

Exchange constants and transfer integrals of spinel ferrites

P.G. Bercoff*, H.R. Bertorello

Facultad de Matemática, Astronomía y Física, Universidad Nacional de Córdoba, Haya de la Torre y Medina Allende, Ciudad Universitaria, 5000 Córdoba, Argentina

Received 1 July 1996; revised 2 December 1996

Abstract

We have studied Fe_3O_4 , CoFe_2O_4 , NiFe_2O_4 and CuFe_2O_4 considering Néel's two-sublattice collinear model and the superexchange theory. We have found that, for this theory to be valid, the interaction between ions in tetrahedral sites should be very weak, and we have proposed a model to find the constants J_{AB} and J_{BB} with the assumption that $J_{AA} = 0$. Using this model, the calculated values of these constants follow the expected tendencies for the four systems under study, as well as the ion-to-ion constants of Anderson's theory which we obtained through the assessment of the transfer integrals.

Keywords: Spinel ferrites; Exchange constants; Transfer integrals

1. Introduction

The exchange energy in ferrites is indirect (superexchange). The predominating exchange energies between the magnetic ions in the ferrites are negative, as would follow from the theory for half-filled or more than half-filled 3d shells. These ions include the ferric ions, as well as the divalent metal ions of the first transition series which can be substituted in ferrites with spinel structure.

The magnitude of the negative exchange energies between two magnetic ions M and M' depends upon the distances from these ions to the oxygen ion O^{2-} , via which the superexchange takes place,

and on the angle $M-\text{O}^{2-}-M'$ (ϕ) (Fig. 1), though no quantitative relationship is known between the exchange interaction and these quantities. Usually, only interactions within the first coordination sphere (both cations in contact with the anion) are considered important and the others are neglected. According to the superexchange theory, the angle $\phi = 180^\circ$ gives rise to the greatest exchange energy, and this energy decreases very rapidly as the distance between the ions increases. If we call A and B the tetrahedral and octahedral ions respectively in a spinel structure, the $A-B$ interaction is the greatest and the $A-A$ exchange interaction is the weakest [1].

Néel postulated a two-sublattice collinear model and analyzed the variation of the saturation magnetization and paramagnetic susceptibility with temperature for a number of ferrites [2]. He

* Corresponding author. E-mail: berto@famaf.fis.uncor.edu; fax: + 54-51-334054.

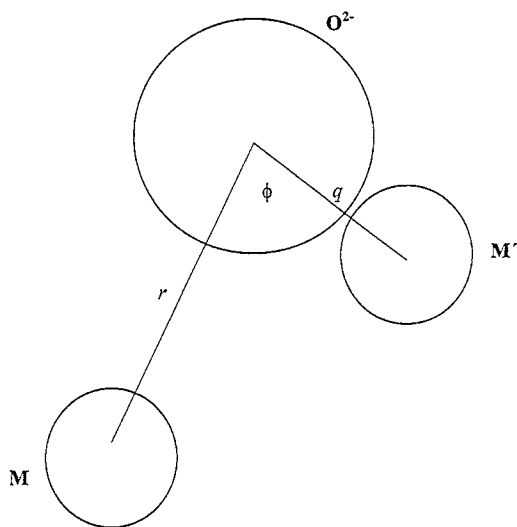


Fig. 1. Schematic representation of ions M and M' and the O^{2-} ion through which the superexchange is made. r and q are the centre-to-centre distances from M and M' (respectively) to O^{2-} , and ϕ is the angle between them.

obtained the exchange constants J_{AA} , J_{AB} and J_{BB} , on the basis of the molecular field theory. However, Smit and Wijn [1] have shown that this theory fails in describing ferrimagnetic materials because it predicts too large values for the interaction between sublattices and particularly for those within the sublattice of lower magnetization, that is, the tetrahedral sublattice. This difficulty is illustrated very clearly in some results of Néel and Brochet [3] on the interaction in Ni–Zn ferrites. From a molecular field analysis of experimental data on susceptibility, they found $|J_{AA}| \geq |J_{BB}|$ in every case. Considering the details of the spinel structure and the current ideas about exchange interactions in oxides [4] we must regard such results as most unlikely. Smit and Wijn's arguments apply specifically to interactions determined from paramagnetic susceptibility data; however different molecular field theory approaches, involving other kind of data, for evaluating exchange interactions lead to the same difficulty, as proved by Rado and Folen [5] who used spontaneous magnetization data.

