off-diagonal matrix element is the Hermitian adjoint of the other.

In the iron garnets, the crystalline and exchange potential have rhombic symmetry with respect to the g-tensor axes. Therefore, (1) the doublet wave functions contain only those states $|JM_J\rangle$ which have their spatial quantum numbers M_J differing by an even number, and (2) only even components (q) of the exchange potential are present. From these facts one deduces that the diagonal matrix elements contain only the z component of the iron sublattice spin, and the off-diagonal elements contain only the x and y components, i.e., the exchange tensor is in principal form. By using the procedure outlined by Griffith[26] and the molecular-field approximation, we find that

$$\langle \mathfrak{IC}_{\mathrm{ex}}\rangle_{\mathrm{doublet}} = 2[M(T)/M(0)]_{\mathrm{YIG}}\hat{M}\cdot\mathbf{A}\cdot\mathbf{J}'(\mathrm{RE}).\quad (4.6)$$

In this formula $J'(\mathrm{RE})$ is the fictitious angular momentum of the doublet, $\hat{M}$ is a unit vector pointing in the direction of the magnetization of the iron sublattice, and $[M(T)/M(0)]_{\mathrm{YIG}}$ represents the ratio of the spin of the iron sublattice at a temperature T to that at absolute zero. The principal values of the exchange tensor $\mathbf{A}$ are

$$a_{xx} = (1/\sqrt{2})[|\eta(1)| - |\eta(-1)|],$$
$$a_{yy} = (1/\sqrt{2})[|\eta(1)| + |\eta(-1)|], \quad (4.7)$$
$$a_{zz} = -|\eta(0)|,$$

where

$$\eta(m') = \sum_{kq} \gamma_{kq}(m')\alpha_{kq} \quad (4.8a)$$

and

$$\gamma_{kq}(m') \equiv 2 \sum_{M_J M'_J} (-)^{J+M_J+1} C(M_J M'_J)$$

$$\times \sum_{\substack{r=|k-1| \\ (r\ \mathrm{odd})}}^{k+1} (2r+1)^{1/2}\bar{V}(JJr; -M_J M'_J m)$$

$$\times \bar{V}(r1k; m, m', -q)$$

$$\times (J\|\sum_{i=1}^{n} [\mathbf{T}^{[k]}(i)\times\mathbf{S}^{[1]}(i)]^{[r]}\|J). \quad (4.8b)$$

[26] J. S. Griffith *The Theory of Transition–Metal Ions* (Cambridge University Press, London, 1961); note that the matrix elements

Here the exchange parameters include the average value of the spin of the iron sublattice at absolute zero. $C(M_J M'_J)$ is a product of the coefficients of the states $|JM_J\rangle$ that enter the Kramers' conjugate states ψ and ψ^*.

When the iron magnetization is parallel to one of the $\mathbf{A}$-tensor principal axes, say q, the value of $J_q'(\mathrm{RE})$ is $\pm\frac{1}{2}$. With the Hamiltonian (4.6) we find

$$(\Delta E_{\mathrm{ex}})_q = 2[M(T)/M(0)]a_{qq}, \quad (4.9)$$

which is the exchange splitting of the doublet along the qth principal axis related to the principal value of the exchange tensor.

V. CONCLUSIONS AND DISCUSSIONS OF RESULTS

The main objective in part I has been achieved; the Hamiltonian (3.2 or 3.3) has been derived that describes the anisotropic exchange interaction between the electrons of one or a cluster of S-state ions and those of an ion whose orbital and spin angular momenta are strongly coupled to form a resultant $\mathbf{J}$. The dependence of this interaction on the orbital state of the ion with the total angular momentum $\mathbf{J}$ is accounted for by a generalized exchange potential (2.5); this potential is applicable to superexchange as well as direct-exchange interactions.

For the Yb^{3+} ion in YbIG the spin-orbit coupling splits the lowest term of the $4f^{13}$ configuration (^2F) into two J states, which are removed from one another by 10 000 cm^{-1}. The crystalline field splittings of these states are about 500 cm^{-1} and the exchange splittings of the lowest doublets are about 25 cm^{-1}. From this we conclude the J is a good quantum number for Yb^{3+} in YbIG. In the case of rare-earth ions for which J is not a good quantum number, as for example, when the crystalline field splittings is of the same order of magnitude as the spin-orbit splitting, the alternate form of the operator $\hat{J}^{[r]}(\mathrm{RE})$ can be used, i.e., $S^{[r]}(\mathrm{RE})$.

