Rare-Earth-Iron Exchange Interaction in the Garnets. II. Exchange Potential for Ytterbium*

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To determine the magnitude of the anisotropy of the ytterbium-iron (Yb-Fe) exchange interaction we have evaluated the exchange splittings of the lowest ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ doublets of ytterbium (Yb³⁺) in ytterbium iron garnet (YbIG). By using the wave functions of Yb³⁺ in yttrium gallium garnet (those for YbIG are not known) we are able to express these splittings in terms of ten parameters which characterize the anisotropy of the exchange interaction. As there are only six experimental splittings it is necessary to reduce the number of unknowns by assuming: (1) that the rare-earth-iron (RE-Fe) exchange interaction takes place through the neighboring eight oxygen ions, and (2) (somewhat more uncertainly) that the rare-earth-oxygen (RE-O) exchange interaction is axial about the RE-O axis. This leads us to express the exchange splittings in two sets of four exchange constants. We find a good four-parameter fit of the experimental exchange splittings by adopting essentially zero values for the rare-earth-ferric ion exchange interactions that take place through the four nearest oxygen ions. This result corroborates qualitative conjectures on the RE-Fe exchange based on superexchange bonding angles. The validity of the extrapolation of the anisotropy of the Yb-Fe exchange interaction to other rare earths is discussed.

I. INTRODUCTION

 \mathbf{I}^{N} a preceding article,¹ we introduced an exchange potential to take into account the anisotropy of the rare-earth-iron cluster (RE-Fe) exchange interaction. Because of the complexity of this interaction, parameters in this potential can only be empirically determined, as, for example, from the dependence of the exchange splittings of doublet levels of the RE ions on the direction of the iron sublattice spin. Heretofore we have not been able to determine these parameters because the number of known splittings is insufficient; there are *ten* exchange potential parameters for the (c)site in the garnet structure and only six experimental exchange splittings, i.e., the splittings of the lowest doublets of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ states of ytterbium (Yb³⁺) in ytterbium iron garnet² (YbIG). Added to this indeterminacy is the lack of precise wave functions for the above-mentioned states. To overcome this difficulty it is reasonable³ to use the wave functions of Yb³⁺ in yttrium gallium garnet (YGaG). These have been determined by White,⁴ and Hutchings and Wolf⁵ and, in Sec. II, we shall use them to evaluate the exchange splittings of the above-mentioned doublets.

The parameters α_{kq} have no simple heuristic interpretation which might permit one to estimate their values. To surmount the insufficiency in amount of experimental data, we must relate the α_{kq} to a new set of parameters on which we can make approximations that are guided by our knowledge of the super-exchange interaction.

By 1962 it was commonly believed^{2,6,7} that the rareearth-ferric ion (RE-Fe³⁺) interaction takes place through the neighboring oxygen ions and that it is possible to write the exchange potential for the RE-Fe cluster exchange interaction in terms of the exchange constants $A(m_l)$ of the RE-Fe³⁺ exchange interaction. With this model we hereby relate the parameters α_{kq} to ones which have more physical significance and on which certain approximations may be made. Wolf and Elliott,⁶ and Koster and Statz⁷ considered that approximation to the RE-Fe³⁺ interaction in which only the state of the RE ion which has maximum overlap on the neighboring oxygen ions contributes significantly to the RE-Fe³⁺ exchange. The exchange splittings of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ doublets of Yb³⁺ in YbIG derived on this assumption did not produce a satisfactory fit to the experimental splittings. Generalizing on the abovementioned model, we will show that the experimental splittings of the Yb³⁺ doublets admit a solution in which the Yb-Fe³⁺ linkages containing the next-nearestneighbor (n.n.n.) oxygen ions carry the major portion of the Yb-Fe cluster exchange interaction. This result is not limited to ytterbium and it is expected to hold for all rare earths at (c) sites in the iron garnets.

As the only experimental data available are those on the Yb-Fe exchange, we will draw on this ion to bring out the features of the anisotropic RE-Fe exchange. In Sec. II we present the evaluation of the exchange splittings Eqs. (I,4.7-I,4.9)⁸ for the lowest doublets of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ states of Yb³⁺ in terms of the unknowns α_{kq} and the wave functions. In Sec. III we develop the RE-Fe cluster exchange potential from the RE-Fe³⁺ linkage potentials, and relate the α_{kq} to new parameters,

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² K. A. Wichersheim and R. L. White, Phys. Rev. Letters 8, 483 (1962).

³ See Ref. 1, footnote 27.

 ⁴ R. L. White (private communication).
 ⁵ M. T. Hutchings and W. P. Wolf, J. Chem. Phys. 41, 617 (1964)

⁶ W. P. Wolf and R. J. Elliott (private communication); for a discussion of this model see P. M. Levy, doctoral thesis, Harvard University, 1963 (unpublished).

⁷ G. F. Koster and H. Statz, in Proceedings of the First International Conference on Paramagnetic-Resonance, Jerusalem, edited by W. Low (Academic Press Inc., New York, 1963), Vol. I, p. 362. ⁸ All equations referred to Ref. 1 have the equation prefixed

with an I.

 $A(m_l)$. In the fourth and final section we present the results of fitting the experimental splittings of the two doublets to the theoretical expressions derived in sections two and three. We find that a good four-parameter fit of the experimental exchange splittings is obtained by adopting essentially zero values for the RE-Fe exchange interactions that take place through the nearest-neighbor oxygen ion. The chief result of the analysis is that the RE-Fe exchange interaction takes place primarily through the next-nearest-neighbor oxygens; the nearest-neighbor oxygens are comparatively inert.

II. EXCHANGE SPLITTINGS OF Yb³⁺ IN YTTERBIUM IRON GARNET

With the formulas derived in Sec. IV of I, it is possible to evaluate empirically the exchange potential parameters for the rare-earth-iron cluster exchange interaction from data on the exchange splittings of Kramers doublets of rare-earth ions provided:

(1) The exchange splittings of a sufficient number of these doublets have been experimentally determined so that the number of unknown parameters α_{kq} is less than the number of empirical exchange splittings.

(2) The wave functions Ψ , Ψ^* of the states for the rare-earth ion's doublets in the crystalline field of the garnets are known.

Neither of these conditions can be fulfilled at the present time. The only experimental data available are for the exchange splittings of the lowest doublets of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ states of Yb³⁺ in YbIG which are insufficient to determine the ten unknowns α_{kq} ; furthermore the wave functions for these states are not known.

Nevertheless one can obtain an estimate of the rareearth-iron cluster exchange potential by reducing the number of unknown parameters with a specific model of the rare-earth-ferric-ion interaction (Sec. III), and by approximating the wave functions of the doublets.

