

Calculation of exchange constants in spinel ferrites with magnetic S-state ions

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The exchange constants in spinel ferrites with *S*-state ions, including magnesium ferrite, lithium ferrite, and manganese ferrite, were calculated using modified Becke's three-parameter density functional, where the percentage of Hartree–Fock exchange in total exchange was introduced as a variable parameter (w) to match the experimental results of exchange constants by controlling the localization and delocalization of the electrons. Consistently, the scaling factor of the $3d$ orbitals of ferric ions was also introduced as a variable parameter (α). From the calculation, the values of parameters w and α matching the experimental results of J_{AB} (nearest-neighbor exchange constant between tetrahedral and octahedral sublattices) were concentrative, while those matching the experimental results of J_{AA} (nearest-neighbor exchange constant inside tetrahedral sublattice) and J_{BB} (nearest-neighbor exchange constant inside octahedral sublattice) were dispersive. Observing that J_{AB} is dominant in most practical ferrimagnetic spinel ferrites and the current accuracy of the measurements of J_{BB} and J_{AA} may be insufficient to support more accurate conclusion, it is suggested that there may be an empirical universal law of parameters w and α for spinel ferrites with *S*-state ions. © 2005 American Institute of Physics. [DOI: 10.1063/1.1850385]

INTRODUCTION

In previous research,¹ we calculated exchange constants in MnFe_2O_4 using Becke's three-parameter density functional. By varying the percentage of Hartree–Fock (HF) exchange in the total exchange (parameter w) and scaling the Fe^{3+} $3d$ orbitals (parameter α), we were able to match the experimental results of J_{AB} (nearest-neighbor exchange constant between tetrahedral and octahedral sublattices) and predict J_{BB} (nearest-neighbor exchange constant inside octahedral sublattice) in the accuracy of experimental results. We were also able to predict the electronic structure and parameters of MnFe_2O_4 as by-products, especially the insulating state (band gap). A fundamental question, however, rose since that research, *whether or not the parameters $w \sim 0.35$ and $\alpha \sim 1.3$ are universal*, although a computational study of nickel (II) oxide (NiO) using similar density functional suggested a close percentage of HF exchange ($\sim 30\%$) in total exchange.² In this article, we are going to answer this question in a narrowed context, spinel ferrites,^{3,4} with *S*-state ions.

The spinel ferrites with *S*-state ions studied here are

magnesium ferrite (MgFe_2O_4) (Ref. 5) and lithium ferrite ($\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$) (Ref. 6) and compared to manganese ferrite (MnFe_2O_4).⁷ These *S*-state spinel ferrites or their derivatives (manganese zinc ferrite, for example) are important practical microwave ferrites⁸ due to their low microwave loss, which is related to the 6S ground state of magnetic ions. The spin configuration of these ferrites is collinear as expected by Néel's theory. Zinc ferrite (ZnFe_2O_4), however, is carefully avoided here, since the spin configuration is still unclear and under study.⁹

APPROACH

The exchange constants were calculated using the Heitler–London approach, where the exchange constants were calculated by substituting spin configurations and corresponding total energies into the Heisenberg model. In the calculation, each unit cell of spinel structure contained two tetrahedral (*A*) sites, four octahedral (*B*) sites, and eight oxygen sites. The calculations of MgFe_2O_4 assumed an inverse spinel structure and three collinear spin configurations [Table I(a)]. The calculations of $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ assumed an ordered inverse spinel structure and three collinear spin configurations [Table I(b)].

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TABLE I. Spin configurations and total energies derived from Heisenberg model.

(a) MgFe ₂ O ₄				
Spin configuration				
Designation	A sites	B sites	Energy	
FM	↑↑	↑↑	$-E_{FM} = 8J_{AA}S_A^2 + 24J_{AB}S_A S_B + 4J_{BB}S_B^2$	
FI-1	↓↓	↑↑	$-E_{FI-1} = 8J_{AA}S_A^2 - 24J_{AB}S_A S_B + 4J_{BB}S_B^2$	
FI-2	↑↓	↑↑	$-E_{FI-2} = -8J_{AA}S_A^2 + 4J_{BB}S_B^2$	
FI-5	↑↑	↑↓	$-E_{FI-5} = 8J_{AA}S_A^2 - 4J_{BB}S_B^2$	