The second major objective in this investigation is the empirical determination of the exchange potential parameters of the RE-Fe exchange interaction from the available experimental data on the exchange splittings of Kramers' doublets. The exchange potential parameters may be determined empirically from data on one J state, on different J states within a L, S multiplet, or even from data on states in the ground multiplets of ions with different numbers of equivalent electrons. These three methods may not give a unique set of parameters, i.e., if the parameters have been determined from data on one J state they may not accurately represent the exchange potential for other states either of the same ion or for ions with different numbers of equivalent electrons. As no additional assumptions were made in deriving the exchange Hamiltonian for different J states in a L, S multiplet of an ion, it seems reasonable to use the exchange potential parameters determined

(4.2) are operators in a space other than that spanned by the wave functions ψ and ψ^*.

for one J state for others within the same multiplet. On the other hand, in the derivation of the exchange Hamiltonian for states in the ground multiplets of ions with different numbers of equivalent electrons, the assumption was made that each electron sees the same exchange potential. This "one-electron" approximation is more appropriate for the angular than the radial part of a wave function, and therefore it is reasonable to extrapolate only the *ratios* of the exchange potential parameters from one ion to another and not their magnitude, i.e., the isotropic component α_{00}.

At the present time it is not possible to determine the parameters α_{kq} nor the extent of their validity. Three reasons can be cited:

(1) The experimental data on Yb^{3+} are insufficient to determine uniquely the parameters without resorting to specific models of the RE-Fe^{3+} exchange interaction.

(2) No direct experimental data, as exchange splittings, exists for the anisotropy of the RE-Fe exchange interaction in ions other than Yb^{3+}.

(3) The wave functions for the Yb^{3+} ion in the crystalline field of YbIG are not accurately known.

The wave functions for Yb^{3+} in the crystal field (excluding exchange field) are not known. Wickersheim[3,5] has concluded, from the effect of a large magnetic field on the $^2F_{5/2}$ and $^2F_{7/2}$ lowest doublet levels, that it is a "safe procedure" to use the wave functions for the doublets of Yb^{3+} in YGaG to represent those in YbIG.[27] These wave functions have just been determined by Hutchings and Wolf,[28] and one could determine the exchange potential parameters with the available data *provided* one uses a specific model of the RE-Fe^{3+} exchange interaction (if more experimental data on the Yb-Fe exchange interaction were available, it would be possible to determine the parameters independent of any model).

A mention should be made about the *relative* signs of the g values for the Zeeman effect and the exchange splittings. The effect of a large magnetic field on the exchange splittings of the $^2F_{5/2}$ and $^2F_{7/2}$ doublets has been measured by Wickersheim.[3,5] He concluded that the g values for the two states have opposite signs. No further experimental information has been obtained on the relative signs, and therefore all g values and splittings for each doublet have been given the same sign. This assignment implies the least amount of anisotropy in the exchange splittings. Whereas it is not possible to assign each g value or splitting a definite sign it has been noted by O'Brien[29] and Pryce[30] that the product

of the principal values of the g tensor or exchange tensor, i.e., $\det g_{ij}$, has a definite sign that can be experimentally determined by using circularly polarized radiation. This information would be very useful in helping one to determine the signs of the g values and exchange splittings; these relative signs affect the values of the empirically determined exchange-potential parameters.

In conclusion, the exchange potential parameters have not been determined, nor has the concept of a unique exchange potential for the RE-Fe interaction been validated. These topics and models of the RE-Fe^{3+} interaction will be discussed in a subsequent paper (part II).