A. The Exchange Splittings of the Lowest Doublets of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ States of Yb³⁺ in Ytterbium Iron Garnet

The splitting of a Kramers doublet under the influence of an anisotropic exchange interaction was discussed in Sec. IV of I. We now apply the results of that section to the lowest doublets of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ states of the Yb³⁺ ion in YbIG.

The calculation of these splittings reduces to an evaluation of Eq. (I,4.8b)

$$\gamma_{kq}(m') = 2 \sum_{M_JM_J'} (-)^{J-M_J+1} C(M_JM_J') \sum_{\substack{r=|k-1|\\(r \text{ odd})}}^{k+1} (2r+1)^{1/2} \bar{V}(JJr; -M_JM_J'm) \\ \times \bar{V}(r1k; m, m', -q) (J \| \sum_{i=1}^n [\mathbf{T}^{[k]}(i) \times \mathbf{S}^{[1]}(i)]^{[r]} \| J), \quad (2.1)$$

and to a determination of the terms $C(M_JM_J')$. The trivalent ytterbium ion has 13 4f electrons. The relation between the reduced matrix element of an operator for n=13 electrons and the same operator for 4l+2-n=1electrons is given by Eq. (I, A.8). With this relation and the reduced matrix element for one electron given by Eq. (I2.21), we find that the reduced matrix element for 13 electrons is (realizing that k is even)

$$(J \| \sum_{i=1}^{13} [\mathbf{T}^{[k]}(i) \times \mathbf{S}^{[1]}(i)]^{[r]} \| J) = (2r+1)^{1/2} (2J+1) (s = \frac{1}{2} \| \mathbf{S}^{[1]} \| s = \frac{1}{2}) X (lsJ/lsJ/k1r), \qquad (2.2)$$

where l=3. With this relation placed in Eq. (I, 4b) we find that

$$\gamma_{kq}(m') = 2(2J+1)(s = \frac{1}{2} \|\mathbf{S}^{[1]}\|_{s} = \frac{1}{2}) \sum_{M_JM_{J'}} (-)^{J-M_J+1} C(M_JM_{J'}) \sum_{\substack{r=|k-1|\\ (r \text{ odd})}}^{k+1} (2r+1)\bar{V}(JJr; -M_JM_{J'}m) \\ \times \bar{V}(r1k; m, m', -q)X(lsJ/lsJ/k1r).$$
(2.3)

To ascertain the magnetic quantum numbers M_J and and $M_{J'}$ and the values of $C(M_JM_{J'})$ that enter the operator matrix element (2.1) it is necessary: to apply the wave functions of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ doublets to the Hamiltonian (I,3.3), to use the properties of the matrix element $E(M_J, M_{J'}; S_{m'})$, Eq. (I, 4.2) given in Sec. IV of I, and to compare the resulting expression with the operator-matrix element

$$\chi = \sum_{M_J M_J'} C(M_J M_J') E(M_J, M_J'; S_{m'}^{[1]}). \quad (2.4)$$

The wave function for a ${}^2\!F_{5/2}$ state in a rhombic crystalline field⁹ is

$$\psi_{5/2} = a \left| \frac{5}{2} \frac{5}{2} \right\rangle + b \left| \frac{5}{2} \frac{1}{2} \right\rangle + c \left| \frac{5}{2} - \frac{3}{2} \right\rangle, \tag{2.5}$$

while that for a ${}^{2}F_{7/2}$ state is

$$\psi_{7/2} = a' \left| \frac{7}{2} \frac{5}{2} \right\rangle + b' \left| \frac{7}{2} \frac{1}{2} \right\rangle + c' \left| \frac{7}{2} - \frac{3}{2} \right\rangle + d' \left| \frac{7}{2} - \frac{7}{2} \right\rangle, \quad (2.6)$$

where $\left|\frac{7}{2}\frac{5}{2}\right\rangle$ means that the total angular momentum

⁹ The point symmetry of the rare-earth (c) site is D_2 .

 $J = \frac{7}{2}$ and $M_J = \frac{5}{2}$. The Kramers conjugate states to $\Psi_{5/2}$ and $\Psi_{7/2}$ are given by the relation

$$|JM_J\rangle^* = (-)^{J+M_J} |J, -M_J\rangle, \qquad (2.7)$$

where the asterisk denotes a time-reversed state. Applying these wave functions to the Hamiltonian (I, 3.3) and comparing the ensuing expression with the form (2.4), we find the permissible values of M_J and M_J' , and the constants $C(M_JM_J')$ that enter the operator-matrix elements $\gamma_{kq}(m')$. The numerical values of the 3-*j* symbols (\overline{V} coefficients) that appear in the matrix elements (2.3) are given by Rotenberg *et al.*,¹⁰ and the values of the 9-*j* symbols are given by Howell.¹¹ The exchange splittings (I, 4.9) of the lowest doublets of the ${}^2F_{5/2}$ and ${}^2F_{7/2}$ states of Yb³⁺ in YbIG are given in Table I [for low temperatures where (M(T)/M(0))=1] in terms of the unknown components of the states $|JM_J\rangle$ in the wave functions (2.5) and (2.6) and the unknown exchange potential parameters α_{kq} .

$$\Delta E_Q = 2a_{QQ},$$

$$a_{QQ} = \frac{1}{2} \sum_{k,q} \gamma_{kq}(Q) \alpha_{kq},$$
(2.8)

where

$$\begin{split} \boldsymbol{\gamma}_{kq}(\boldsymbol{x}) &\equiv (1/\sqrt{2}) \big[\left| \boldsymbol{\gamma}_{kq}(1) \right| - \left| \boldsymbol{\gamma}_{kq}(-1) \right| \big], \\ \boldsymbol{\gamma}_{kq}(\boldsymbol{y}) &\equiv (1/\sqrt{2}) \big[\left| \boldsymbol{\gamma}_{kq}(1) \right| + \left| \boldsymbol{\gamma}_{kq}(-1) \right| \big], \\ \boldsymbol{\gamma}_{kq}(\boldsymbol{z}) &\equiv - \left| \boldsymbol{\gamma}_{kq}(0) \right|, \end{split}$$

$$(2.9)$$

and $\gamma_{kq}(m')$ is given by Eq. (2.3). The splittings of the two doublets lead to six inhomogeneous equations with ten unknowns: the parameters α_{kq} .

B. Doublet Wave Functions

At present the wave functions for the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ lowest doublet states of the Yb³⁺ ion in the crystalline field of YbIG are not known. Whereas the crystalline field of YbIG is "approximately cubic," the use of wave functions appropriate to a cubic crystalline field leads to an isotropic g tensor for the doublet. If we used cubic wave functions and then compared the calculated exchange splittings (Table I) with the observed (Table II), we would attribute all the anisotropy in the observed exchange splittings to the rare-earth-iron exchange interaction. This gives the exchange potential an exaggerated anisotropy.

