

Computational study of copper ferrite (CuFe_2O_4)

Xu Zuo^{a)}

College of Information Technical Science, Nankai University, 94 Weijin Road, Tianjin 300071, China

Aria Yang, Carmine Vittoria, and Vincent G. Harris

Department of Electrical and Computer Engineering, Northeastern University, 360 Huntington Avenue, Boston, Massachusetts 02115

(Presented on 2 November 2005; published online 24 April 2006)

Magnetic properties and electronic structure of copper ferrites in both normal and inverse spinel structures are studied using a principle spin-polarized band structure calculation method with a modified Becke's three-parameter exchange correlation. The calculated exchange constants show that the Néel configuration may be unstable for both normal and inverse structures. The local magnetic moments are calculated using Mülliken population analysis and show that the normal structure may achieve very high magnetization. The calculated density of states show that copper ferrite in both normal and inverse spinel structure may be half metallic. © 2006 American Institute of Physics. [DOI: 10.1063/1.2170048]

I. INTRODUCTION

In previous research, we studied artificial manganese ferrite (MnFe_2O_4) theoretically and experimentally. Experimentally, using a modified pulse laser deposition technique, we prepared artificial manganese ferrite, where the distribution of magnetic ions was artificially controlled by growth conditions.¹⁻⁴ Theoretically, using a spin-polarized band calculation method with a modified Becke's three-parameter exchange correlation, we studied the magnetic properties and electronic structure of manganese ferrite, which predicts that artificial manganese ferrite in an inverse spinel structure may be stable.⁵⁻⁸ In fact, as manganous (Mn^{2+}) and ferric (Fe^{3+}) ions are almost identical, it can be expected that the spinel structure and Néel configuration are still stable after the redistribution of these ions among *A* and *B* sites. However, the identicalness of these ions, especially the spin $-5/2$ state, may result in little variation of magnetization. Therefore, manganese ferrite is only a prototype in such a sense that our original driving force to develop artificial ferrite is to enhance magnetization.

Copper ferrite⁹ may be a promising candidate for the artificial ferrite with enhanced magnetization. Copper ferrite is mostly in inverse spinel structure. Statistically, about 6%–24% Cu^{2+} occupy *A* sites depending on the sample preparation.¹⁰ The corresponding magnetization is about 1.48–2.92 μ_B per chemical formula according to the ionic model. However, if copper ferrite is in normal spinel structure, where 100% Cu^{2+} occupy *A* sites, its magnetization will be 9 μ_B per chemical formula according to the ionic model. This is obviously a significant enhancement of magnetization. Recently, we investigated copper ferrite films prepared by pulse laser deposition and observed the enhancement of magnetization and redistribution of magnetic ions in the

experiment.¹¹ However, limited by a film deposition technique, regular pulse laser deposition, the magnetization enhancement is only about 40%.

In contrast to Mn^{2+} , Cu^{2+} is quite different from Fe^{3+} in terms of the electronic state. We expect that redistribution of Cu^{2+} from the octahedral *B* site to the tetrahedral *A* site may significantly affect both crystal and spin structures. On the crystal structure, Cu^{2+} on the *B* site may result in a cooperative Jahn–Teller distortion with $c/a > 1$.¹⁰ On the contrary, Cu^{2+} on the *A* site may result in a distortion with $c/a < 1$.¹⁰ On the spin structures, as the t_{2g} bands of Cu^{2+} on *B* sites are fully occupied, the intersite direct hopping is absent and results in a ferromagnetic or weak antiferromagnetic exchange coupling between *B* sites, which stabilizes the Néel configuration. However, as Cu^{2+} are redistributed on *A* sites, Fe^{3+} occupies *B* sites and results in an antiferromagnetic exchange coupling between *B* sites, which frustrates the Néel configuration. If the exchange coupling between Cu^{2+} on the *A* site and Fe^{3+} on the *B* site is weak enough, the redistribution may result in spin canting or other complex spin structures. In addition, redistribution of Cu^{2+} from *B* to *A* sites alters the ground multiplet from doublet to triplet. This effect, combined with the large spin-orbital coupling constant, may result in different magnetic anisotropy.

