

Influence of spin orbit coupling and lanthanide contraction on the exchange interaction in rare earth garnets

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Abstract. The exchange constants observed in the rare earth iron garnets, obtained from fitting magnetization and paramagnetic susceptibility as a function of temperature have been analysed in terms of Anderson's theory of superexchange. The transfer integrals and covalency parameters have been obtained for various rare earth ions overlapping with oxygen.

Keywords. Exchange constants; superexchange; transfer integrals; covalency parameters; molecular field constants.

1. Introduction

In an earlier paper (Srivastava *et al* 1982) we had reported the simultaneous fitting of saturation magnetisation (M_s) and paramagnetic susceptibility (χ) for the ferrimagnetic garnets $R_3Fe_5O_{12}$ where R is yttrium or a trivalent rare earth ion with configuration (Xe) $4f^n$ ($7 \leq n \leq 13$). We had used the molecular field constants to determine the exchange constants by means of the equation

$$J_{ij} = \frac{g_i g_j \mu_B^2 n_j \lambda_{ij}}{2 Z_{ij}}, \quad (1)$$

where g_i , g_j are the g factors of the sublattices i and j , λ_{ij} are the molecular field constants, n_j is the number of j ions per unit mole and Z_{ij} is the number of $n - n_j$ ions to an ion on i th sublattice. But if one of the ions involved is a rare earth ion then (1) is not the correct expression to convert the molecular field constants to J_{ij} . This is because for the rare earths the orbital momentum is not quenched and hence the exchange energy is

$$E_i = -2n_j Z_{ij} J_{ij} (g_i - 1) \bar{J}_i \cdot \bar{S}_j. \quad (2)$$

Here, we have assumed that the i th ion is a rare earth and the factor $(g_i - 1)$ comes because the rare earth spin has to be projected on J_i the angular momentum. In terms of λ_{ij} , E_i is given by

$$\begin{aligned} E_i &= -\mu_i \cdot \mu_j = -g_i \bar{J}_i \mu_B \cdot \lambda_{ij} \bar{M}_j, \\ &= -n_j g_i g_j \mu_B^2 n_j \lambda_{ij} \bar{J}_i \cdot \bar{S}_j \end{aligned} \quad (3)$$

From (2) and (3) we get

$$J_{ij} = \frac{g_i g_j \mu_B^2 n_j \lambda_{ij}}{2 Z_{ij} (g_i - 1)}. \quad (4)$$

Table 1. Exchange constants ($^{\circ}\text{K}$) in garnets ($\text{R}_3\text{Fe}_5\text{O}_{12}$).

R	Values in $^{\circ}\text{K}$		
	$-J_{ac}$	$-J_{dc}$	$-J_{cc}$
Y	0	0	0
Gd	0.60	1.8	0
Tb	1.12	2.0	0
Dy	2.97	2.97	-0.9
Ho	2.64	2.80	0
Er	2.70	3.40	0
Tm	2.64	3.96	0
Yb	21.00	16.1	-0.2

The $-J_{aa}$, $-J_{dd}$ and $-J_{dd}$ values are 6.45, 30.40 and 12.05 respectively in all the cases.

Equation (4) differs from (1) because of the factor $(g_i - 1)$ in the denominator. Hence the exchange constants have to be corrected by dividing the values reported earlier (Srivastava *et al* 1982) by $(g_i - 1)$ where g_i is the g factor of the rare earth site. These are shown in table 1.

2. Exchange constants from Anderson's theory

We give below the calculation of exchange constants from Anderson's theory of superexchange for these garnets. For the exchange between a rare earth and Fe^{3+} ions in garnets Levy (1966) has shown that if the Z axis for the interaction is chosen as the RE-O^{2-} bond direction then the only orbital on the RE ion contributing to the exchange is the one with $m_l = 0$ (*i.e.* f_z orbital). Following the same convention we find that the only transfer integral in Anderson's expression for 180° superexchange interaction is $b_{\sigma\sigma}$ arising from the overlaps of f_z orbital on RE ion and $e_g(d_z^2)$ on Fe^{3+} with a p_z orbital on the O^{2-} ion. Similarly the only transfer integral for the 90° exchange is $b_{\pi\sigma}$ arising from overlaps of t_{2g} and f_z orbitals with p_z orbital on oxygen. Thus we have (ignoring direct overlap of magnetic orbitals)

