

Northeastern University

Electrical and Computer Engineering Faculty Publications Department of Electrical and Computer Engineering

May 15, 2003

Calculation of exchange integrals and electronic structure of manganese ferrite ($MnFe_2O_4$)

X. Zuo

C. Vittoria Northeastern University

Recommended Citation

Zuo, X. and Vittoria, C., "Calculation of exchange integrals and electronic structure of manganese ferrite (MnFe₂O₄)" (2003). *Electrical and Computer Engineering Faculty Publications*. Paper 27. http://hdl.handle.net/2047/d20002197

This work is available open access, hosted by Northeastern University.

AP Applied Physics

Calculation of exchange integrals and electronic structure of manganese ferrite (MnFe2O4)

Xu Zuo and Carmine Vittoria

Citation: J. Appl. Phys. **93**, 8017 (2003); doi: 10.1063/1.1558200 View online: http://dx.doi.org/10.1063/1.1558200 View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v93/i10 Published by the American Institute of Physics.

Related Articles

Optically driven method for magnetically levitating diamagnetic material using photothermal effect J. Appl. Phys. 111, 023909 (2012)

Simultaneous observation of magnetostatic backward volume waves and surface waves in single crystal barium ferrite platelets with in-plane easy axis J. Appl. Phys. 111, 023901 (2012)

The effect of Fe2+ ions on dielectric and magnetic properties of Yb3Fe5O12 ceramics J. Appl. Phys. 111, 014112 (2012)

Direct observation of magnetic phase coexistence and magnetization reversal in a Gd0.67Ca0.33MnO3 thin film Appl. Phys. Lett. 100, 022407 (2012)

Epitaxial thin films of p-type spinel ferrite grown by pulsed laser deposition Appl. Phys. Lett. 99, 242504 (2011)

Additional information on J. Appl. Phys.

Journal Homepage: http://jap.aip.org/ Journal Information: http://jap.aip.org/about/about_the_journal Top downloads: http://jap.aip.org/features/most_downloaded Information for Authors: http://jap.aip.org/authors

ADVERTISEMENT

■LakeShore Model 8404 TOYO Corporation NEW AC/DC Hall Effect System Measure mobilities down to 0.001 cm²/Vs

Calculation of exchange integrals and electronic structure of manganese ferrite $(MnFe_2O_4)$

Xu Zuo^{a)} and Carmine Vittoria

The Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115

(Presented on 14 November 2002)

The exchange integrals of manganese ferrite (MnFe₂O₄) are calculated with the density functional theory method for both normal and inverse spinel structures. The functional is chosen to be a mixture of Becke exchange and Fock exchange with variable weight (*w*). The exchange integrals J_{AB} (the exchange integral between the nearest neighbor A and B sites) and J_{BB} (the exchange integral between nearest neighbor B sites) are calculated by substituting the total energies of different magnetic ground states into the Heisenberg model. The calculated value of J_{AB} is in agreement with experimental values measured by neutron diffraction and nuclear magnetic resonance. Also, the parameters *U* (Coulomb repulsion energy) and E_g (band gap) are extracted from density of states plotted versus *w*. Our calculated band gap shows that MnFe₂O₄ is a complex insulator in contrast to previous local spin density approximation and generalized gradient approximation calculations which predicted it to be metallic. © 2003 American Institute of *Physics.* [DOI: 10.1063/1.1558200]

I. INTRODUCTION

Manganese (MnFe₂O₄) is a ferrite material with a spinel crystallographic structure (space group Fd3m), in which O^{2-} forms tetragonal and octagonal local symmetries that are referred to as A and B sites, respectively.¹ A normal spinel structure, per primary cell, consists of two A sites occupied by two Mn²⁺ and four B sites each occupied by four Fe³⁺. On the other hand, 100% inverse spinel structure, per primary cell, consists of two A sites occupied by two Fe³⁺ and four B sites occupied by two Fe³⁺ and four B sites occupied by two Fe³⁺ and four B sites occupied by two Fe³⁺ ions. MnFe₂O₄ is known to be approximately 20% inverse. The exact percentage depends on the details of material preparation.²