Srivastava et al. [6] observed that in many cases more than one set of exchange constants can fit the saturation magnetization M_s versus T curves

equally well. They showed in particular the case of Lithium ferrite, where the results obtained by Rado and Folen, Dionne et al. and themselves all give a good fit to the magnetization data, while the exchange constants varied markedly from one set to another.

In order to better define the set of exchange constants, Srivastava et al. [6] have proposed a three-sublattice model to describe interactions in spinel ferrites. They have considered the octahedral sublattice as two different sublattices: one composed of the divalent ions (B') and the other formed with the trivalent ions (B''). These authors found a set of six exchange constants using paramagnetic susceptibility and magnetization data simultaneously. However, the superexchange constants obtained on the basis of the three-sublattice model show a great discrepancy with what was expected. The values of $|J_{AA}|$ for a number of ferrites are indeed too high and both $|J_{B'B'}|$ and $|J_{B''B''}|$ are too low. It also predicted a too strong ferromagnetic interaction between ions in sites B' , and according to Anderson [7] the ferromagnetic interaction for ions in octahedral sites should be very weak.

We think that the main reason for this behavior is that usually there exist two magnitudes to be fitted: magnetization and Curie temperature, but at least three available parameters. We have more variables than equations and different sets of the parameters can give equally good results. The fitting can always be optimized but the exchange constants obtained in this way do not have a coherent physical meaning, according to the superexchange theory.

If we consider that even for the simplest cases of pure ferromagnets as Fe, Ni or Co, with only one parameter to fit, the molecular field model does not lead to a fit for $M_T(T)$ versus T as accurate as that for ferrites with three or more coefficients [6], it emerges that something is not completely right.

In the case of spinel ferrites, what is not completely right is that the negative values obtained for J_{AA} , when three or more coefficients are considered, are too high.

In the literature concerning this subject, there are several cases where the assumption that $J_{AA} = 0$ is made [8] but this was not used systematically in studies of spinel ferrites.

In this paper we make the assumption that $J_{AA} = 0$ in spinel ferrites. This is based on the usual idea that superexchange interaction occurs between the metal ions via the nearest oxygen ions. A two-sublattice model for the magnetization as a function of temperature is used to calculate the values of the other exchange constants for several spinel ferrites. These constants were used in Anderson's model of superexchange interactions to evaluate the ion-to-ion exchange energies.

2. Two-sublattice model

In spinel ferrites the metal ions are separated by the oxygen ions and the exchange energy between spins of neighboring metal ions is found to be negative, that is, antiferromagnetic.

This is explained in terms of superexchange interaction of the metal ions via the intermediate oxygen ions [7].

However, there are a few points to line out about the interaction between two ions in tetrahedral (A) sites:

- The distance between two A ions ($\sim 3.5 \text{ \AA}$) is very large compared with their ionic radius (0.67 \AA for Fe^{3+}),
- the angle $\text{A}-\text{O}^{2-}-\text{A}$ ($\phi = 79^\circ 38'$) is unfavorable for superexchange interaction [1], and
- the distance from one A ion to O^{2-} is not the same as the distance from the other A ion to O^{2-} as there is only one A nearest neighbor to an oxygen ion (in Fig. 1 M and M' are A ions, $r \approx 3.3 \text{ \AA}$ and $q \approx 1.7 \text{ \AA}$ (Ref. [1])). As a result, two nearest A ions are connected via two oxygen ions.

These considerations led us to the conclusion that superexchange interaction between A ions is very unlikely. This conclusion, together with the observation that direct exchange is also unlikely in this case [1] support our assumption that $J_{AA} = 0$ in spinel ferrites.

On this basis, we apply Néel's two-sublattice collinear model for the magnetization and calculate the values for the exchange constants J_{AB} and J_{BB} for MFe_2O_4 (M being Fe, Ni, Co and Cu) with the aid of magnetization and Curie temperature data from Pauthenet [9].