(b) Li _{0.5} Fe _{2.5} O ₄				
Spin configuration				
Designation	A sites	B sites	Energy	
FM	↑↑	↑↑↑	$-E_{FM} = 8J_{AA}S_A^2 + 36J_{AB}S_A S_B + 12J_{BB}S_B^2$	
FI-1	↓↓	↑↑↑	$-E_{FI-1} = 8J_{AA}S_A^2 - 36J_{AB}S_A S_B + 12J_{BB}S_B^2$	
FI-2	↑↓	↑↑↑	$-E_{FI-2} = -8J_{AA}S_A^2 + 12J_{BB}S_B^2$	
FI-5	↑↑	↑↑↓	$-E_{FI-2} = 8J_{AA}S_A^2 + 12J_{BB}S_A S_B - 4J_{BB}S_B^2$	

The total energies were calculated using Becke's three-parameter density functional¹⁰ with a variable percentage of HF exchange in total exchange (parameter w). The parameter w controlled the localization and delocalization of the electrons, which can be related to the exchange constants through its effects on hopping integral (t) and effective on-site Coulomb repulsion energy (U). As the linear combination of atomic orbitals was used to construct the Bloch functions, the parameter α was consistently introduced to control the localization and delocalization on the wave-function side by scaling the Fe³⁺ 3d orbitals. The basis functions were optimized for MgO,¹¹ LiF,¹² and Fe₂O₃.¹³

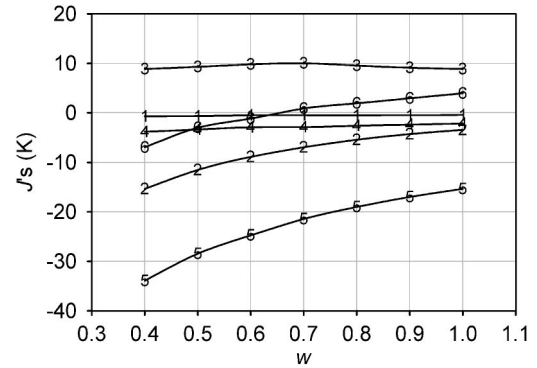
The lattice constant also affects the calculated results of exchange constants, since modifying the lattice constant is equivalent to scaling basis functions. We adopted an experimental lattice of Li_{0.5}Fe_{2.5}O₄ ($a = 8.33$ Å).¹⁴ In addition, we extrapolated the lattice constant of 100% inverse MgFe₂O₄ ($a = 8.370$ Å) from the dependence of the lattice constant on cation distribution.¹⁵

RESULTS

The experimental results of exchange constants of MgFe₂O₄ were calculated from the dependence of hyperfine field (measured by Mössbauer spectrum) on cation distribution¹⁶ (Table II). Those of Li_{0.5}Fe_{2.5}O₄ were calculated from the curve of saturation magnetization and magnetic susceptibility as a function of temperature (M - T curve)¹⁷ (Table II). The major approximation in calculating these experimental results is mean field approximation.

TABLE II. Comparison between experimental and calculated exchange constants in MgFe₂O₄ and Li_{0.5}Fe_{2.5}O₄.

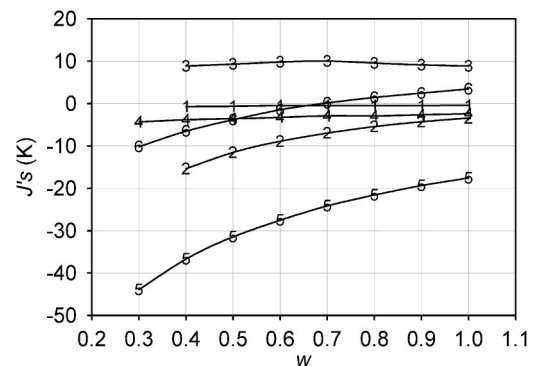
		J_{AB}	J_{BB}	J_{AA}
MgFe ₂ O ₄	Exp.	-22.5	-11.5	-7.0
	$w = 0.7, \alpha = 1.3$	-21.4	0.9	-2.9
Li _{0.5} Fe _{2.5} O ₄	Exp.	-29.0	-10.0	-20
	$w = 0.6, \alpha = 1.3$	-27.5	-1.5	-3.3

FIG. 1. Calculated exchange constants of MgFe₂O₄ as a function of parameters w and α . Curves (1), (2), and (3) represent J_{AA} , J_{AB} , and J_{BB} calculated with $\alpha = 1.0$, respectively. Curves (4), (5), and (6) represent J_{AA} , J_{AB} , and J_{BB} calculated with $\alpha = 1.3$, respectively.