Three investigators, Hutchings and Wolf,⁵ and White⁴ have determined the wave functions (Table III) for the lowest doublets of the Yb³⁺ ion's ${}^{2}F_{7/2}$ and ${}^{2}F_{5/2}$ states in YGaG. White found the constants in the wave functions (2.5) and (2.6) by optimizing the fit of these wave functions to the experimental g values (Table II). This procedure does not guarantee that the wave functions fit the crystalline field energy levels, which is a necessary



FIG. 1. The coordination of oxygen ions around the rare-earth (c) site of garnet. The crystallographic axes are x,y,z; p,q,r are the g-tensor axes (axes of local D_2 symmetry). The p,q axes are in the xy plane but rotated 45° from the x,y axes. All angles are referred to the g-tensor (p,q,r) axes. For a perfect cubic coordination, type-1 ions lie in the pr plane and type-2 ions lie in the pq or xy plane.

requirement for wave functions describing the state of an electron in a crystalline field.

As it is experimentally impossible to distinguish the x and y axes of the g tensor with respect to the crystallographic axes for the garnet structure,⁵ White fitted his wave functions to the two possible assignments of g values: g_x to g_p , g_y to g_q , and vice versa (see Fig. 1).

Hutchings and Wolf (H-W) found the wave functions for the lowest doublets by fitting them to the g values of the two doublets (Table II) and to the crystallinefield energy levels of the $J = \frac{5}{2}$ state. They found that the only reasonable fit of the energy levels is obtained by assigning g_x to g_p and g_y to g_q . Whereas their wave functions fit the energy levels of the $J = \frac{5}{2}$ state, they do not provide a good fit to the g values of the doublets.⁵

The wave functions are given by H-W in an L, S, M_L , M_S representation; written in an L, S, J, M_J representation the $J = \frac{5}{2}$ state contains a small admixture of the $\frac{7}{2}$ state and vice versa. In our formalism we have considered only the splittings of pure J states¹²; therefore we only used those parts of the wave functions corresponding to pure J state. The admixture of other J states is very small and the errors incurred by neglecting this admixture are probably less than the error introduced by using the wave functions of Yb³⁺ in YGaG in lieu of those for Yb³⁺ in YbIG.

III. REDUCING THE NUMBER OF UNKNOWN PARAMETERS

In our model of the RE-Fe exchange interaction we make the basic assumption that this cluster interaction

¹⁰ M. Rotenberg, R. Bivins, N. Metropoulis, and J. K. Wooten, Jr., 3-j and 6-j Symbols (Technology Press, Cambridge, Massachusetts, 1959).

 $^{^{}n}$ K. M. Howell, University of Southampton Mathematics Department, Research Report 59-2, 1959 (unpublished).

¹² In our approximation we consider only pure J states and neglect the cross terms between different J states.

		$\Delta E_{Q} = \sum_{kq} \gamma_{kq}(Q) \alpha_{kq}$
 		² F _{5/2}
Ь	a	$\boldsymbol{\gamma}_{kq}(x)$
ñ	q	$- [7/7(7)^{1/2}][7/(5)^{1/2}a_c + 3b^2 + 4\sqrt{2}b_c]$
2	0	$[2/7(3)^{1/2}](b^{2} + \sqrt{2}b_{c})$
2	2	$- [4\sqrt{7}(35)]^2](5) + \sqrt{207}$ $- [4/7(35)]^2 [(5)]^2 ab \pm 5bc \pm (10)]^2 ac \pm 2\sqrt{7}b^2 \pm \sqrt{7}c^2]$
A	2	$- \begin{bmatrix} \frac{1}{2} / (35) + \frac{1}{2} \end{bmatrix} \begin{bmatrix} 35 + 36 + 36 + (15) + 46 + 2426 \end{bmatrix}$ $- \begin{bmatrix} 2\sqrt{5} / 21 / (75) \sqrt{2} + 75 \end{bmatrix} \begin{bmatrix} 36 + 36 + 76 + 76 + 76 + 76 + 76 + 76 +$
4	2	$\begin{bmatrix} 2\sqrt{2}/21 (11)^{4/3} \\ [2](3)^{4/$
	2	$\left[2\sqrt{2}/21(11)^{n-2} \right] \left[3u^{2} + 5(3)^{n-2}u^{2} - 18\sqrt{2}u^{2} + 4(10)^{n-2}u^{2} + 2(10)^{n-2}u^{2} \right]$
(4	$-\lfloor 2/21(11)^{1/2} \rfloor (5)^{1/2} d^{\alpha} + 5(5)^{1/2} d^{\alpha} + 12\sqrt{2} d^{\beta} \rfloor$
0	0	$\begin{bmatrix} 4\sqrt{3}/1 (1001)^{3/2} \end{bmatrix} \begin{bmatrix} (5)^{3/2} dc + 50^{\circ} - 5\sqrt{20}c \end{bmatrix}$
	2	$\begin{bmatrix} 4/7(143)^{1/2} \\ 1/2 c^2 \end{bmatrix} \begin{bmatrix} 2\sqrt{2ab} + 2(10)^{1/2} bc - 2ac - 2(5)^{1/2} b^2 - (5)^{1/2} c^2 \end{bmatrix}$
	4	$\left[\frac{2\sqrt{3}}{(143)^{1/2}}\right]\left[\sqrt{2a^2+5\sqrt{2c^2-4(5)^{1/2}ab}}\right]$
	6	$-\lfloor 12/7(13)^{1/2} \rfloor a^2$
L	_	$\boldsymbol{\gamma}_{kq}(y)$
R	q	
0	0	$-\left\lfloor 2/7(7)^{3/2} \rfloor \left\lfloor 2(5)^{3/2} dc + 30^{2} - 4\sqrt{20} c \right\rfloor$
2	0	$\left[\frac{4\sqrt{3}}{(35)^{1/2}}\right](b^2 - \sqrt{2}bc)$
	2	$\left[\frac{4}{7}(35)^{1/2}\right]\left[-(5)^{1/2}ab-5bc+(10)^{1/2}ac+2\sqrt{2}b^2+\sqrt{2}c^2\right]$
4	0	$[2\sqrt{2}/21(77)^{1/2}][7(5)^{1/2}ac-9b^2+2\sqrt{2}bc]$
	2	$[2\sqrt{2}/21(77)^{1/2}][3ab+3(5)^{1/2}bc+18\sqrt{2}ac-4(10)^{1/2}b^2-2(10)^{1/2}c^2]$
	4	$- [2/21(11)^{1/2}] [(5)^{1/2}a^2 + 5(5)^{1/2}c^2 - 12\sqrt{2}ab]$
6	0	$[4\sqrt{3}/7(1001)^{1/2}][(5)^{1/2}ac+5b^2+5\sqrt{2}bc]$
	2	$[4/7(143)^{1/2}][2\sqrt{2}ab+2(10)^{1/2}bc+2ac+2(5)^{1/2}b^2+(5)^{1/2}c^2]$
	4	$[2\sqrt{3}/7(143)^{1/2}][\sqrt{2}a^2+5\sqrt{2}c^2+4(5)^{1/2}ab]$
	6	$[12/7(13)^{1/2}]a^2$
		$oldsymbol{\gamma}_{kq}(z)$
k	q	
0		$[2/7(7)^{1/2}](5a^2+b^2-3c^2)$
2	0	$[2\sqrt{3}/7(35)^{1/2}](5a^2-c^2)$
	2	$[4/7(35)^{1/2}][(5)^{1/2}ab-bc]$
4	0	$[\sqrt{2}/21(77)^{1/2}](25a^2 - 14b^2 + 37c^2)$
	2	$[2\sqrt{2}/21(77)^{1/2}][39ab-5(5)^{1/2}bc]$
	4	$[4/21(11)^{1/2}]ac$
6	0	$[4\sqrt{3}/7(1001)^{1/2}](a^2+10b^2+5c^2)$
	2	$[16\sqrt{2}/7(143)^{1/2}](ab+(5)^{1/2}bc)$
	4	$[8(30)^{1/2}/7(143)^{1/2}]ac$
	6	0
		2F7.19
		$\gamma_{ko}(x)$
k	q	
0		$-[4/7(7)^{1/2}][2\sqrt{3}a'c'+2b'^{2}+(7)^{1/2}a'd'+(15)^{1/2}b'c']$
2	0	$[2/7(105)^{1/2}][8b'^2 - 5(7)^{1/2}a'd' + 3(15)^{1/2}b'c']$
	2	$- \big[2\sqrt{2}/7 (105)^{1/2} \big] \big[4(5)^{1/2} b'c' + 4(15)^{1/2} a'b' + 5a'c' + 3\sqrt{3}b'^2 + (105)^{1/2} b'd' + 5\sqrt{3}c'^2 \big]$
4	0	$ [2\sqrt{2}/7 (231)^{1/2}] [14a'c' - 4\sqrt{3}b'^2 - (21)^{1/2}a'd' - (5)^{1/2}b'c'] $
	2	$[4/21(231)^{1/2}][6b'c'+6\sqrt{3}a'b'-9(5)^{1/2}a'c'+3(15)^{1/2}b'^2-9(21)^{1/2}b'd'+5(15)^{1/2}c'^2]$
	4	$- [4/21(33)^{1/2}] [3(15)^{1/2}a'^2 + (15)^{1/2}c'^2 + 3\sqrt{3}a'b' + 3(35)^{1/2}c'd']$
6	0	$ [2/7 (3003)^{1/2}] [12\sqrt{3}a'c' + 40b'^2 - (7)^{1/2}a'd' - 15(15)^{1/2}b'c'] $
	2	$[2/7(429)^{1/2}][16b'c'+16\sqrt{3}a'b'-2(5)^{1/2}a'c'-3(15)^{1/2}b'^2-2(21)^{1/2}b'd'-5(15)^{1/2}c'^2]$
	4	$[2\sqrt{2}/7(143)^{1/2}][6\sqrt{3}a'^2 + 2\sqrt{3}c'^2 - (15)^{1/2}a'b' - 5(7)^{1/2}c'd']$
	6	$-[2/7(13)^{1/2}](a'^2+7d'^2)$