According to Néel's theory, the total magnetization of a ferrite divided into two sublattices A and B is:

$$M_T(T) = M_B(T) - M_A(T) \quad (1)$$

where T is the temperature and both $M_B(T)$ and $M_A(T)$ are given in terms of the Brillouin function $B_{Si}(x_i)$:

$$M_B(T) = M_B(T=0)B_{SB}(x_B), \quad (2)$$

$$M_A(T) = M_A(T=0)B_{SA}(x_A), \quad (3)$$

with

$$B_{Si}(x_i) = \text{Brillouin function},$$

$$S_{A(B)} = \text{spin quantum number of ions A(B)},$$

$$x_A = \frac{\mu_B g_A S_A}{k_B T} M_B N_{AB}, \quad (4)$$

$$x_B = \frac{\mu_B g_B S_B}{k_B T} (M_B N_{BB} + M_A N_{AB}), \quad (5)$$

k_B = Boltzmann constant.

The molecular field coefficients, N_{ij} , are related to the exchange constants J_{ij} by the following expression:

$$J_{ij} = \frac{n_j g_i g_j \mu_B^2}{2z_{ij}} N_{ij} \quad (6)$$

with n_j the number of magnetic ions per mole in the j th sublattice, g_i the Landé factor, μ_B is Bohr magneton, and z_{ij} the number of nearest neighbors on the j th sublattice that interact with the i th ion.

According to Néel's theory and using $J_{AA} = 0$ (or, following Eq. (6), $N_{AA} = 0$), equating the inverse susceptibility $1/\chi = 0$ at $T = T_c$ (the Curie temperature) we obtain for the coefficients of the molecular field theory N_{AB} and N_{BB} the following expression:

$$N_{BB} = \frac{T_c}{C_B} - \frac{C_A N_{AB}^2}{T_c}, \quad (7)$$

where C_A and C_B are the Curie constants for each sublattice.

Eqs. (1) and (7) constitute a set of equations with two unknowns, N_{AB} and N_{BB} , provided that M_A and M_B are a known function of T . If this is the

case, it is possible to find the molecular field coefficients.

However, the available experimental data are the curves M_T versus T for the different ferrites so that M_A and M_B are underdetermined with the only condition that $M_B - M_A = M_T$ for each value of T .

The procedure we used to obtain N_{AB} and N_{BB} is the following: for a given pair of experimental values T and $M_T(T)$, we proposed an initial value of M_B (we call it M_B^{inic}) considering that it could only vary between $M_B^{\text{min}} = M_T(T)$ and $M_B^{\text{max}} = M_B(T=0)$. With this arbitrary value of M_B^{inic} we calculated x_B from Eq. (2). Then using Eq. (7) into Eq. (5) both N_{AB} and N_{BB} were calculated. Knowing N_{AB} , the value of x_A was obtained with (4) and used in Eq. (3) to give M_A^{calc} .

This value was compared with $M_A^{\text{inic}} = M_B^{\text{inic}} - M_T(T)$ and if there was a percentile discrepancy between M_A^{inic} and M_A^{calc} over 0.5%, we changed M_B^{inic} and repeated the loop until we found the desired agreement.

We applied this procedure to several $M_T(T)$, T pairs along the curve $M_T(T)$ versus T of the different ferrites and for each point we obtained a set of N_{AB} , N_{BB} coefficients. We found that the coefficients obtained for $T/T_c = 0.5$ were the ones that gave the best fit to the whole experimental curve.

3. Results and discussion

From the calculated N_{ij} coefficients we obtained the exchange constants J_{ij} with the help of Eq. (6). These results are shown in Table 1 and the calculated values of the curve $M_T(T)/M_T(0)$ versus T/T_c are compared with experimental curves of Pauthenet [9] in Figs. 2–5.

The general agreement between the measured and calculated values of the magnetization is not as good as that obtained by using $J_{AA} \neq 0$, especially for low temperatures. In our case, for each temperature T_i , we deal with only two adjustable parameters (N_{AB} and N_{BB}) and two magnitudes ($M_T(T_i)$ and T_c) to fit and the iteration process gives only one pair of coefficients N_{AB} and N_{BB} .