Manganese ferrite has been discussed for a long time^{1,3} and there have been numerous qualitative arguments made for the existence of superexchange interactions in this material and oxide magnetic materials.^{4,5} The most recent generalized gradient approximation (GGA) calculation⁶ showed that $J_{AB} = -39.3$ K compared to $J_{AB} = -22.7$ K obtained experimentally from nuclear magnetic resonance⁷ and J_{AB} = - 19.1 K from magnon dispersion measurements.^{8,9} Both local spin density approximation (LSDA)¹⁰ and GGA⁶ calculations predicted a metallic state for MnFe₂O₄, although MnFe₂O₄ is known to be an insulator as confirmed by activation energy measurement.¹¹ On the other hand, it is known that Hartree–Fock (HF) overestimates U and E_g , and underestimates the exchange integrals for transition metal oxides.^{12,13} In a previous paper by the current authors,¹⁴ a Hamiltonian, which is a mixture of HF and LSDA, was utilized and led to J_{AB} close to the experimental value, if the radial part of the 3d orbit of Fe^{3+} was extended to 130%. However, it was shown that J_{BB} was sensitive to the extension and that the calculated $J_{\rm BB}$ was larger than experimental value for inverse spinel structure with an extension of 130%. In this paper, we calculated the exchange integrals and electronic structure with an extension of 120%.

II. APPROACH

We chose a modified version of Becke's parametrization of the exchange-correlation functional, which is examined for a wide range of atoms and molecules.¹⁵ In this approximation, the correlation part is given by

$$E_c = E_c^{\text{SDA}} + a_c \Delta E_c^{\text{PW}},\tag{1}$$

where E_c^{LSDA} and ΔE_c^{PW} are LSDA correlation¹⁶ and PWGGA correction,¹⁷ respectively. The exchange part is given by

$$E_x = (1 - w)(E_x^{\text{LSDA}} + a_x \Delta E_x^B) + w E_x^{\text{exact}}, \qquad (2)$$

where E_x^{exact} , E_x^{LSDA} , and ΔE_x^B are exact exchange, LSDA exchange, and Becke exchange-only GGA correction,18 respectively. In Becke's original parametrization, $a_c = 0.81$, $a_x = 0.9$, and w = 0.2 are determined from the least-squares fitting of atomization energies, ionization potentials, and proton affiliates.¹⁵ In this paper, we are allowing w to vary between 0 and 1 to fit the experimental value of J_{AB} and U. In the calculation, E_x^{exact} is replaced by the Fock exchange (E_x^F) .¹⁵ We choose Gaussian basis sets for Mn²⁺, Fe³⁺, and O²⁻. The basis sets of Mn²⁺ and Fe³⁺ were optimized for MnO^{12} and Fe_2O_3 ,¹³ respectively. The basis set of O^{2-} was optimized for a wide range of oxide materials including MnO and NiO.¹² The calculations were implemented by CRYSTAL98 code¹⁹ at experimental geometry,²⁰ lattice constant a = 8.511 Å and position of O^{2-} u = 0.3846. The calculations were performed self-consistently in spin-dependent scheme, in which the net spin in a primary cell is locked at the theoretical value of ionic model, i.e., the net spin of Fe³⁺ and Mn^{2+} is 5/2 and that of O^{2-} is 0.

0021-8979/2003/93(10)/8017/3/\$20.00

8017

^{a)}Electronic mail: xzuo@ece.neu.edu



FIG. 1. Calculated exchange integrals using optimized (opt) and extended (ext) basis sets for normal spinel structure.