TABLE I. The exchange splittings of the lowest doublets of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ states of Yb³⁺ in YbIG, in terms of the components of the states $|JM_{J}\rangle$ in the wave functions in (2.5) and (2.6).

		$\Delta E_Q = \sum_{kq} \gamma_{kq}(Q) \alpha_{kq}$
7		$oldsymbol{\gamma}_{kq}(\mathrm{y})$
ĸ	q	$r_{A,B}$
0		$- \lfloor \frac{4}{7} / \frac{7}{7} \rfloor \lfloor \frac{2}{3} \sqrt{3} d^2 c^2 + 2b^2 - \frac{7}{7} (1)^{4/2} d^2 - \frac{1}{10} (1)^{4/2} d^2 c^2 \rfloor$
2	0	$\left[\frac{2}{7}(105)^{1/2}\right]\left[\frac{8b^{2}+5(7)^{1/2}a^{\prime}a^{\prime}-3(15)^{1/2}b^{\prime}c^{\prime}\right]$
	2	$[2\sqrt{2}/7(105)^{1/2}][-4(5)^{1/2}b'c'-4(15)^{1/2}a'b'+5a'c'+3\sqrt{3}b'^{2}+(105)^{1/2}b'd'+5\sqrt{3}c'^{2}]$
4	0	$[2\sqrt{2}/7(231)^{1/2}][14a'c'-4\sqrt{3}b'^{2}+(21)^{1/2}a'd'+(5)^{1/2}b'c']$
	2	$[4/21(231)^{1/2}][6b'c'+6\sqrt{3}a'b'+9(5)^{1/2}a'c'-3(15)^{1/2}b'^{2}+9(21)^{1/2}b'd'-5(15)^{1/2}c'^{2}]$
	4	$- [4/21(33)^{1/2}] [3(15)^{1/2}a'^{2} + (15)^{1/2}c'^{2} - 3\sqrt{3}a'b' - 3(35)^{1/2}c'd']$
6	0	$[2/7(3003)^{1/2}][12\sqrt{3}a'c'+40b'^2+(7)^{1/2}a'd'+15(15)^{1/2}b'c']$
	2	$[2/7(429)^{1/2}][16b'c'+16\sqrt{3}a'b'+2(5)^{1/2}a'c'+3(15)^{1/2}b'^2+2(21)^{1/2}b'd'+5(15)^{1/2}c'^2]$
	4	$[2\sqrt{2}/7(143)^{1/2}][6\sqrt{3}a'^2+2\sqrt{3}c'^2+(15)^{1/2}a'b'+5(7)^{1/2}c'd']$
	6	$[2/7(13)^{1/2}](a'^2+7d'^2)$
		$oldsymbol{\gamma}_{kq}(z)$
k	q	
0		$-\lfloor 2/7(7)^{1/2} \rfloor (5a'^2 + b'^2 - 3c'^2 - 7d'^2)$
2	0	$[1/7(105)^{1/2}](5a'^2+7b'^2-15c'^2+35d'^2)$
	2	$- [2\sqrt{2}/7(21)^{1/2}] [3\sqrt{3}a'b' - 2b'c' - (35)^{1/2}c'd']$
4	0	$[2/21(154)^{1/2}](45a'^2-21b'^2+19c'^2+21d'^2)$
	2	$[4/7(231)^{1/2}][5\sqrt{3}a'b'-8b'c'+3(35)^{1/2}c'd']$
	4	$- [4/7(33)^{1/2}] [(5)^{1/2}a'c' - (21)^{1/2}b'd']$
6	0	$[1/7(3003)^{1/2}](37a'^2+125b'^2+87c'^2+7d'^2)$
	2	$[4/7(429)^{1/2}][9\sqrt{3}a'b'+23b'c'+(35)^{1/2}c'd']$
	4	$[2\sqrt{2}/7(143)^{1/2}][17a'c'+(105)^{1/2}b'd']$
	6	$[4/(91)^{1/2}]a'd'$

TABLE II. Principal values of g tensors and exchange splittings for ytterbium in the garnets. The principal value g_x is along the local p axis, g_y along the local q axis, and g_z along the r or z axis (see Fig. 1).