$$J_{ij} = -\frac{1}{4(g_i - 1)J_i S_j} 2 \frac{b_{\sigma\sigma}^2}{U} \text{ for } 180^{\circ} \text{ superexchange} \quad (5a)$$

$$J_{ij} = -\frac{1}{4(g_i - 1)J_i S_j} 2 \frac{b_{\pi\sigma}^2}{U} \text{ for } 90^{\circ} \text{ superexchange} \quad (5b)$$

In rare earths the spin orbit interaction is very strong compared to the crystal field energy, hence the ground state wavefunction will have admixtures of states with all values of m_l . However, as explained above only the $m_l = 0$ state contributes to the superexchange. Hence if we assume that all the m_l states have equal probability of being occupied then the probability that the state $m_l = 0$ has unpaired electron is $1 - (n - 7)/7 = 2 - (n/7)$ where n is the number of electrons in the $4f$ shell ($n \geq 7$). Using this in (5) and noting that J_{ac} is a predominantly 90° exchange while J_{dc} is a 180°

exchange we get for a $f^n - d^5$ superexchange interaction

$$J_{ac} = -\frac{1}{4(g_i - 1) J_i S_j} 2 \frac{b_{\sigma\sigma}^2}{U} \left(2 - \frac{n}{7} \right), \quad (6a)$$

$$J_{ac} = -\frac{1}{4(g_i - 1) J_i S_j} 2 \frac{b_{\pi\sigma}^2}{U} \left(2 - \frac{n}{7} \right). \quad (6b)$$

The values of the coulomb energy can be estimated by a procedure used by Anderson (1959) to evaluate U for the 3d series transition metal ions. Taking the free ion ionisation potential (IP) for these ions we find that $I_4 - I_3$ i.e. the difference between the 4th and 3rd IP gives the free ion U . This has to be corrected in the solid. Firstly the transfer of electrons take place through a finite distance and not to infinity as is the case for calculating IP. Anderson estimated this correction to be 4 eV for 3d electrons. We shall assume the same correction for R^{3+} ions. The next correction is the dielectric polarisation correction because the coulomb repulsion takes place in a dielectric medium and not in vacuum. This gives another correction of 4 eV. Finally because of covalency another 10% correction is required. Using the IP calculated by Sugar and Reader (1973) and using the above method we get $U = 10 \text{ eV} \pm 1 \text{ eV}$ for all the rare earth ions except Gd^{3+} as shown in table 2. Since the ground state of Gd^{2+} is $5d^2 f^7$ and not f^8 , the U value for Gd will reduce if the correct IP for $4f^7 - f^8$ transition is taken. Hence we can assume $U = 10 \text{ eV}$ for all the heavy rare earths. Using (4) instead of (1) as was used in our earlier work (Srivastava *et al* 1982) to get the correct values of J_{ij} we have obtained the values of $b_{\sigma\sigma}$ and $b_{\pi\sigma}$ using (7) for all these garnets which are given in table 3. In table 3 we also give the distance of closest approach of the rare earth and oxygen orbitals

$$S^{-1} = \frac{r_{R-O} - (r(R^{3+}) + r(O^{2-}))}{r(R^{3+}) + r(O^{2-})}.$$

The values of r_{R-O} , $r(R^{3+})$, $r(O^{2-})$ are from Tch  ou *et al* (1970), Khattak and Yang (1979) and CRC handbook (1980) respectively. Figure 1 gives a plot of b^2 against S^{-1} for both $b_{\sigma\sigma}^2$ and $b_{\pi\sigma}^2$. This curve resembles the curve obtained by Slater (1953) for metals. However, $b_{\sigma\sigma}^2$ does not show the peak in the observed region of overlap. Yb does not fit in the above scheme because as shown by Copland (1970) the 5p shell plays a

Table 2. Coulomb energy U (eV) for rare earth ions.

