

Exchange in insulators

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MS received 9 February 1981

Abstract. The exchange constants obtained using the three sublattice model for ferrites and garnets have been analysed using Anderson's theory of superexchange. The transfer integrals for the 180° and 90° interactions obtained from the experimental values of exchange constants give approximate values of the covalency parameters which are consistent with the chemical theory of covalency.

Keywords. Superexchange interaction; ferrimagnetic materials; transfer integrals; covalency parameters.

1. Introduction

The superexchange interaction in magnetic insulators has been discussed by a number of authors (Anderson 1959; Blasse 1964; Neel 1948; Dionne 1976; de Gennes 1960 and Kanamori 1959). However, only in simple systems where it can be represented by one or two exchange constants it has been possible to obtain some agreement of the experimental data with theory. In systems like ferrites and garnets the number of exchange interactions varies from three to six and it is only recently that some success has been achieved in the understanding of exchange phenomena in these ferrimagnetics. In this paper we present the results obtained for these systems using the approach followed by Srivastava *et al* (1979) where a set of exchange constants is obtained which explains simultaneously the magnetization as well as the paramagnetic susceptibility data. The experimental estimates of exchange constants are then used to obtain the values of the transfer integrals using Anderson's theory of superexchange. These transfer integrals are found to be in general agreement with the chemical theory of covalency.

The 90° and 180° superexchange interactions between Fe^{3+} ions are present in both ferrites and garnets with very nearly the same bond lengths and bond angles. As expected the experimental values of these exchange constants are found to be nearly equal.

The analysis of the rare earth iron garnets gives the experimental values of T-T, T-R and R-R interactions, where T is a transition series and R is a rare earth ion. Similar exchange constants are also obtained in the study of rare-earth transition series intermetallics. On comparison the two sets of exchange constants are found to be very nearly equal.

The systems which we discuss in this paper are spinel ferrites, $M^{2+}Fe_2^{3+}O_4$ ($M = Mn, Fe, Co, Ni, Cu, Li_{0.5}^+, Fe_{0.5}^{3+}$) and rare earth garnets $R_3^{3+}Fe_5^{3+}O_{12}$ ($R = Y, Gd, Tb, Dy, Ho, Er, Tm$ and Yb).

2. Exchange constants based on three-sublattice model

The Neel two sublattice (A and B) collinear model for spinel ferrites (Neel 1948) did not yield exchange constants in agreement with the theory of superexchange. The reason is that in inverse spinels the B sublattice has two types of magnetic ions whose ground states are generally very different. Consequently the analysis can only be done if the B sublattice is split in two, B_1 and B_2 , each with only one type of ion. The expressions for magnetization and paramagnetic susceptibility for the three sublattice model and the method of obtaining a set of exchange constants which simultaneously satisfies both the magnetization and susceptibility data have been discussed by Srivastava *et al.* The exchange constants obtained using this procedure are given in table 1 for spinel ferrites (Srivastava *et al* 1979) and table 2 for rare earth iron garnets (Srivastava *et al* 1980).

Some of the conclusions which can be drawn from these tables are as follows:

- (i) In spinel ferrites the (d^5-d^5) 180° exchange constant for ($Fe^{3+}-Fe^{3+}$) is -28 K while for ($Fe^{3+}-Mn^{2+}$) it is only -19.1 K.

Table 1. The value of the direct exchange J_π is 0.025 eV. Values of exchange constants (K) in spinel ferrites in K.

Composition	n	J_{AA} d^5-d^5	$J_{AB'}$ d^5-d^n	$J_{AB''}$ d^5-d^5	$J_{B'B'}$ d^n-d^n	$J_{B'B''}$ d^5-d^n	$J_{B''B''}$ d^5-d^5
$Li_{0.5}Fe_{2.5}O_4$	-	-20	-	-29	-	-	-8
$MnFe_2O_4$	5	-14.6	-19.1	-	-	-	-10
Fe_3O_4	6	-21	-23.8	-28	48.4	-13.2	-10
$CoFe_2O_4$	7	-15	-22.7	-26	46.9	-18.5	-7.5
$NiFe_2O_4$	8	-15	-27.4	-30.7	30.0	-2.7	-5.4
$CuFe_2O_4$	9	-15	-28	-24	20	-6	-8