	Principal		g values		Hutchingsd	Fypori	Exchange spli White's	ttings (cm ⁻¹) Theo- retical	Theo-
State	value	YbIGª	YGaG ^b	White	Wolf	mental ^a	eter fit ^e	(White's Ψ)	$(H-W's \Psi)$
Lowest ${}^2F_{7/2}$ doublet	x y z	3.7 ± 0.15 3.6 ± 0.15 2.8 ± 0.1	3.73 3.60 2.85	3.82 3.63 2.90	3.69 3.29 2.87	30.6 ± 0.2 26.1 ± 0.1 11.8 ± 0.2	27.9 25.8 23.9	30.6 26.8 18.7	34.3 21.8 11.8
Lowest ${}^{2}F_{5/2}$ doublet	x y z	1.8 ± 0.2 1.8 ± 0.2 ≤ 0.4	1.80 1.98 0.35	$1.81 \\ 1.98 \\ 0.43$	1.88 1.92 0.26	29.8 ± 0.2 5.6 ± 0.2 15.2 ± 0.1	23.3 8.1 13.0	29.8 5.6 15.2	29.8 5.6 15.2

See Ref. 2. The erroneous ordering of the principal values of the ²F_{5/2} state has been corrected.
See Ref. 5.
R. L. White (private communication).
^d These g values differ slightly from those given in Ref. 5, as only those parts of the wave functions were used that corresponded to pure J states.

TABLE III. The wave functions for the lowest doublets of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ states of Yb³⁺ in YGaG, referred to the system of axes described in Table II. Referred to these axes, the Hamiltonian appropriate to a cubic potential is of the form $\mathcal{H} \propto O_4^0 + 20O_4^2 - 15O_4^4$, where the O_n^m are the standard operator equivalents.

Reference	a	ь	с	<i>a</i> ′	b'	- c'	d'
Cubic Field ^a White ^b Hutchings & Wolf ^e Thomas ^d	$-0.612 \\ -0.463 \\ -0.461 \\ \cdots$	-0.646 -0.663 -0.671	0.456 0.558 0.583	0.216 0.256 0.241	0.484 0.513 0.509	-0.625 -0.638 -0.634	-0.573 -0.517 -0.519

^a The signs of the g values differ, e.g., the cubic-field wave functions give three positive g values, whereas the wave functions given by White have two negative and one positive g value. ^b R. L. White (private communication). ^c See Ref. 5. It is not possible to obtain unique coefficients for the ${}^{2}F_{7/2}$ wave function in an J, M_J representation. ^d J. Thomas, thesis, Université de Grenoble, 1962 (unpublished). The ${}^{2}F_{6/2}$ doublet was not considered by Thomas.

can be resolved into interactions of the RE ion with individual Fe ions (RE-Fe³⁺). The model we adopt is a generalization of the one Wolf and Elliott first proposed⁶; in it we assume that:

(1) the rare-earth-ferric-ion (RE-Fe³⁺) interaction takes place through the intermediary oxygen ions,

(2) with respect to the rare-earth-oxygen (RE-O) axis the RE-Fe³⁺ exchange is axial,

(3) as there are two types of oxygen ions that neighbor on a rare-earth, it is reasonable to assign a different exchange constant $A_{K}(m_{l})$ to each.

The cluster exchange potential based on this model can be found by the following procedure.

(1) The Hamiltonian for a rare-earth-ferric-ion exchange interaction is given by Eq. (I,2.4)

$$\mathfrak{K}_{\mathrm{ex}} = -2A_{i}(l, m_{l}, m_{l}')_{\mathrm{op}}\mathbf{s}(i) \cdot \mathbf{S}(\mathrm{Fe}^{3+}), \qquad (3.1)$$

where i = RE electron, and $S(\text{Fe}^{3+}) = \text{total spin of ferric}$ ion. As it is assumed that the exchange-potential operator (I, 2.5) for a RE-Fe³⁺ interaction is axial when referred to the RE-O axis,13 we can write it as

$$A_{i}(m_{l})_{op} = \sum_{n=0}^{l} \alpha_{n} T_{0}^{[2n]}(i), \qquad (3.2)$$

where the parameters α_n are given by Eq. (I, 2.8)

$$\alpha_{n} = (4n+1) \sum_{m_{l}=0}^{l} (-)^{l-m_{l}} (2-\delta_{m_{l}}) A(m_{l}) \\ \times \bar{V}(ll2n; -m_{l}, m_{l}, 0) \quad (3.3)$$

and $A(m_l) \equiv (lm_l | A_{op} | lm_l)$ is an exchange constant of the rare-earth-ferric-ion interaction for an orbital state m_l of a RE 4f electron referred to the RE-O axis.¹⁴

(2) As the scalar product of the spins is an invariant, the only part of the Hamiltonian (3.1) that changes under rotation is the exchange potential (3.2). The transformation of an irreducible tensorial set under a coordinate transformation is given as¹⁵

$$T_0^{[2n]'} = \sum_{\mu} \mathfrak{D}_{0\mu}^{(2n)} T_{\mu}^{[2n]}, \qquad (3.4)$$

where $T_0^{[2n[']} = axial$ tensor referred to the line joining the rare-earth and oxygen ions and $T_{\mu}^{[2n]} = \text{tensor re-}$

$$\alpha_n = (-1)^n \frac{(2n)!(3+n)!(4n+1)}{(n!)^2(3-n)!} \left[\frac{(6-2n)!}{(7+2n)!} \right]^{1/2} A.$$

¹⁵ A. R. Edmonds, Angular Momentum in Quantum Mechanics (Princeton University Press, Princeton, New Jersey, 1957), p. 22, Eq. (5.3).

ferred to g-tensor axes. The transformation matrix elements $\tilde{D}_{0\mu}^{(2n)}$ are given by Edmonds,¹⁶ and the rotated exchange potential (3.2) is

$$RA_{\rm op}(i)R^{-1} = \sum_{n=0}^{1} (4\pi/(4n+1))^{1/2} \alpha_n^K \\ \times \sum_{\mu=-2n}^{2n} Y_{\mu}^{2n}(\theta^K, \phi^K) T_{\mu}^{[2n]}(i), \quad (3.5)$$

where θ^{K} and ϕ^{K} are given in Appendix A, and the spherical harmonics are defined by Edmonds.¹⁷