III. RESULTS

A. Exchange integrals

On the calculation of exchange integrals, only J_{AB} and J_{BB} were considered, since there is no experimental data on J_{AA} . To determine J_{AB} and J_{BB} , we calculated the ground state energies of three different magnetic structures denoted as FM, FI-1, and FI-3. FM is the assumed ferromagnetic structure. FI-1 is the observed ferrimagnetic structure in experiments. FI-3 is an assumed ferrimagnetic structure, in which spins in the A sublattice are aligned parallel to each other, spins within B sublattice are aligned antiparallel. Assuming the spin arrangement to be collinear and substituting each magnetic structure into the Heisenberg model, we obtain

$$J_{AB} = \frac{1}{96S^2} (E_{FI-1} - E_{FM}),$$

$$J_{BB} = \frac{1}{32S^2} \left[E_{FI-3} - \frac{(E_{FI-1} + E_{FM})}{2} \right],$$
(3)

where S = 5/2 is assumed according to the ionic model. The calculated J_{AB} and J_{BB} are plotted as a function of w in Figs. 1 and 2 for normal and inverse structure, respectively. The calculated J_{AB} is negative (antiferromagnetic) for all values of w, and becomes stronger when w decreases. $J_{AB} = -15.3$ K is obtained for normal spinel structure at w = 0.4 and $J_{AB} = -14.5$ is obtained for inverse spinel structure at w = 0.5, which are reasonable when compared to experimental value.⁷⁻⁹ However, calculated J_{BB} 's are about 10 K for normal spinel structure and 7 K for inverse spinel structure, compared to $J_{BB} = -3.0$ K from magnon dispersion measurement.⁹

As w decreases, the weight of LSDA in Hamiltonian increases. Since the above-given basis sets are optimized by HF, the divergence occurs when w is smaller than a critical value of 0.40. Since self-consistent wave functions of LSDA are more extensive than those of HF, it is reasonable to expect that more extensive basis sets may improve the convergence of the calculation. Thus, we extended the 3*d* basis



FIG. 2. Calculated exchange integrals using optimized (opt) and extended (ext) basis sets for inverse spinel structure.

functions of Fe³⁺ to 120% in the radial direction. Using extended basis sets, we obtain J_{BB} =4.5 K for normal spinel structure at w=0.3 and J_{BB} =1.9 K for inverse structure at w=0.4, which are closer to the experimental value of -3.0 K.

B. Electronic structure

On the electronic structure, we calculated the density of states (DOS) using the extended basis sets for normal spinel structure with experimentally observed FI-1 structure at different values of *w*. The site projected DOS at w = 0.3 is plotted in Fig. 3. Compared to the DOS calculated by LSDA¹⁰ or GGA,⁶ the DOS given by our calculation is quite different. First, the DOS calculated by LSDA or GGA implied that MnFe₂O₄ is metallic, where the spin-down Mn²⁺ *d* bands and the spin-down Fe³⁺ *d* bands overlapped with each other and crossed over the Fermi level. However, in our calculation, the DOS shows that MnFe₂O₄ is a typical insulator with a band gap between the spin-down Mn²⁺ *d* bands and spin-down Fe³⁺ *d* bands, which is qualitatively in agreement with



FIG. 3. Projected DOS calculated using extended basis set for normal spinel structure and FI-1 magnetic structure at w = 0.30, where the definitions of E_g and U are schematically shown.



FIG. 4. Coulomb repulsion parameters for Fe^{3+} (U_{Fe}) and Mn^{2+} (U_{Mn}), and band gap (E_{e}) calculated using extended basis sets.

experiment.¹¹ Second, the DOS given by LSDA or GGA implied that $MnFe_2O_4$ is a typical Mott insulator for both Fe^{3+} and Mn^{2+} , in which the *p* band of O^{2-} is located at a lower energy than the lower Hubbard bands of Fe^{3+} and Mn^{2+} . On the other hand, in our previous calculation,¹⁴ the DOS implied that the Fe–O system in $MnFe_2O_4$ is a typical charge transfer insulator, in which the *p* band of O^{2-} is located between the upper and lower Hubbard bands of Fe^{3+} . However, in this calculation, both Fe–O system and Mn-O system are the interim state between Mott insulator and charge transfer insulator, in which the *p* band of O^{2-} overlaps the *d* band of Fe^{3+} and Mn^{2+} at the top of valence band.