The calculated J_{AB} in MgFe₂O₄ and Li_{0.5}Fe_{2.5}O₄ showed similar dependence on parameters w and α in MnFe₂O₄; J_{AB} became more negative as w decreased or α increased (Fig. 1 and 2). This behavior can be attributed to the definition of w and α . As w (the percentage of HF exchange in total exchange) decreased, more local spin density approximation (LSDA) entered total exchange, which decreased effective Coulomb repulsion (U) energy and increased hopping integral (t). As a result, the superexchange interaction was enhanced and J_{AB} became more negative. Increasing α had similar effects like decreasing w , but directly operated on wave functions of the magnetic ions.

With $w = 0.7$ and $\alpha = 1.3$, the calculated J_{AB} in MgFe₂O₄ matched the experimental result (Table II). For Li_{0.5}Fe_{2.5}O₄, matching the experimental result of J_{AB} led to $w = 0.6$ and $\alpha = 1.3$ (Table II). Although these optimal values were different from those ($w \sim 0.35$ and $\alpha = 1.3$) deduced from MnFe₂O₄, they were concentrated in a small parameter space. This implies that there is at least a set of values of parameters w and α , which could possibly be universal for Fe³⁺ only spinel ferrite.

The obvious difference between $w \sim 0.35$ and 0.6 (or 0.7) seems to answer the fundamental question negatively. However, since $w \sim 0.35$ was deduced from the calculated J_{AB} in normal MnFe₂O₄, it might be underestimated. In nor-

FIG. 2. Calculated exchange constants of Li_{0.5}Fe_{2.5}O₄ as a function of parameters w and α . Curves (1), (2), and (3) represent J_{AA} , J_{AB} , and J_{BB} calculated with $\alpha = 1.0$, respectively. Curves (4), (5), and (6) represent J_{AA} , J_{AB} , and J_{BB} calculated with $\alpha = 1.3$, respectively.

mal MnFe_2O_4 , J_{AB} is the exchange interaction between Mn^{2+} on A sites and Fe^{3+} on B sites. Since α only scaled the Fe^{3+} $3d$ orbitals, the Mn^{2+} orbitals was still optimized by HF, which overestimated effective Coulomb repulsion energy on Mn^{2+} and underestimated the hopping integral between Mn^{2+} and O^{2-} . As a result, a small w (percentage of HF in total exchange) was required to compensate the effect of HF optimized orbitals in order to match the experimental result. This implies that another parameter similar to α be required to scale the $3d$ orbitals of Mn^{2+} .

The calculated J_{AA} and J_{BB} for both MgFe_2O_4 and $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ were smaller than corresponding experimental values at any value of w (Table II). This is insufficient to overthrow the above conclusion of parameters w and α . In fact, the accuracy of both current calculation and experiments is insufficient to draw solid conclusion on J_{AA} and J_{BB} . In current calculation, a threshold for an electron overlapping integral was set up, which cut off all overlapping integrals between A sites. However, since the direct hopping may be a major contribution to superexchange if the bonding angle is close or smaller than 90° ($\angle AOA' \sim 80^\circ$), J_{AA} is obviously underestimated by current calculation. Also, the threshold cut off the overlapping integral between a B site and its second neighbor oxygen, which contributed to the superexchange between B sites ($\angle BOB'' \sim 125^\circ$). Thus, J_{BB} was underestimated too. Cation randomness can happen in both MgFe_2O_4 and $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, which blocks the ferromagnetic order inside one magnetic sublattice and is equivalent to overestimate the J_{BB} and J_{AA} .

CONCLUSION

A set of empirical universal values of parameters w and α was deduced from matching experimental results of J_{AB} in MgFe_2O_4 and $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$. Observing the short-range nature of superexchange interaction, this set of values may also be applicable to garnets and hexaferrites, where Fe^{3+} is dominant.

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