(3) As the iron sublattice is ferrimagnetically coupled we can write

$$\mathbf{S}(j) = \pm \mathbf{S}(K),$$

when j refers to the equivalent oxygen ions (with respect to a RE ion) of a specific type K. By applying the symmetry operations Eqs. (A1) to the Hamiltonian (3.1) we find¹⁸

$$(\mathfrak{K}_{ex})_{K} = -2\langle RA_{K}(i)_{op}R^{-1}\rangle \mathbf{s}(i)\cdot \mathbf{S}(K), \quad (3.6)$$

where the potential $\langle RA_{K}(i)_{op}R^{-1}\rangle$ differs from (3.5) in that it contains the sum

$$\sum_{j=1}^{4} Y_{\mu}^{2n}(\theta_{j}^{K},\phi_{j}^{K}).$$

With the relations (A1) and the properties of the spherical harmonics¹⁷ we relate the transformation matrices for the various oxygens of a specific type K to one another. We find that the above sum vanishes for odd values of μ ; the result for even μ together with Eq. (3.5) gives

$$\langle RA_{K}(i)_{\rm op}R^{-1}\rangle = 2 \sum_{n=0}^{i} (4\pi/(4n+1))^{1/2} \alpha_{n}^{K}$$
$$\times \sum_{\mu=-2n}^{2n} [Y_{\mu}^{2n}(\theta^{K}, \phi^{K}) + Y_{-\mu}^{2n}(\theta^{K}, \phi^{K})] T_{\mu}^{[2n]}(i). \quad (3.7)$$

This is the RE-Fe cluster exchange potential through one type of oxygen.

(4) By summing the Hamiltonian (3.6) over the different types of oxygen ions present in the complex surrounding the rare-earth ion, we have

$$\mathcal{K}_{\mathbf{ex}} = -2\sum_{K} \langle RA_{K}(i)_{\mathrm{op}} R^{-1} \rangle \mathbf{s}(i) \cdot \mathbf{S}(K) \,. \quad (3.8)$$

The spins S(K) are related as follows¹⁹

$$\mathbf{S}(K)\rangle/|\langle \mathbf{S}(K)\rangle| \equiv \hat{M}, K=1, 2,$$

where \hat{M} is a unit vector in the direction of the magnetization of the iron sublattice, and the molecularfield approximation is used on the spin of the iron sub-

¹³ It is possible to replace the two successive rotations of the exchange potential from the RE-O to the Re-Fe³⁺ axis to the axis of the magnetic g tensor by one direct rotation which circumvents the rotation to the Re-Fe³⁺ axis. With the forethought that the exchange potential must ultimately be referred to the g-tensor axis, we talk about a RE-Fe³⁺ exchange Hamiltonian in which the exchange potential is referred to the Re-O axis, because it is most simply expressed when referred to the latter axis. ¹⁴ Wolf and Elliott (see Ref. 6) assumed that only the state

 $m_l=0$ has a significant exchange; therefore Eqs. (I,2.5) and (I,2.8) are written as $A(m_l) = A\delta_{m_l}^0$ and

¹⁶ A. R. Edmonds, Ref. 15, p. 25, Eqs. (5.14) and (5.18).
¹⁷ A. R. Edmonds, Ref. 15, pp. 21, 24.
¹⁸ The brackets about the exchange potential denote an *algebraic* average, not a quantum-mechanical (trace) average.
¹⁹ The brackets about the spin operators denote a *quantum-transit of another and the spin operators*.

mechanical average.

lattice. The average value of the spin of the iron sublattice is absorbed in the constants α_n^K . We can thus write the Hamiltonian (3.8) as

$$\mathcal{K}_{\text{ex}} = -2\langle A(i)_{\text{op}} \rangle \mathbf{s}(i) \cdot \hat{M}, \qquad (3.8')$$

$$\langle A(i)_{\rm op} \rangle \equiv \sum_{\kappa} \langle RA_{\kappa}(i)_{\rm op} R^{-1} \rangle.$$
 (3.9)

The Hamiltonian for the rare-earth exchange interaction with the neighboring ferric ions through the oxygen atoms may also be written in a form similar to Eq. (I,2.4). Applying the molecular-field approximation to that Hamiltonian, we find

$$\mathcal{GC}_{\mathbf{ex}} = -2[M(T)/M(0)]_{\mathbf{YIG}} \times A_i(l,m_l,m_l')_{op}\mathbf{s}(i)\cdot\hat{M}, \quad (3.10)$$

where $A_i(l,m_l,m_l')_{op}$ is the exchange potential operator. The average value of the spin of the iron sublattice is incorporated in the exchange parameters as in Eq. (I,4.8a). By comparing the Hamiltonians (3.10) and (3.8') and from the definition of the exchange potential Eq. (I, 2.5), we find that

$$\langle A(i)_{\rm op} \rangle = \sum_{k=0}^{2l} \sum_{q=-k}^{k} \alpha_{kq} T_q^{[k]}(i).$$
 (3.11)

Upon placing Eqs. (3.7) and (3.9) in (3.11) we find the exchange potential parameters are related to the $A_K(m_l)$ as follows.

For k,q even:

$$\alpha_{kq} = 2(4\pi/(2k+1))^{1/2} \times \sum_{K=1}^{2} \alpha_{k/2} [Y_{q}^{k}(\theta^{K}, \phi^{K}) + Y_{-q}^{k}(\theta^{K}, \phi^{K})], \quad (3.12)$$

where

$$\alpha_{k/2}{}^{K} = (2k+1)^{1/2} \sum_{m_{l}=0}^{l} (-)^{l-m_{l}} (2-\delta_{m_{b}}{}^{0}) A_{K}(m_{l}) \\ \times \bar{V}(llk; m_{l}, -m_{l}, 0). \quad (3.13)$$

For k,q odd:

IV. SOLUTION FOR EXCHANGE POTENTIAL PARAMETERS

 $\alpha_{kq}=0.$

The exchange splittings of the two doublets provide six inhomogeneous equations with ten unknowns α_{kq} . The relations (3.12) and (3.13) not only reduce the number of unknowns to eight, but they also express the splittings in terms of the $A_k(m_l)$ on which it is possible to make some approximations (of physical significance) and thereby reduce the number of unknowns to less than six. The approximation which allows us to fit the experimental data with the least number of unknowns is the most desirable.