Table 2. Values of exchange constants in garnets. The $J(T-T)$ for all garnets including YIG are the same and are as follows:

$$J_{aa}(d^5-d^5) = -6.45 \text{ K} \quad J_{ad}(d^5-d^5) = -30.40 \text{ K}$$

$$J_{dd}(d^5-d^5) = -12.05 \text{ K}$$

Values of $J(R-T)$ and $J(R-R)$ in K

R	n	$-J_{ac}$ (d^5-f^n)	$-J_{dc}$ (d^5-f^n)	$-J_{cc}$ (f^n-f^n)
Gd	7	0.60	1.80	0
Tb	8	0.56	1.01	0
Dy	9	0.99	0.99	-0.10
Ho	10	0.66	0.70	0
Er	11	0.55	0.68	0
Tm	12	0.44	0.66	0
Yb	13	3.0	2.30	0.04

(ii) The 90° superexchange interaction $J_{B'B'}$ ($d^n - d^n$) ($9 \geq n \geq 6$) in spinel ferrites is large and ferromagnetic.

(iii) In rare-earth iron garnets the exchange interactions between the transition series atoms are unaffected by the presence of the type of rare earth ion on the c -sub-lattice. Moreover, $J(T-T) > J(T-R) > J(R-R)$.

(iv) The $J_{AB''}$ ($d^5 - d^5$) interaction in spinel ferrites is very nearly the same as for J_{ad} ($d^5 - d^5$) interaction in garnets.

3. Analysis of exchange constants

The relation between the exchange constants (J_{AB}) and transfer integrals (b_k) as obtained by Anderson is first discussed in this section and is then used to obtain the values of b_k from the experimental values of J_{AB} .

The 180° superexchange interaction between two cations A and B with an intervening anion C requires consideration of ground and excited states which are as shown in figure 1 where A and B are the cations and C is an anion. The appropriate electronic wavefunctions are the antibonding molecular orbitals for the metal ions and a bonding orbital for the cation orthogonal to the antibonding orbitals. So

$$\begin{aligned} \phi_A &= N_a (u_a - \lambda_{ac} u_c) \\ \phi_B &= N_b (u_b - \lambda_{bc} u_c) \\ \phi_C &= N_c (u_c + \gamma_{ac} u_a + \gamma_{bc} u_b), \end{aligned} \tag{1}$$

where u_a and u_b are atomic d functions and u_c is the atomic orbital for the anion. λ and γ are measures of covalency and N_i ($i = a, b, c$) are the normalisation constants.

Anderson has shown that in this case the superexchange interaction is given by

$$H_{\text{ex}} = -2 J_{AB} \mathbf{S}_A \cdot \mathbf{S}_B, \tag{2}$$

where $J_{AB} = g_{AB,BA} - \frac{b^2_{A \rightarrow B}}{U_{A \rightarrow B}} - \frac{b^2_{B \rightarrow A}}{U_{B \rightarrow A}},$ (3)

$$g_{AB,BA} = \int \phi_A^* (1) \phi_B^* (2) \frac{e^2}{r_{12}} \phi_B (1) \phi_A (2) d\tau_1 d\tau_2, \tag{4}$$

and $b_{A \rightarrow B}$ is the transfer integral and is given by

$$b_{A \rightarrow B} = f_{AB} + (2 g_{AC,BC} - g_{AC,CB}) + g_{AB,BB}. \tag{5}$$

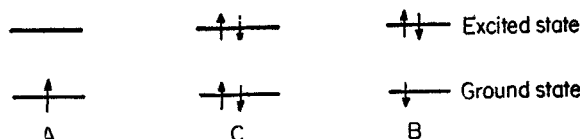


Figure 1. Spin configuration in the ground and excited states of the cation and anion in Anderson's theory of superexchange.

Here g 's are two-electron coulomb matrix elements as in equation (4) and f is a one-electron matrix element

$$f_{AB} = \int \phi_A^*(1) \frac{Z_{\text{eff}} e^2}{r_1} \phi_B(1) d\tau, \quad (6)$$

$U_{A \rightarrow B}$ is the increase in coulomb energy when the electron from ion A is taken and placed on B .

Equation (5) may be expressed in terms of the atomic orbitals u_a , u_b and u_c (Zeiger and Pratt 1973)

$$b_{A \rightarrow B} = \lambda_{ac} \lambda_{bc} (f_{cc} + g_{cc,ac}) - \lambda_{ac} (f_{bc} + g_{cc,bc} + g_{bb,cb}) \\ - \lambda_{bc} (f_{ac} + g_{cc,ac}) - g_{aa,cb}.$$

Since $g_{cc,cc} \gg g_{cc,bc} \gg g_{ab,cb}$ the first term in $b_{A \rightarrow B}$ is the largest. Therefore,

$$b_{A \rightarrow B} \simeq \lambda_{ac} \lambda_{bc} \Delta E_c, \quad (7)$$

where ΔE_c is of the order of a one-electron ionisation energy of the anion.