When $J_{AA} \neq 0$, there are still two magnitudes to fit but now there are three parameters. In this case

Table 1

Exchange constants for spinel ferrites, calculated with the assumption that $J_{AA} = 0$

Ferrite	J_{AA} (K)	J_{AB} (K)	J_{BB} (K)
Fe_3O_4	0	-14.7	-11.7
CoFe_2O_4	0	-17.6	-5.7
NiFe_2O_4	0	-20.6	-9.9
CuFe_2O_4	0	-20.3	-9.0

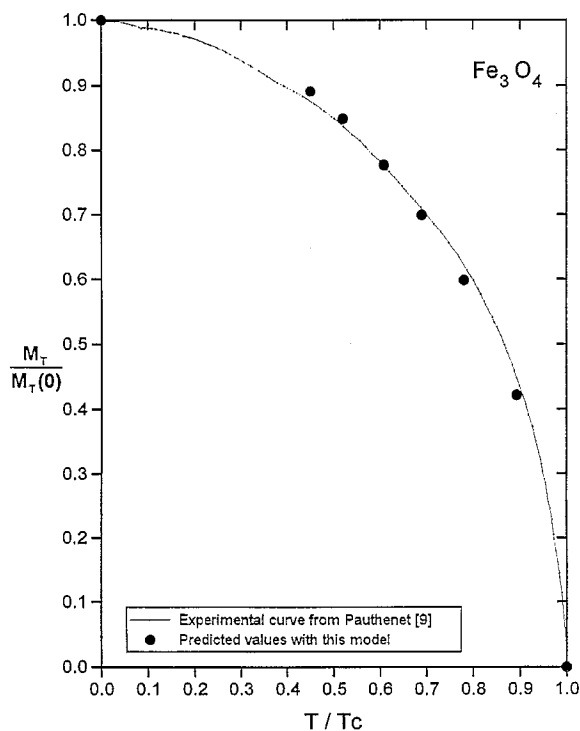


Fig. 2. Reduced magnetization as a function of reduced temperature for magnetite. The solid curve corresponds to experimental values [9] and the dots are the values predicted with $J_{AA} = 0$; $J_{BB} = -11.7$ K; $J_{AB} = -14.7$ K.

the $M_T(T)$ versus T curves are better reproduced by using three coefficients (there are more variables than equations) but the values of the exchange constants obtained in this way do not have a coherent physical meaning, according to the superexchange theory.

In the following, we analyze the problem from a point of view based on superexchange interaction.

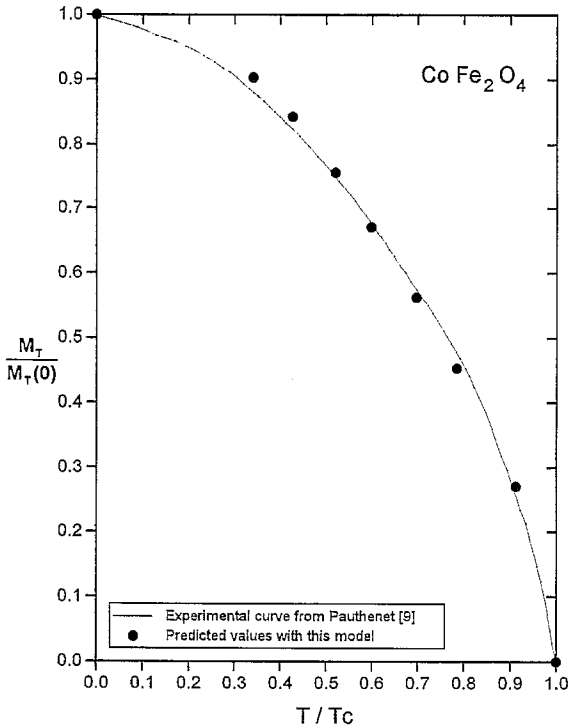


Fig. 3. Reduced magnetization as a function of reduced temperature for cobalt ferrite. The solid curve corresponds to experimental values [9] and the dots are the values predicted with $J_{AA} = 0$; $J_{BB} = -5.7$ K; $J_{AB} = -17.6$ K.

The difference of energy between a parallel and an anti-parallel spin arrangement of the two interacting atomic ions is called the exchange energy and can be expressed, according to Anderson [7] in the form:

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

We have kept the same nomenclature as Anderson's; the summation k is over the different routes of the superexchange (indirect) interaction via the ligand (oxygen ion), and l is over the different ferromagnetic (direct) interactions. The b_k 's are the coefficients of the Fourier expansion of the magnetic ion's wave function and the U_k 's are constants which Anderson estimated for different ions. Using the Heisenberg–Dirac Hamiltonian, we have the following expression for the ion-to-ion exchange