With the doublet wave functions of White, and Hutchings and Wolf (Table III) we evaluated the exchange splittings, i.e., the $\gamma_{kg}(Q)$ in Table I. The angles θ^{K} , ϕ^{K} with g_{z} parallel to r given in Appendix A

(Table V) were used to evaluate the relations (3.12) and (3.13) which relate the cluster exchange potential parameters α_{kq} to the individual RE-Fe³⁺ exchange parameters $A_K(m_l)$. The resulting set of six equations for the splittings in terms of the unknown $A_K(m_l)$ is written in a matrix form as

$$\Delta \mathbf{E} = \mathbf{\Gamma} \times \mathbf{A}, \qquad (4.1)$$

where ΔE is a 6×1 column matrix of the experimental exchange splittings, A is an 8×1 column matrix of the unknowns $A_K(m_l)$, and Γ is a 6×8 matrix

$$\mathbf{\Gamma} = \mathbf{\Gamma}' \times (\mathbf{B} \times \mathbf{C}) \,. \tag{4.2}$$

The 6×10 matrix Γ' has for its elements the $\gamma_{kq}(Q)$ given in Table I. The elements of the 10×8 matrix **B** are given by Eq. (3.12) and those of the 8×8 matrix C are given by Eq. (3.13). In analogy to the g tensor, it is impossible experimentally to distinguish the principal x and y axes of the exchange tensor for the iron garnets. It is therefore necessary to try the two possible assignments ΔE_x to p, ΔE_y to q, and vice versa.²⁰ The signs of the exchange splittings are not known, and we must try all combinations of signs to find a best fit.

As a first attempt to solve the set of equations (4.1)we made the Wolf and Elliott approximation¹⁴ of neglecting all $A_K(m_l)$ other than those for $m_l=0$. We were unable to find a fit with this approximation. We next solved for six of the unknowns $A_K(m_l)$ in terms of the remaining two, but were unable to find a solution in which $A_K(m_l)$ decreases as m_l increases.²¹

The solution we found was to totally neglect the $A_K(m_l)$ for K=1, i.e., no exchange via the type-1 oxygen ions. Neglecting $A_1(m_l)$ leaves four unknowns in six equations. Solving for the unknowns by using four of the six equations, we use the remaining two equations to determine the consistency of the solution, i.e., how well the solution fits the two remaining exchange splittings. We concluded that better fits are consistently found (1) by assigning ΔE_x and g_x to the p axis and ΔE_y and g_y to the q axis²² (see Fig. 1); and (2) when the exchange splittings are of the same sign as the g values for the $J = \frac{5}{2}$ doublet and of opposite sign for the $J = \frac{7}{2}$ doublet²³ (in the $\frac{7}{2}$ state, L and S are parallel, whereas in the $\frac{5}{2}$ state they are antiparallel). The best fits to the experimental exchange splittings obtained with White's, and Hutchings' and Wolf's wave functions are given in Table II and the $A_2(m_l)$ that produce these fits $[A_1(m_l) \equiv 0]$ are given in Table IV. The exchange

$$\langle \mathcal{K}_{\mathrm{ex}} \rangle = -\beta \mathbf{H}_{\mathrm{eff}} \cdot \mathbf{g}' \cdot \mathbf{J} = 2M \cdot \mathbf{A} \cdot J,$$

we have the signs of the magnetic g and exchange (A) tensors the same for $J = \frac{T}{2}$ and opposite for $J = \frac{5}{2}$.

²⁰ When assigning ΔE_x to p and ΔE_y to q it is necessary to use the appropriate wave functions, i.e., g_x to g_p and g_y to g_q . ²¹ This is in keeping with a model of an axial RE-Fe³⁺ interaction in which the exchange is related to the overlap of the RE ion on

the oxygen.

²² This assignment of g_x and g_y agrees with the one found by Hutchings and Wolf (see Ref. 5).

²³ By our definition of the splittings, Eq. (I,4.1):

TABLE IV. Exchange potential parameters for Yb3+ in ytterbium iron garnet.

Parameters for RE-Fe exchange through a n.n.n. oxygen ion (cm ⁻¹)						Parameters for entire RE-Fe exchange interaction (cm ⁻¹)								
Wave functions used	$A(m\iota=0)$	$A(m\iota = \pm 1)$	$A(m_l = \pm 2)$	$A(m_l=\pm 3)$	α_{00}	α 20	a 22	α¥0	α42 `	a44	CC 60	α62	cx 64	α66
White's Hutchings' and Wolf's	8.48 6.41	8.60 6.52	-29.4 -29.6	4.43 6.17	-36.6 -41.4	19.2 1.43	6.76 0.50	156 154	47.4 47.1	-207 -206	-46.1 -44.6	-13.6 -13.2	50.2 48.5	71.3 68.9

potential is derived from the exchange constants $A_K(m_l)$ by the relation

$$\boldsymbol{\alpha} = (\mathbf{B} \times \mathbf{C}) \times \mathbf{A}, \qquad (4.3)$$

where $(\mathbf{B} \times \mathbf{C})$ is the 10×8 matrix in Eq. (4.2), α is a 10×1 column matrix whose elements are the familiar α_{kq} and the 8×1 column matrix A has for its elements $A_K(m_l)$. The exchange potentials, corresponding to the sets of $A_{\kappa}(m_l)$ that give the best fits, are given in Table IV. As we will see in the next section, the spherical component α_{00} forms an independent check on the merit of our fit.

V. DISCUSSION OF RESULTS

On the basis of our model of the RE-Fe exchange interaction, we have found a good four-parameter fit of the exchange splittings of the lowest doublets of the ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$ states of Yb³⁺ in YbIG, only by neglecting the type-1 exchange constants $A_1(m_l)$. We conclude from this that the RE-Fe exchange interaction takes place primarily through the next-nearest neighbor (n.n.n.) oxygens (type 2), whereas the nearest neighbor (n.n.) oxygens (type 1) are comparatively inert. This result is not unexpected. In their analysis of the RE-O-Fe super-exchange angles in the garnets, Geller and Gilleo²⁴ suggest, first that the tetrahedrally coordinated iron-RE exchange J_{cd} is larger than the octahedrally coordinated iron-RE exchange J_{ca} ; and second that the two nearestneighbor ferric ions, in the tetrahedral sites, are ineffective in the RE-Fe exchange. The experimental results of LeCraw et al., 25 and Hutchings et al. 26 are also compatible with our result. The experiments of LeCraw have demonstrated that the exchange field at the rareearth $\{c\}$ site depends primarily on the number of ferric ions in the tetrahedral (d) sites; those of Hutchings show that the field is relatively unaffected by the number of ferric ions in the octahedral [a] sites. These results lead them to conclude that J_{cd} is much greater than J_{ca} , but they do not necessarily indicate that the two nearest neighbor ferric (d) ions are inactive in the RE-Fe exchange.