From DOS, we extracted the values of band gap (E_g) and Coulomb repulsion (U). We plotted E_g and U vs w in Fig. 4. As shown in Fig. 4, U depends on w linearly. The optimal fitting of U to experimental values^{21,22} is obtained at $w \approx 0.20$, which is the original parametrization by Becke. In contrast to the linear dependence of E_g on w given by optimized basis sets,¹⁴ there is a knee point around w = 70% in

the E_g-w curve given by extended basis sets, which implies a transition of DOS from typical charge insulator to the interim state between charge transfer insulator and Mott insulator as w decreases.

IV. CONCLUSION

By admixing Fock and Beck exchange-correlation functional, the calculated exchange integrals by us are in reasonable agreement with experimental values. Also, our calculations yield an insulating state for $MnFe_2O_4$ as confirmed by experiments.

- ¹E. W. Gorter, Philips Res. Rep. 9, 295 (1954).
- ²J. M. Hasting and L. M. Corliss, Phys. Rev. **104**, 328 (1956).
- ³J. Smit and H. P. J. Wijn, *Ferrites* (Wiley, New York, 1959), p. 136.
- ⁴J. B. Goodenough, *Magnetism and Chemical Bond* (Interscience, New York, 1963).
- ⁵P. W. Anderson, Phys. Rev. **115**, 2 (1959).
- ⁶D. J. Singh, M. Gupta, and R. Gupta, Phys. Rev. B 65, 064432 (2002).
- ⁷A. J. Heeger and T. W. Houston, Phys. Rev. **133**, A661 (1964).
- ⁸ V. C. Rakhecha, L. M. Rao, N. S. S. Murthy, and B. S. Srinivasan, Phys. Lett. **40A**, 101 (1972).
- ⁹W. Wegener, D. Scheerlinck, E. Legrand, and S. Hautecler, Solid State Commun. **15**, 345 (1974).
- ¹⁰ M. Pénicaud, B. Siberchicot, C. B. Sommers, and J. Kübler, J. Magn. Magn. Mater. **103**, 212 (1992).
- ¹¹F. K. Lotgering, J. Phys. Chem. Solids 25, 95 (1964).
- ¹² M. D. Towler, N. L. Allan, N. M. Harrison, V. R. Saunders, W. C. Mackrodt, and E. Aprà, Phys. Rev. B 50, 5041 (1994).
- ¹³ M. Catti, G. Valerio, and R. Dovesi, Phys. Rev. B **51**, 7441 (1995).
- ¹⁴X. Zuo and C. Vittoria, Phys. Rev. B 66, 184420 (2002).
- ¹⁵A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- ¹⁶S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980).
- ¹⁷J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B 46, 6671 (1992).
- ¹⁸A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
- ¹⁹ V. R. Saunders, R. Dovesi, C. Roetti, M. Causà, N. M. Harrison, R. Orlando, and C. M. Zicovich, CRYSTAL98 User's Manual (1999).
- ²⁰ R. W. G. Wyckoff, *Crystal Structure*, 2nd ed. (Wiley, New York, 1967), Vol. 3, p. 75.
- ²¹A. Fujimori, M. Saeki, N. Kimizuka, M. Taniguchi, and S. Suga, Phys. Rev. B **34**, 7318 (1986).
- ²² A. Fijimori, N. Kimizuka, T. Akahane, T. Chiba, S. Kimura, F. Minami, K. Siratori, M. Taniguchi, S. Ogawa, and S. Suga, Phys. Rev. B **42**, 7580 (1990).