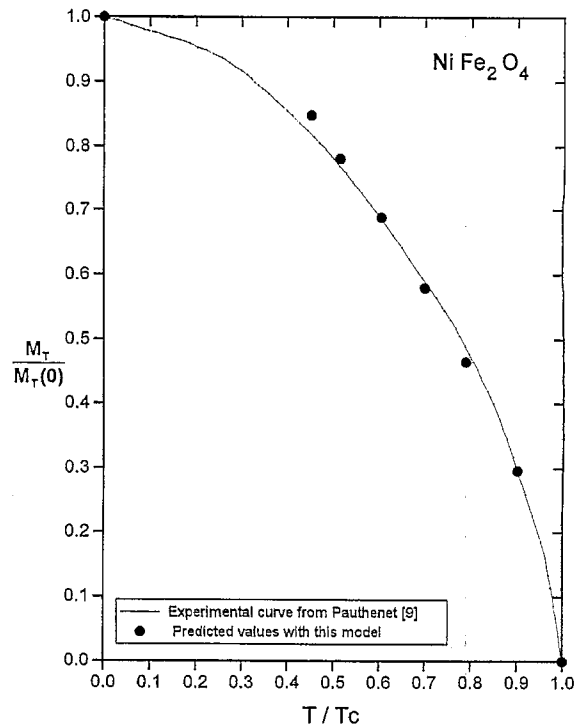


Fig. 4. Reduced magnetization as a function of reduced temperature for nickel ferrite. The solid curve corresponds to experimental values [9] and the dots are the values predicted with $J_{AA} = 0$; $J_{BB} = -9.9$ K; $J_{AB} = -20.6$ K.

constants:

$$J_{ij}^{\text{ion1-ion2}} = \frac{1}{4S_i S_j} \left(\sum_k \frac{2b_k^2}{U_k} - \sum_l J_l \right). \quad (9)$$

The kind of ferrites that we have considered are of the normal type: $\text{Fe}^{3+}[\text{M}^{2+}\text{Fe}^{3+}]\text{O}_4^{2-}$, where the ions between brackets are in B sites. The constants shown in Table 1 are average values of the exchange interaction between the different ions. We have expressed the constants J_{AB} and J_{BB} as a weighted average of the corresponding ion-to-ion constants in Eqs. (10) and (11).

$$J_{AB} = \frac{1}{2} (J_{AB}^{\text{Fe}^{3+}\text{-Fe}^{3+}} + J_{AB}^{\text{Fe}^{3+}\text{-M}^{2+}}), \quad (10)$$

$$J_{BB} = \frac{1}{4} (J_{BB}^{\text{Fe}^{3+}\text{-Fe}^{3+}} + 2J_{BB}^{\text{Fe}^{3+}\text{-M}^{2+}} + J_{BB}^{\text{M}^{2+}\text{-M}^{2+}}). \quad (11)$$

According to Eq. (9) the expressions for the interactions between electrons in orbitals d^n and

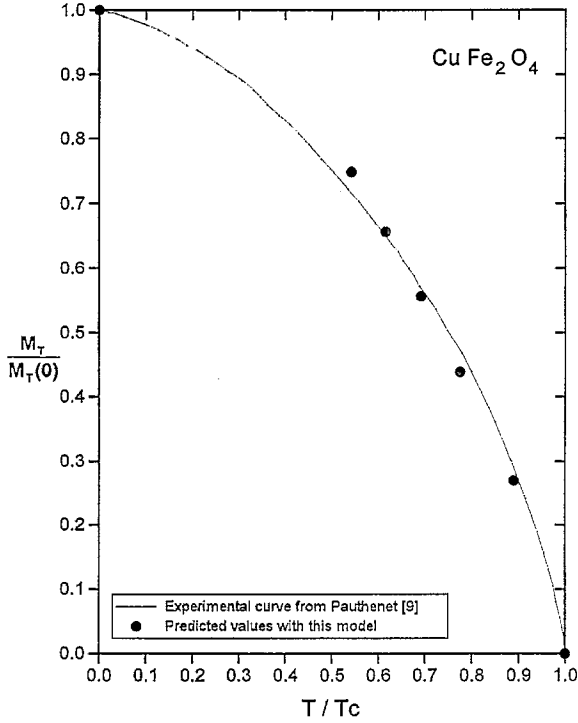


Fig. 5. Reduced magnetization as a function of reduced temperature for copper ferrite. The solid curve corresponds to experimental values [9] and the dots are the values predicted with $J_{AA} = 0$; $J_{BB} = -9.0$ K; $J_{AB} = -20.3$ K.