APPENDIX A: EVALUATION OF REDUCED MATRIX ELEMENTS FOR STATES OF MAXIMUM MULTIPLICITY USING UNSYMMETRIZED PRODUCTS OF SINGLE-ELECTRON WAVE FUNCTIONS

In evaluating the reduced matrix element (3.5) for a configuration of equivalent electrons it is irrelevant whether an antisymmetrized wave function or a set of products of single-electron wave functions is used, because the operators $T_q{}^{[k]}(i)$ and $S_{q'}{}^{[\kappa]}(i)$ yield the same result. For a state of maximum multiplicity the set of product wave functions reduces to *one*, that one for which

$$n \leqslant 2l+1; \; |S, M_S = S\rangle = \prod_{r=1}^{n} |\tfrac{1}{2}, \tfrac{1}{2}\rangle_r$$

and   (A1)

$$4l+2 \geqslant n > 2l+1; \; |S, M_S = S\rangle$$

$$= \prod_{r=1}^{2l+1} \prod_{r'=2l+2}^{n} |\tfrac{1}{2}, \tfrac{1}{2}\rangle_r |\tfrac{1}{2}, -\tfrac{1}{2}\rangle_{r'}.$$

For this state it is particularly simple to evaluate the reduced matrix elements with the product type wave function.

For states of maximum multiplicity not only are the reduced matrix elements for the second half of the $4f$ shell related to those of the first half [see Eqs. (3.7)], but also within each half-shell the reduced matrix elements of a double tensor are related. These relations were given by Van Vleck[24] and Judd[25] for the special

[27] Perhaps there is a slight difference in the wave functions; and it is possible that the RE-Fe exchange interaction is sensitive to this difference, in which case the g values of the lowest doublets of the $^2F_{5/2}$ and $^2F_{7/2}$ states of Yb^{3+} in YbIG must be re-evaluated with a better accuracy than has been obtained in past experiments.

[28] M. T. Hutchings and W. P. Wolf, J. Appl. Phys. 35, 1060 (1964).

[29] M. C. M. O'Brien, Doctoral thesis, University of Oxford, 1955 (unpublished).

[30] M. H. L. Pryce, Phys. Rev. Letters 3, 375 (1959).

case of tensorial operators acting only on the orbital variables, and will be generalized to include the reduced matrix element relations for double tensors,

$$\sum_i \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i).$$

Before proceeding with the derivation of the relations it will be necessary to derive a simple formula for the reduced matrix element of a double tensor. Let us consider the matrix element

$$\sum_{i=1}^{n} \langle L, M_L = L | T_0^{[k]}(i) | L, M_L = L \rangle$$

$$\times \langle S, M_S = S | S_0^{[\kappa]}(i) | S, M_S = S \rangle. \quad (A2)$$

For $n \leqslant 2l+1$, the product wave functions are

$$|L, M_L = L\rangle = \prod_{r=1}^{n} |l,(l+1-r)\rangle_r, \qquad (A3)$$

and $|S, M_S = S\rangle$ is given above. The matrix element may be evaluated by using the Wigner-Eckart theorem[17] or the product wave functions. Upon comparing the results obtained by these two methods, one finds that for $n \leqslant 2l+1$

$$(l^n LS \| \sum_{i=1}^{n} \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i) \| l^n LS)$$

$$= \frac{(\tfrac{1}{2} \| \mathbf{S}^{[\kappa]} \| \tfrac{1}{2}) \bar{V}(\tfrac{1}{2}\tfrac{1}{2}\kappa; -\tfrac{1}{2}\tfrac{1}{2}0)}{\bar{V}(LLk; -LL0)\bar{V}(SS\kappa; -SS0)}$$

$$\times \sum_{i=1}^{n} (-1)^{i-1} \bar{V}(llk; -(l+1-i)(l+1-i)0). \quad (A4)$$

With this formula we will now derive the desired relations.

(1) Relation between the configurations $l^{(2l+1-n)}$ and l^n for the first half of a shell, i.e., $2l+1 \geqslant n \geqslant 1$. For states of maximum spin multiplicity the orbital angular momentum for the configurations $l^{(2l+1-n)}$ and l^n are related as follows:

$$L(l^n) = L(l^{(2l+1-n)}).$$

Evaluating Eq. (A4) for the configuration $l^{(2l+1-n)}$, one finds

$$(l^{(2l+1-n)}LS_m' \| \sum_{i=1}^{2l+1-n} \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i) \| l^{(2l+1-n)}LS_m')$$

$$= \frac{(\tfrac{1}{2} \| \mathbf{S}^{[\kappa]} \| \tfrac{1}{2}) \bar{V}(\tfrac{1}{2}\tfrac{1}{2}\kappa; -\tfrac{1}{2}\tfrac{1}{2}0)}{\bar{V}(LLk; -LL0)\bar{V}(S_m'S_m'\kappa; -S_m'S_m'0)}$$

$$\times \sum_{i=1}^{2l+1-n} (-1)^{i-1} \bar{V}(llk; -(l+1-i)(l+1-i)0). \quad (A5)$$