Ion	Ionisation potential (eV)		Free ion	Corrected U (eV)	Covalency correction (10%)	Corrected U in solid (eV)
	I_3	I_4	$U = I_4 - I_3$ (eV)			
Gd	20.63	44.01	23.78	15.38	1.54	13.84
Tb	21.91	39.79	12.88	9.88	0.99	8.89
Dy	22.79	41.47	18.68	10.68	1.07	9.61
Ho	22.84	42.48	19.64	11.68	1.17	10.57
Er	22.74	42.65	19.91	11.91	1.19	10.92
Tm	23.68	42.69	19.01	11.01	1.10	9.91
Yb	25.03	43.74	18.71	10.71	1.07	9.64

The correction for $n - n$ and dielectric polarization was 8 in all the cases.

Table 3. Transfer integrals in garnets $R_3Fe_5O_{12}$.

R	J_i	$b_{\sigma\sigma}^2$ (eV) ²	$b_{\pi\sigma}^2$ (eV) ²	S^{-1}
				$\frac{r(R-O) - r(R^{3+}) - r(O^{2-})}{r(R^{3+}) + r(O^{2-})}$
Gd	3.5	0.0271	0.0091	0.016
Tb	6.0	0.0295	0.0168	0.022
Dy	7.5	0.0448	0.0448	0.024
Ho	8.0	0.0419	0.0398	0.026
Er	7.5	0.0513	0.0408	0.032
Tm	6.0	0.0596	0.0398	0.035
Yb	3.5	0.0240	1.15	0.037

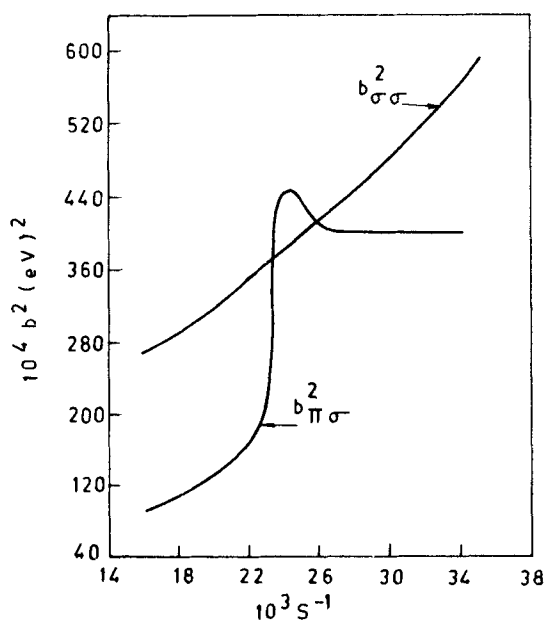


Figure 1. Transfer integrals in garnets.

dominant role in superexchange in YbIG, unlike the other garnets where the 4f shell is the dominant orbital contributing to superexchange.

3. Covalency parameters

Zeiger and Pratt (1973) have shown that the transfer integrals b_{ij} are related to the covalency parameters λ_{ic} and λ_{jc} , where c refers to the intervening anion by

$$b_{ij} = \lambda_{ic}\lambda_{jc}\Delta E_c$$

where ΔE_c is the one electron ionization energy of the anion. For the $Fe^{3+}-Fe^{3+}$

Table 4. Covalency parameters and transfer integrals in garnets.