d^m (with $n, m = 5, 6, 7, 8$ and 9) are the following:

$$d^5-d^5: J_{AB}^{Fe^{3+}-Fe^{3+}} = -\frac{1}{25} \left(\frac{2b_{\sigma}^2}{U} + \frac{4b_{\pi}^2}{U} \right), \quad (12a)$$

$$d^5-d^6: J_{AB}^{Fe^{3+}-M^{2+}} = -\frac{1}{20} \left(\frac{2b_{\sigma}^2}{U} + \frac{4}{3} \frac{2b_{\pi}^2}{U} \right), \quad (12b)$$

$$d^5-d^7: J_{AB}^{Fe^{3+}-M^{2+}} = -\frac{1}{15} \left(\frac{2b_{\sigma}^2}{U} + \frac{2}{3} \frac{2b_{\pi}^2}{U} \right), \quad (12c)$$

$$d^5-d^8: J_{AB}^{Fe^{3+}-M^{2+}} = -\frac{1}{10} \left(\frac{2b_{\sigma}^2}{U} \right), \quad (12d)$$

$$d^5-d^9: J_{AB}^{Fe^{3+}-M^{2+}} = -\frac{1}{5} \left(\frac{b_{\sigma}^2}{U} \right), \quad (12e)$$

$$d^5-d^6: J_{BB}^{Fe^{3+}-M^{2+}} = -\frac{1}{20} \left(\frac{5}{3} \frac{2b_{\pi}^2}{U} - \frac{4b_{\sigma}^2}{U} \right), \quad (13a)$$

$$d^5-d^7: J_{BB}^{Fe^{3+}-M^{2+}} = -\frac{1}{15} \left(\frac{4}{3} \frac{2b_{\pi}^2}{U} - \frac{4b_{\sigma}^2}{U} \right), \quad (13b)$$

$$d^5-d^8: J_{BB}^{Fe^{3+}-M^{2+}} = -\frac{1}{10} \left(\frac{2b_{\pi}^2}{U} - \frac{4b_{\sigma}^2}{U} \right), \quad (13c)$$

$$d^5-d^9: J_{BB}^{Fe^{3+}-M^{2+}} = -\frac{1}{5} \left(\frac{b_{\pi}^2}{U} - \frac{2b_{\sigma}^2}{U} \right), \quad (13d)$$

$$d^5-d^5: J_{BB}^{Fe^{3+}-Fe^{3+}} = -\frac{1}{25} \left(\frac{4b_{\pi}^2}{U} - \frac{4b_{\sigma}^2}{U} \right), \quad (13e)$$

$$d^6-d^6: J_{BB}^{M^{2+}-M^{2+}} = -\frac{1}{16} \left(\frac{4}{3} \frac{2b_{\pi}^2}{U} - \frac{4b_{\sigma}^2}{U} \right), \quad (13f)$$

$$d^7-d^7: J_{BB}^{M^{2+}-M^{2+}} = -\frac{1}{9} \left(\frac{2}{3} \frac{2b_{\pi}^2}{U} - \frac{4b_{\sigma}^2}{U} \right), \quad (13g)$$

$$d^8-d^8: J_{BB}^{M^{2+}-M^{2+}} = -\frac{1}{4} \frac{4b_{\sigma}^2}{U}, \quad (13h)$$

$$d^9-d^9: J_{BB}^{M^{2+}-M^{2+}} = -\frac{1}{4} \frac{2b_{\sigma}^2}{U}. \quad (13i)$$

In these equations, $U = 10$ eV, $\bar{U} = 8$ eV and $\bar{U} = 6$ eV, as given in Ref. [7]; $b_{\sigma}^2(b_{\pi}^2)$ is the transfer integral for the electron in the $e_g(t_{2g})$ state of one atom to the $e_g(t_{2g})$ state on the other; b_{π}^2 takes part in the antiferromagnetic term of the J_{BB} exchange constant and it is a contribution between a t_{2g} state on one and z^2 state on the other magnetic ion through a single p orbital of the ligand with π for t_{2g} and σ for e_g bonding states; b_{σ}^2 is the transfer integral for the ferromagnetic interaction which involves two p orbitals (σ and σ') of the ligand and z^2 orbitals of the magnetic ions in σ -bonding states. We neglect direct exchange J_l from Eq. (9) because, due to the symmetry of these compounds, it is very unlikely to have this kind of interaction [1, 6].