The sum in Eq. (A5) can be rewritten as

$$\sum_{i=1}^{2l+1-n} = \sum_{i=1}^{2l+1} - \sum_{i=2l+2-n}^{2l+1}.$$

The first sum on the right-hand side is zero as the orbital angular momentum is zero for a state of maximum spin multiplicity if the shell is half-filled, i.e., $L(l^{(2l+1)}) = 0$. With the substitution $i = 2l+2-j$, one finds

$$\sum_{i=2l+2-n}^{2l+1} (-1)^{i-1} \bar{V}(llk; -(l+1-i)(l+1-i)0)$$

$$= (-1)^k \sum_{j=1}^{n} (-1)^{j-1} \bar{V}(llk; -(l+1-j) \times (l+1-j)0). \quad (A6)$$

Placing the result (A6) in Eq. (A5) and comparing with Eq. (A4) gives one the result for $2l+1 \geqslant n \geqslant 1$

$$(l^{(2l+1-n)}LS_m' \| \sum_{i=1}^{2l+1-n} \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i) \| l^{(2l+1-n)}LS_m')$$

$$= (-1)^{k+1} \frac{\bar{V}(S_m S_m \kappa; -S_m S_m 0)}{\bar{V}(S_m' S_m' \kappa; -S_m' S_m' 0)}$$

$$\times (l^n LS_m \| \sum_{i=1}^{n} \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i) \| l^n LS_m), \quad (A7)$$

where $S_m = \tfrac{1}{2}n$ and $S_m' = \tfrac{1}{2}(2l+1-n)$, $0 \leqslant k \leqslant 2l$, and $\kappa = 0$ or 1.

(2) To find the relation between the configurations $l^{(2l+1-n)}$ and l^n for $4l+2 \geqslant n > 2l+1$, we use the relation (A.7). In place of n, we substitute the new variable p which is defined as follows: $p \equiv 4l+2-n$ and $p \leqslant 2l+1$. Using Eq. (3.7a) to relate the configurations $l^{(4l+2-n)}$ and l^n, gives us the desired relation

$$(l^n LS_m \| \sum_{i=1}^{n} \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i) \| l^n LS_m)$$

$$= (-1)^k \frac{\bar{V}(S_m' S_m' \kappa; -S_m' S_m' 0)}{\bar{V}(S_m S_m \kappa; -S_m S_m 0)}$$

$$\times (l^{[n-(2l+1)]}LS_m' \| \sum_{i=1}^{n-(2l+1)} \mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i) \| l^{[n-(2l+1)]}LS_m'), \quad (A8)$$

where

$$S_m = \tfrac{1}{2}(4l+2-n)$$

and

$$S_m' = \tfrac{1}{2}(2l+1) - S_m = \tfrac{1}{2}[n-(2l+1)].$$

With the relations (A7) and (A8), the reduced matrix elements of the double tensor $\mathbf{T}^{[k]}(i)\mathbf{S}^{[\kappa]}(i)$ of only $l+1$ configurations are needed to fully determine the remaining $3l+1$ provided the state considered is of maximum multiplicity. As an example, consider the

rare-earth $(4f^n)$ series; the reduced matrix elements for the configurations f^0, f^1 and f^2, f^3 suffice to determine the remaining ones. As the configuration f^0 is trivial, three reduced matrix elements define the remaining ten.

APPENDIX B: THE RESTRICTIONS OF THE HAMILTONIAN FOR AN EXCHANGE INTERACTION

A Hamiltonian that describes an exchange interaction is Hermitian, and even under time reversal provided the states of the system have the same parity. The first is a requirement for an operator to represent a physical observable; the second is required when one realizes that reversing the time does not affect the exchange interaction in any discernable way; it only reverses the rotation of *both* electrons.

As the direct product (2.4) of two operators that commute with each other will be Hermitian, and even under time reversal if both operators have these properties, the exchange potential operator (2.5) must have the same properties as the Hamiltonian (2.4). The restrictions on the terms that enter the Hamiltonians (3.2) and (3.3) and exchange potential (2.5) so that they are Hermitian, and even under time reversal will now be derived.