II. APPROACH

In this research, the spin-polarized band calculation technique, realized by the CRYSTAL 98 code,¹² is the fundamental tool used to study artificial copper ferrite. The exchange correlation is based on Becke's three-parameter hybrid exchange correlation,¹³ which is a mixture of Fock exchange, local spin density approximation (LSDA) exchange, Becke generalized gradient approximation (GGA) correction on exchange, LSDA correlation, and PWGGA (GGA by J. P. Perdew and Y. Wang) correction on correlation. We modify the original parameterization of the Becke's exchange correlation by adjusting the weight of Fock exchange (w) from 0.2 to 0.4. Our previous study on manganese ferrite showed that

^{a)}Author to whom correspondence should be addressed; electronic mail: xzuo@nankai.edu.cn

TABLE I. Calculated exchange constants of the inverse structures using $\alpha = 1.3$ (unit: K).

w	J_{FeFe}^{AA}	J_{FeCu}^{AB}	J_{FeFe}^{AB}	J_{CuCu}^{BB}	J_{CuFe}^{BB}	J_{FeFe}^{BB}
0.40	-9.1	-16.9	-39.4	-508.6	-88.4	-41.2
1.00	-2.3	-5.9	-18.0	22.5	8.0	3.7

the modified parametrization may fit the experimental result of exchange constants.⁵ Linear combination of atomic Orbitals (LCAO) is the method to construct the crystal orbitals. The atomic orbitals are linear combinations of Gaussian type functions, which are optimized for CuO and Fe₂O₃ by Hartree–Fock (HF) calculations, respectively. As LSDA-based terms present in exchange correlation (when $w \neq 1.0$), the basis sets optimized by HF need to be modified. Our previous study on manganese ferrite showed that introducing the scaling factor of Fe³⁺ 3*d* orbital (α) and using $\alpha=1.3$ may fit the experimental result of exchange constants.⁵

Artificial copper ferrite in both normal and inverse spinel structures are studied in this article. As quenched copper ferrite is mostly in inverse cubic spinel structure, we assume that inverse structure is in the same structure.⁹ An experimental lattice constant ($a=8.37$ Å) and oxygen parameter ($u=0.38$) are adopted in the calculation.⁹ Although redistribution of Cu²⁺ to A sites may result in instability of spinel structure or even crystal phase transition, in this article we temporarily assume that redistribution of magnetic ions only distorts the spinel structure at most. Thus, the normal structure may be in a distorted spinel structure. Referring to the c/a value of CuCr₂O₄,¹⁴ and CuRh₂O₄,¹⁵ we assume $c/a=0.9$ for artificial copper ferrite after the redistribution. In addition, we assume that the volume of the cubic unit cell and the oxygen parameter remained constant after the lattice distortion.

III. RESULTS

Exchange interactions between magnetic ions play an important role in determining the spin structure of the artificial copper ferrite. In this research, we calculated nearest neighbor exchange constants intra- and intersublattices of A and B. In the inverse structure, there are six nearest neighbor exchange interactions, denoted as J_{FeFe}^{AA} , J_{FeCu}^{AB} , J_{FeFe}^{AB} , J_{CuCu}^{BB} , J_{CuFe}^{BB} , and J_{FeFe}^{BB} . In these notations, the superscripts indicate the interacting sites and the subscripts indicate the interacting ions. We compute the total energies of seven collinear spin configurations, the ferromagnetic alignment, and six ferrimagnetic alignments, and calculate the exchange constants from the energy differences of ferrimagnetic alignments from the ferromagnetic alignment. As the unit cell of the normal structure is distorted from the cubic structure, B sites split in to two equivalent sites, B₁ and B₂. This results in six nearest neighbor exchange interactions in the normal structure, denoted as J_{CuCu}^{AA} , $J_{\text{CuFe}}^{AB_1}$, $J_{\text{CuFe}}^{AB_2}$, $J_{\text{FeFe}}^{B_1B_1}$, $J_{\text{FeFe}}^{B_1B_2}$, and $J_{\text{FeFe}}^{B_2B_2}$. In fact, these exchange constants can be mapped to those of the inverse structure one to one.