We considered N Eqs. (10) and (11) for Fe_3O_4 and one of the other three ferrites at a time. Using Eqs. (12a), (12b), (12c), (12d), (12e), (13a), (13b), (13c), (13d), (13e), (13f), (13g), (13h) and (13i) we obtained a set of four equations with four unknowns (b_{σ}^2 , b_{π}^2 , $b_{\sigma'}^2$ and $b_{\pi'}^2$), for each pair of ferrites: Fe_3O_4 - $NiFe_2O_4$; Fe_3O_4 - $CoFe_2O_4$; and Fe_3O_4 - $CuFe_2O_4$. They were solved by using the data from Table 1.

We obtained a different set of values for the transfer integrals depending on what ferrite we used

Table 2
Transfer integrals for the antiferromagnetic interactions in spinel ferrites, calculated with the data from Table 1

b_{σ}^2 (eV ²)	b_{π}^2 (eV ²)	b_{σ}^2 (eV ²)	b_{π}^2 (eV ²)
0.1028	0.0130	0.0004	0.0477

for the calculation, and we chose a particular set (given in Table 2) that gave the exchange constants J_{AB} and J_{BB} which better reproduced the magnetization curves.

With these values we calculated the d^5-d^5 , d^5-d^n and d^n-d^n exchange interaction constants and the results are shown in Table 3 (A and B), together with the results obtained by Srivastava et al. [6].

All the ion-to-ion exchange constants, except $|J_{BB}|(d^n-d^n)$, for $NiFe_2O_4$ and $CuFe_2O_4$ are the same, according to Eqs. (13c) and (13d) which are identical, as in both cases the number of different routes of superexchange interaction divided by the corresponding product $S_i S_j$ gives the same result.

It is remarkable that $J_{BB}(d^n-d^n)$ for Cu and Ni ferrites turns out to be slightly ferromagnetic, as predicted by Anderson's theory. Also, this exchange constant for Fe and Co ferrites results antiferromagnetic and its magnitude is comparable with the other exchange constants. This is an important success of the model that proposes $J_{AA} = 0$. In contrast, the values obtained in Ref. [6] for $J_{BB}(d^n-d^n)$ are strongly ferromagnetic and higher than all the other exchange constants involved. This behavior can not be accounted for by any theory of superexchange interaction.

The values of $|J_{AB}|(d^5-d^n)$ and $|J_{BB}|(d^5-d^n)$ also satisfy Anderson's theory, as the first constant increases with n and the second decreases as n grows.

The exchange constants between ferric ions $|J_{AB}|(d^5-d^5)$ and $|J_{BB}|(d^5-d^5)$ are the same for all the ferrites since we are considering just ion-to-ion interactions, neglecting interactions with the other nearest neighbors.

The ion-to-ion constants from Table 3 were used in Eqs. (10) and (11) in order to predict J_{AB} and J_{BB} and the results are given in Table 4. With these values, the Curie temperatures were calculated by

Table 3
Comparison between ion-to-ion exchange constants for spinel ferrites, calculated with the transfer integrals from Table 2 and the values obtained by Srivastava et al. [6]

A	Ferrite	n	J_{AA} (K) (d^5-d^5)		J_{AB} (K) (d^5-d^5)		J_{AB} (K) (d^5-d^n)	
			This work	Ref. [6]	This work	Ref. [6]	This work	Ref. [6]
	Fe_3O_4	6	0	-14.0	-12.0	-28.0	-17.4	-20.2
	$CoFe_2O_4$	7	0	-14.0	-12.0	-28.0	-20.7	-22.7
	$NiFe_2O_4$	8	0	-14.0	-12.0	-28.0	-29.8	-27.4
	$CuFe_2O_4$	9	0	-14.0	-12.0	-28.0	-29.0	-27.0
B	Ferrite	n	J_{BB} (K) (d^5-d^5)		J_{BB} (K) (d^5-d^n)		J_{BB} (K) (d^n-d^n)	
			This work	Ref. [6]	This work	Ref. [6]	This work	Ref. [6]
	Fe_3O_4	6	-8.8	-9.0	-11.4	-11.0	-15.2	+44.0
	$CoFe_2O_4$	7	-8.8	-9.0	-12.2	-10.0	-13.3	+46.0
	$NiFe_2O_4$	8	-8.8	-9.0	-13.6	-10.0	+0.8	+29.0
	$CuFe_2O_4$	9	-8.8	-9.0	-13.6	-10.0	+0.4	+29.0