	Type of exchange	Transfer integral	Value of b_k (eV)	λ_σ ($\text{Fe}^{3+}\text{-O}^{2-}$)	λ_π ($\text{Fe}^{3+}\text{-O}^{2-}$)	λ_σ ($\text{R}^{3+}\text{-O}^{2-}$)
Fe^{3+}	J_{ad}	$b_{\sigma\sigma}$	0.48	0.24		
		$b_{\pi\pi}$	0.18		0.14	
	J_{dd}	$b_{\sigma\sigma'}$	0.12	0.12		
$b_{\pi\sigma}$		0.30	0.25	0.14		
Gd^{3+}	J_{ac}	$b_{\pi\sigma}$	0.095		0.14	0.078
	J_{dc}	$b_{\sigma\sigma}$	0.16	0.25		0.08
Tb^{3+}	J_{ac}	$b_{\pi\sigma}$	0.13		0.14	0.107
	J_{dc}	$b_{\sigma\sigma}$	0.17	0.25		0.08
Dy^{3+}	J_{ac}	$b_{\pi\sigma}$	0.21		0.14	0.17
	J_{dc}	$b_{\sigma\sigma}$	0.21	0.25		0.098
HO^{3+}	J_{ac}	$b_{\pi\sigma}$	0.20		0.14	0.16
	J_{dc}	$b_{\sigma\sigma}$	0.20	0.25		0.094
Er^{3+}	J_{ac}	$b_{\pi\sigma}$	0.20		0.14	0.17
	J_{dc}	$b_{\sigma\sigma}$	0.22	0.25		0.105
Tm^{3+}	J_{ac}	$b_{\pi\sigma}$	0.20		0.14	0.16
	J_{dc}	$b_{\sigma\sigma}$	0.24	0.25		0.11
Yb^{3+}	J_{ac}	$b_{\pi\sigma}$	1.07		0.14	0.8
	J_{dc}	$b_{\sigma\sigma}$	0.15	0.25		0.07

exchange we have

$$\begin{aligned}
 b_{\sigma\sigma} &= \lambda_\sigma(\text{Fe}^{3+})\lambda_\sigma(\text{Fe}^{3+})\Delta E_c \\
 b_{\pi\pi} &= \lambda_\pi(\text{Fe}^{3+})\lambda_\pi(\text{Fe}^{3+})\Delta E_c \\
 b_{\pi\sigma} &= \lambda_\pi(\text{Fe}^{3+})\lambda_\sigma(\text{Fe}^{3+})\Delta E_c \\
 b_{\sigma\sigma'} &= \lambda_\sigma(\text{Fe}^{3+})\lambda_\sigma(\text{Fe}^{3+})\Delta E_c
 \end{aligned}
 \tag{7}$$

For $\text{Fe}^{3+} - \text{R}^{3+}$ exchange we have

$$\begin{aligned}
 b_{\pi\sigma} &= \lambda_\sigma(\text{R}^{3+})\lambda_\pi(\text{Fe}^{3+})\Delta E_c \\
 b_{\sigma\sigma} &= \lambda_\sigma(\text{R}^{3+})\lambda_\sigma(\text{Fe}^{3+})\Delta E_c
 \end{aligned}
 \tag{8}$$

The electron affinity of oxygen is -1.47 eV and for O^- it is 7.2 eV so that $\Delta E_c = 8.67$ eV. Using this in (7) and (8) we obtain the λ values which are listed in table 4.

We observe that $\lambda_\sigma > \lambda_\pi$ for Fe^{3+} exchange as expected from chemical bond theory. Also λ_σ values for the rare earth ions are generally lower than that for the Fe^{3+} bonds. This also agrees with the chemical theory of covalent bonds where it is known that the covalent bonds involving the $3d$ orbitals are stronger than those involving the $4f$ orbitals.

References

- Anderson P W 1959 *Phys. Rev.* **115** 2
 Copland G M 1970 *Chem. Phys. Lett.* **7** 175

- CRC Handbook of Chemistry and Physics 1980–81, 61st (CRC Press Florida) p. F.216
- Khattak C P and Yang F F Y 1979 *Handbook of physics and chemistry of rare earths* (ed.) Schneider Jr and L Eyrings (Amsterdam: North Holland) Vol. 3 p. 565
- Levy P M 1966 *Phys. Rev.* **147** 311
- Slater J C 1953 *Rev. Mod. Phys.* **25** 199
- Srivastava C M, Srinivasan C and Aiyar R 1982, *J. Appl. Phys.* **53** 781
- Sugar J and Reader J 1973 *J. Chem. Phys.* **59** 2083
- Tchéou F, Fuess H and Bertaut H 1970 *Solid State Commun.* **8** 1745
- Zeiger H J and Pratt G W 1973 *Magnetic interactions in solids* (Oxford: Clarendon) p. 242