The calculated exchange constants of the inverse structure are listed in Table I. As observed in the previous com-

TABLE II. Calculated exchange constants of the normal structure using $\alpha = 1.3$ (unit: K).

w	J_{CuCu}^{AA}	$J_{\text{CuFe}}^{AB_1}$	$J_{\text{CuFe}}^{AB_2}$	$J_{\text{FeFe}}^{B_1B_1}$	$J_{\text{FeFe}}^{B_1B_2}$	$J_{\text{FeFe}}^{B_2B_2}$
0.40	-84.3	-60.0	-12.0	-3365.3	-109.4	-132.7

putational results of S-state ferrites (manganese, magnesium, and lithium ferrites),¹⁶ J^{AA} is weak and antiferromagnetic (negative) and J^{AB} s are strong and antiferromagnetic. Both J^{AA} and J^{AB} s become stronger as w decreases. In fact, as w decreases, the covalency between magnetic ion and the oxygen increases and the intrasite Coulomb repulsion of magnetic ions decreases, and they result in a stronger antiferromagnetic superexchange contribution to the exchange constant. In contrast to the S-state ferrites, the J^{BB} s of the inverse structure shows a significant change as w decreases. At $w=1.0$, J^{BB} s are ferromagnetic (positive) and J_{CuCu}^{BB} are the strongest interaction in all of the exchange interactions, which implies that Néel configuration may be stable. However, at $w=0.4$, J^{BB} s are antiferromagnetic and J^{BB} s are stronger than J^{AB} s, which implies that Néel configuration is unstable. More calculations on the other values of w between 0.4 and 1.0 show that J_{CuCu}^{BB} oscillates with the amplitude of 4500 K at $w=0.7$. This phenomenon may be related to orbital degeneracy of Cu²⁺. As the e_g doublet is split by weak next nearest neighbor crystal field, the occupied orbital may change as the exchange correlation is changing from HF ($w=1.0$) toward LSDA ($w=0.4$).

The calculated exchange constants of the normal structure are listed in Table II. At $w=0.4$, the antiferromagnetic J^{BB} s are much stronger than J^{AB} s, which suggests that Néel configuration is unstable.

Local magnetic moments of magnetic ions are calculated for both normal and inverse structures with Néel configuration by Mülliken population analysis (Fig. 1). As w decreases, the local magnetic moments of magnetic ions decrease, which implies a stronger covalency between magnetic ion and oxygen. At $w=0.4$, the magnetization of the normal structure with Néel configuration is $8.4 \mu_B$ per chemical formula.

There is a stair in the curve of local magnetic moment of Cu²⁺ of the inverse structure from $w=0.7$ to 0.6, which is

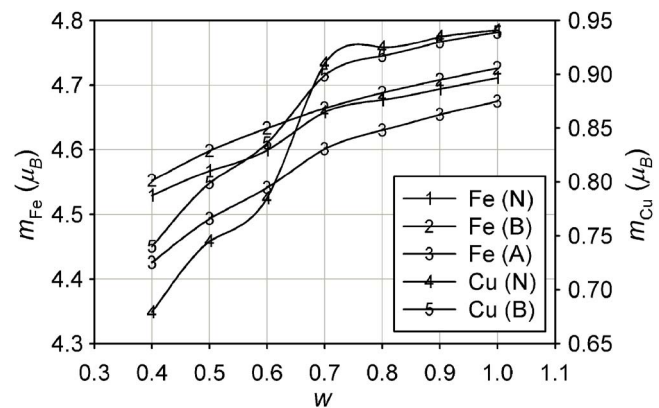


FIG. 1. Calculated local magnetic moments for both normal and inverse structures.

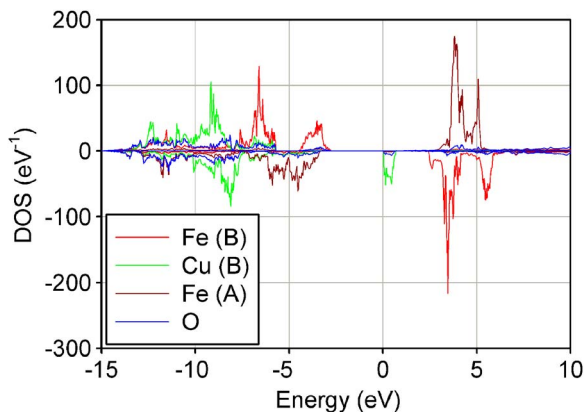


FIG. 2. Calculated DOS of the inverse structure with Néel configuration at $w=0.4$.

concurrent with the oscillation of J_{CuCu}^{BB} and may be related to the change of the occupied orbital of Cu^{2+} . A similar stair in the curve local magnetic moment of Cu^{2+} is also observed in the normal structure around the same value of w .