From the definition of irreducible tensors as given by Fano and Racah[9] the Hermitian adjoint of a "self-adjoint" irreducible tensor operator is given as

$$(T_q^{[k]})^\dagger = (-1)^{k+q} T_{-q}^{[k]}. \qquad (B1)$$

The reduced matrix elements of a self-adjoint operator are related by[31]

$$((j\|(\mathbf{T}^{[k]})^\dagger\|j'))^* = (-1)^{j-j'-k}(j'\|\mathbf{T}^{[k]}\|j). \qquad (B2)$$

From this relation it may be seen that the diagonal elements of the reduced matrix of a self-adjoint operator are *real* if the rank k is *even*, and *imaginary* if k is *odd*.

The time reverse of an irreducible tensor operator is found by taking the time reverse of the "physical" operators comprising it. For irreducible tensor operators referring to *angular momentum*, one has

$$(T_q^{[k]})^T = (-1)^q T_{-q}^{[k]}. \qquad (B3)$$

Finally, let us note that the irreducible tensors defined by Fano and Racah[9] have the property: The irreducible product of two commuting self-adjoint tensors will be self-adjoint.[32]

Taking the Hermitian adjoint and time reverse of the exchange potential operator (2.5), one finds

$$A_{\text{op}}^\dagger = \sum_{k=0}^{2l} \sum_{q=-k}^{k} (-1)^{k+q} \alpha_{k,-q}^* T_q^{[k]} \qquad (B4)$$

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[31] See Ref. 9, p. 80.
[32] A. R. Edmonds *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, 1957), see p. 78.

and

$$A_{\text{op}}^T = \sum_{k=0}^{2l} \sum_{q=-k}^{k} (-1)^q \alpha_{k,-q}^* T_q^{[k]}. \qquad (B5)$$

As the exchange potential operator should be self-adjoint one has

$$\alpha_{k,-q} = (-1)^{k+q} \alpha_{kq}^*. \qquad (B6)$$

Using this relation in Eq. (B.5) and equating the time-reversed exchange potential to itself, one finds that

$$k = \text{even integer}.$$

As k is restricted by time-reversal symmetry to be even the diagonal elements of the reduced matrix (B2) of the operators $T_q^{[k]}$ must be real, and one is justified in defining the reduced matrix element (2.7) real.

The exchange potential now fulfills the necessary conditions on it and it remains to see what further restrictions must be placed on the Hamiltonian (3.3) to make it Hermitian and even under time reversal. Taking the Hermitian adjoint of the Hamiltonian (3.3), and using the relation (B3), one finds

$$\mathcal{H}_{\text{ex}}^\dagger \doteq 2 \sum_{r=0}^{2l+1} \sum_{mm'} (-1)^{r+1-m-m'} (\tilde{\beta}_r(-m, -m'))^*$$
$$\times \tilde{J}_m^{[r]}(i) S_{m'}^{[1]}(j). \qquad (B7)$$

From the definition (3.3) of the coefficient $\tilde{\beta}_r(m,m')$, and some manipulations of the terms, one finds

$$(\tilde{\beta}_r(-m-m'))^* = (-1)^{m+m'} \tilde{\beta}_r(mm'). \qquad (B8)$$

Combining Eqs. (B7) and (B8) and equating the Hermitian adjoint of the Hamiltonian (3.3) to itself, one finds that only odd ranks of the irreducible tensor operator $\tilde{J}_m^{[r]}(i)$ are allowable, i.e.,

$$r = \text{odd integer}.$$

Upon taking the time reverse of the Hamiltonian (3.3) and using the conditions that k is even and r is odd, one finds that the Hamiltonian is equal to itself; therefore no further restrictions are needed to make the Hamiltonian (3.3) even under time reversal.

There is one more requirement that an exchange Hamiltonian must satisfy; it must be invariant under spatial rotations. This condition requires the exchange potential parameters α_{kq} to transform *contragrediently* to the irreducible tensorial operators $T_q^{[k]}$. That is, if

$$T_q^{[k]} = \sum_{q'} \mathfrak{D}_{q'q}^{[k]} T_{q'}^{[k]'}, \qquad (B9)$$

then

$$\alpha_{kq}' = \sum_{q'} \mathfrak{D}_{qq'}^{[k]} \alpha_{kq'},$$

where $\mathfrak{D}_{q'q}^{[k]}$ is a matrix element of the rotation operator that takes the unprimed coordinates into the primed coordinates.