There may be more than one route through which the ions A and B may be interacting. Assuming $b_{A \rightarrow B} = b_{B \rightarrow A} = b_K$ and $U_{A \rightarrow B} = U_{B \rightarrow A} = U_k$ and denoting $g_{AB,BA}$ as J_l the energy difference between the parallel and antiparallel spin directions of ions A and B can be expressed in the form

$$\Delta E(\uparrow\downarrow - \uparrow\uparrow) = - \sum_k \frac{2b_k^2}{U_k} + \sum_l J_l, \quad (8)$$

where the summation is over all the available routes of superexchange between the ions A and B . This result can be expressed in the form of the Heisenberg-Dirac Hamiltonian,

$$E_{\text{cx}} = - \sum_{ij} 2J_{ij} S_i \cdot S_j. \quad (9)$$

From equations (6) and (7)

$$J_{ij} = - \frac{1}{4S_i S_j} \left(\sum_k \frac{2b_k^2}{U_k} - \sum_l J_l \right). \quad (10)$$

It is possible to express J_l in terms of the covalency parameters as given below (Zeiger and Pratt 1973)

$$J_l = \lambda_{ac}^2 \lambda_{bc}^2 \Delta E_c. \quad (11)$$

3.1 Transfer integrals and covalency parameter

Using equation (8) Srivastava *et al* (1979) have obtained the values of the transfer integrals from the experimental values of J_{ij} given in table 1. From these values of

the transfer integrals and estimate of the covalency parameter has been made. From equation (7)

$$\begin{aligned} b_{\sigma\sigma} &= \lambda_{\sigma} \lambda_{\sigma} \Delta E_c, \\ b_{\pi\pi} &= \lambda_{\pi} \lambda_{\pi} \Delta E_c, \end{aligned} \quad (12)$$

$$b_{\sigma\sigma'} = \lambda_{\sigma} \lambda_{\sigma'}, \Delta E_c \text{ with } \lambda_{\sigma} = \lambda_{\sigma'},$$

and $b_{\pi\sigma} = \lambda_{\sigma} \lambda_{\pi} \Delta E_c.$

The electron affinity for oxygen is -1.47 eV and for O^{-1} it is $+7.2$ eV. Hence ΔE_c is 8.67 eV. Using this value in equation (12) we obtain the values of λ_{σ} and λ_{π} which are given in table 3. In J_{BB} an average over (d^5-d^5) , (d^5-d^n) and (d^n-d^n) interactions has been assumed.

The direct exchange J_{π} which dominates in $J_{B'B}$ (d^n-d^n) interaction has a magnitude of 0.025 eV. As in this case the two bonds are similar, we obtain from equation (11) a value of $\lambda_{ac} = \lambda_{bc} = 0.23$ as given in table 3.

We observe the following from table 3.

- (i) If only one p orbital is involved, and if the ions are alike the value of λ_{σ} is large ($0.25 \geq \lambda_{\sigma} \geq 0.23$) for all the three types of interactions. For dissimilar ions λ_{σ} has the values 0.19 and 0.20
- (ii) If there are two p orbitals, λ_{σ} is reduced by about a factor of 2
- (iii) λ_{π} is smaller than λ_{σ} and is the same in all cases
- (iv) The λ 's for direct exchange are of the same order as for the superexchange.

Table 3. Transfer integrals and covalency parameters.

Type of exchange	Exchange constant J_{ij} ($a-b$)	Transfer integral b_k	Expt. value of b_k (eV)	λ_{σ}	λ_{π}
180° exchange	$J_{AB'}$	$b_{\sigma\sigma}$	0.31	0.19	—
	(d^5-d^n)	$b_{\pi\pi}$	0.18	—	0.14
	$J_{AB''}$	$b_{\sigma\sigma}$	0.48	0.24	—
	(d^5-d^5)	$b_{\pi\pi}$	0.18	—	0.14
90° exchange	J_{AA}	$b_{\sigma\sigma'}$	0.12	0.12	—
	(d^5-d^5)	$b_{\pi\sigma}$	0.30	0.25	0.14
	J_{BB} (d^5-d^5)	$b_{\sigma\sigma'}$	0.12	0.12	—
	(d^5-d^n) (d^n-d^n)	$b_{\pi\sigma}$	0.25	0.20	0.14
direct	J_{π} (d^n-d^n)	—	—	0.23	—

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