Table 4
Exchange constants for spinel ferrites, calculated using the ion-to-ion exchange constants

Ferrite	J_{AA} (K)	J_{AB} (K)	J_{BB} (K)
Fe ₃ O ₄	0	− 14.7	− 11.7
CoFe ₂ O ₄	0	− 16.4	− 11.6
NiFe ₂ O ₄	0	− 20.9	− 8.8
CuFe ₂ O ₄	0	− 20.9	− 8.9

Table 5
Curie temperatures for spinel ferrites calculated with the values shown in Table 4, compared with experimental values from Smit and Wijn [1]

Ferrite	T_c^{calc} (K)	T_c^{exp} (K) (Ref. [1])
Fe ₃ O ₄	858	858
CoFe ₂ O ₄	826	793
NiFe ₂ O ₄	857	858
CuFe ₂ O ₄	739	728

solving Eq. (7) for T_c and are presented in Table 5 together with the experimental values taken from Smit and Wijn [1].

Comparing the exchange constants given in Tables 1 and 4, a good agreement between the values can be observed, except for cobalt ferrite, where the values estimated using the ion-to-ion exchange constants exceed those given in Table 1, which were obtained by fitting the magnetization versus temperature curve for this ferrite. As a consequence of this, the estimated Curie temperature is higher than the experimental one. This behavior is also observed in CoO by Anderson [10] who states it is due to the effect of orbital degeneracy in Co.

4. Conclusions

On the basis of the superexchange theory and Néel's ideas of ferrimagnetism we propose a model which neglects any interaction between ions in A sites.

We show a procedure for obtaining the exchange constants and the so-obtained values agree with the

results expected by the superexchange theory, as $|J_{AB}| \geq |J_{BB}|$ for every studied system.

With the use of Anderson's model and the mentioned results, we obtain ion-to-ion interactions which are reasonable and in agreement with what Anderson predicts in his theory.

The values of the exchange constants $|J_{AB}|(d^5-d^n)$ increase with the number of d-electrons of the divalent metal, whereas the values of $|J_{BB}|(d^5-d^n)$ decrease.

The constant $|J_{BB}|(d^n-d^n)$ for the different ferrites tends to be more ferromagnetic as the number of d-electrons increases. For the systems with $n = 8$ and $n = 9$, this constant is positive and small in magnitude.

It is remarkable the fact that using the exchange constants found for each system their Curie temperatures are accurately reproduced, except for Cobalt ferrite, where the theory fails apparently due to orbital degeneracy in the Co ions.

We think that the results obtained in this work strongly support the fact that using too many parameters when limited experimental data is available is inadequate. In the case of spinel ferrites, considering too many parameters to describe the interactions leads to erroneous results.

Acknowledgements

The authors would like to thank Prof. L. Fabietti for helpful discussions on this paper.

This work was partially supported by CONICET, PID-BID II N° 79. P.G. Bercoff acknowledges a fellowship from Consejo de Investigaciones Científicas y Tecnológicas de la Provincia de Córdoba (CONICOR).

References

- [1] J. Smit and H.P.J. Wijn, Ferrites, Philips Technical Library (Wiley, New York, 1959).
- [2] L. Néel, Ann. Phys. 3 (1948) 137.
- [3] L. Néel and C. Brochet, Compt. Rend. Acad. Sci. 230 (1950) 280.
- [4] E.W. Gorter, Philips Res. Rep. 9 (1954) 295.
- [5] G.T. Rado and V.J. Folen, J. Appl. Phys. 31 (1960) 62.
- [6] C.M. Srivastava, G. Srinivasan and N.G. Nanadikar, Phys. Rev. B 19 (1979) 499.

- [7] P.W. Anderson, in: *Magnetism*, Vol. I, Eds. G.T. Rado and H. Suhl (Academic Press, New York, 1963).
- [8] S. Krupicka and P. Novák, in: *Ferromagnetic Materials – A Handbook on the Properties of Magnetically Ordered Substances*, Vol. III, Ed. E.P. Wohlfarth (North-Holland, Amsterdam, 1987) p. 189–304.
- [9] F. Pauthenet, *Compt. Rend. Acad. Sci.* 230 (1950) 1848.
- [10] P.W. Anderson, *Phys. Rev.* 115 (1959) 2.