An alternative way of rationalizing that the n.n. O-RE (type 1) linkages are comparatively inert is to note that the angle that this type linkage makes with the plane of the Fe(a)-O-Fe(d) linkage (67°) is much larger than the corresponding angle for the n.n.n. O-RE (type 2) linkage (31°) , the ratio of the squares of the cosines being six. The RE-O overlap for the latter linkage will be much larger, and the RE-Fe superexchange through this linkage will be concomitantly bigger. This alternative does not require us to assume that J_{cd} is much greater than J_{ca} .

The exchange constants $A_2(m_l)$ derived from our analysis (Table IV) by using the wave functions of White, or those of Hutchings and Wolf, are similar. This is especially true for the large antiferromagnetic $m_l = \pm 2$ (relative to the Re-O axis) constants. Despite this qualitative similarity of the exchange constants obtained with the two wave functions, the exchange splittings derived from the H-W wave functions agree more closely with experimental values. This agreement with exchange splittings unfortunately requires some sacrifice of the agreement with g values. Nevertheless, considering both g values and exchange splittings, the H-W wave functions appear to be the more satisfactory, and we consequently adopt the parameters $A(m_l)$ and α_{kq} so derived.

The exchange potentials (Table IV) are similar except for their second-rank components. The sensitivity of this component to the wave functions used is reminiscent of the sensitivity displayed by the crystal field parameter $A_2^m \langle r^2 \rangle$ to environment.²⁷ In order to extrapolate the values of α_{kq} calculated here to other rareearths, we believe it prudent to use only the ratios²⁸ α_{kq}/α_{00} . As the second-rank components α_{2q} appear to be particularly sensitive to the wave functions, extrapolation of their values would be questionable. As no other data are available on the anisotropy of the RE-Fe, exchange, it is impossible at this time to check the validity of extrapolating the ratios α_{kq}/α_{00} for k=4, 6.

It seems to us that the assumption of an axial exchange potential (about the RE-O axis) for the individual RE-Fe³⁺ interactions is the weakest assumption in our model. Although it is true that two-center exchange is axial about the line connecting the centers. the RE ion is influenced not only by the nearest neighbor oxygens but also by more distant ions.²⁹

As an independent check on the spherical component of the exchange potential, we have used the parameter α_{00} to calculate the isotropic component of the exchange

²⁴ S. Geller and M. A. Gilleo, J. Phys. Chem. Solids 3, 30 (1957). ²⁵ R. C. LeCraw, J. P. Remeika, and H. Matthews, Phys. Letters 12, 9 (1964).
 ²⁶ M. T. Hutchings, C. G. Windsor, and W. P. Wolf, Bull. Am. Phys. Soc. 10, 329 (1964).

²⁷ See Hutchings and Wolf, Ref. 5.

²⁸

²⁸ This has been pointed out by us in Ref. 1.
²⁹ Hutchings and Wolf have shown (see Ref. 5) that the crystalline field at the RE(c) site in gallium garnet has major contribu-tions from other than the nearest neighbors.

$$\alpha_{00} = (1/\sqrt{7})\beta H_{\text{ex}}.$$
 (4.4)

The calculated values of 19.9°K and 22.5°K for the two sets of wave functions, respectively, compare very favorably with the value found experimentally by Caspari et al.³¹ (20°K for Yb³⁺ in YbIG). A verification of the other parameters in the exchange potential must wait for new experimental data on the anisotropy of the RE-Fe exchange interaction. This should preferably be on Yb³⁺; otherwise there enters the questionable extrapolation of the exchange potential from one rare-earth to another.

VI. CONCLUSIONS

We have evaluated the exchange potential parameters α_{kq} which characterize the anisotropy of the Yb-Fe exchange interaction. These parameters may be provisionally used to estimate the anisotropy of RE-Fe exchange interactions for other rare-earths. This evaluation of the exchange potential corroborates the current belief that the exchange interaction J_{cd} is much greater than J_{ca} and further refines this model. Specifically we conclude that the RE-Fe exchange interaction takes place primarily through the n.n.n. oxygen ions; the n.n. oxygen ions are comparatively inert. Finally it should be emphasized that in contradistinction to the 3d-transition-element ions, the exchange interactions involving 4*f*-rare-earth ions may be highly anisotropic. This is due to their large spinorbit couplings and, as is often the case, relatively small crystalline fields.

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APPENDIX A

The oxygen ions are situated at the corners of an approximate cube with the rare-earth ion at the center; see Fig. 1. The position of an ion is given by the angle θ it makes with a chosen g-tensor axis called the z axis of the spherical polar coordinates, and the angle ϕ it makes with the axis obtained from rotating the chosen z axis 90° clockwise about one of the two remaining axes. Which axis, p, q, or r, is called the z axis is not a trivial matter. As crystal-field wave functions for the rare-earth ion's electrons will be applied to the exchange Hamiltonian, it is helpful to have both referred to the same axes of quantization; otherwise they would have to be rotated to a common set of axes.

The angles that an oxygen ion makes with the g-tensor axes are given in Table V32 for three different coordinate

TABLE V. The position of one oxygen ion of each type with respect to g-tensor axes (axes of local D_2 symmetry) in yttrium iron garnet.⁴

g_x parallel g_y parallel	to: <i>r</i> to: <i>q</i>	r Þ	$\stackrel{p}{q}$	For a cubic coordination $p \\ q$
Type 1				
θ^1	125° 36'	80° 48′	37° 09′	35° 16′
ϕ^1	11° 22′	36° 07′	15° 25′	0
r_{1}^{b}	2.37 Å	2.37 Å	2.37 Å	
Type 2				
θ^2	126° 30′	37° 32′	82° 50′	90°
ϕ^2	81°	78° 06′	53° 06′	54° 44′
$r_2^{\rm b}$	2.43 Å	2.43 Å	2.43 Å	

^a See Ref. 32. ^b The lattice constant for YbIG is 12.302 Å while that for YIG is 12.376 Å; therefore r_1 and r_2 for YbIG will be proportionately smaller than the values given for YIG.

systems. The positions of the remaining three oxygen ions of the same *type* are related to the original ion by the following relations:

$$\begin{aligned} \theta_1 &= \theta, \, \phi_1 = \phi; \quad \theta_3 = \pi - \theta, \, \phi_3 = -\phi; \\ \theta_2 &= \theta, \, \phi_2 = \phi + \pi; \quad \theta_4 = \pi - \theta, \, \phi_4 = \pi - \phi. \end{aligned}$$
(A1)

³⁰ This relation is given in footnote 12 of Ref. 1.

³¹ M. E. Caspari, A. Koicki, S. Koicki, and G. T. Wood, Phys. Letters 11, 195 (1964).

³² The coordination of the oxygen ions about the rare-earth (c)site was supplied by W. P. Wolf (private communication) for g_x parallel to p and g_y parallel to q. The polar axis is g_z .