Density of states (DOS) is calculated as the core electronic structure result for both inverse and normal structures with Néel configuration at $w=0.4$. In the calculated DOS of the inverse structure (Fig. 2), the spin-down Cu^{2+} d band is right above the Fermi level in energy. As we adopt the level-shift technique to guarantee the insulating states, which shifts the conduction bands up by 0.3 hartree in self-consistent cycles and shifts back after the cycles, the Fermi level is very likely to fall into the spin-down Cu^{2+} d band in fact. If this is

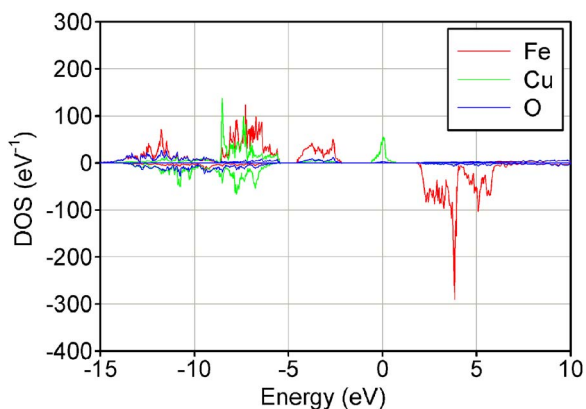


FIG. 3. Calculated DOS of the normal structure with Néel configuration at $w=0.4$.

true, the inverse structure may be half metallic. However, in calculated DOS of the normal structure (Fig. 3), the Fermi level directly falls into the spin-up Cu^{2+} d band. This suggests that the normal structure may also be half metallic.

IV. CONCLUSION

The calculated exchange constants at $w=0.4$ show that Néel configuration may be unstable for both normal and inverse structures. The calculated DOS with Néel configuration at $w=0.4$ shows that both normal and inverse structures may be half metallic. The calculated local magnetic moments of magnetic ions of the normal structure with Néel configuration show that the normal structure may achieve a high magnetization.

ACKNOWLEDGMENTS

Xu Zuo's research is sponsored by the Research Initiation Fund granted by Human Resource and Beneficial Office of Nankai University and Nankai Innovation Fund granted by Nankai University. Vincent G. Harris and Carmine Vittoria are funded by the U.S. National Science Foundation under Grant No. DMR-0400676.

- ¹X. Zuo, S. D. Yoon, and C. Vittoria, *J. Magn. Magn. Mater.* **272–276**, 1795 (2004).
- ²X. Zuo, F. Yang, R. Mafhoum, R. Karim, A. Tebano, G. Balestrino, V. G. Harris, and C. Vittoria, *IEEE Trans. Magn.* **40**, 2811 (2004).
- ³A. Yang, V. G. Harris, S. Calvin, X. Zuo, and C. Vittoria, *IEEE Trans. Magn.* **40**, 2802 (2004).
- ⁴X. Zuo, A. Yang, S. D. Yoon, J. A. Christodoulides, V. G. Harris, and C. Vittoria, *J. Appl. Phys.* **97**, 10G103 (2005).
- ⁵X. Zuo and C. Vittoria, *Phys. Rev. B* **66**, 184420 (2002).
- ⁶X. Zuo and C. Vittoria, *J. Appl. Phys.* **93**, 8017 (2003).
- ⁷X. Zuo and C. Vittoria, *IEEE Trans. Magn.* **39**, 3133 (2003).
- ⁸X. Zuo, B. Barbiellini, and C. Vittoria, *J. Magn. Magn. Mater.* **272–276**, 306 (2004).
- ⁹V. J. Folen, in *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology, New Series*, edited by K.-H. Hellwege and A. M. Hellwege (Springer, New York, 1970), Group III, Vol. 4, Part b, Chap. 6, p. 343.
- ¹⁰S. Krupička and P. Novák, in *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North-Holland, New York, 1982), Vol. 3, Chap. 4, p. 215.
- ¹¹A. Yang, X. Zuo, L. Chen, Z. Chen, C. Vittoria, and V. G. Harris, *J. Appl. Phys.* **97**, 10G107 (2005).
- ¹²R. Saunders, R. Dovesi, C. Roetti, M. Causa, N. M. Harrison, R. Orlando, and C. M. Zicovich, *Computer Code CRYSTAL98, User's Manual* (Theoretical Chemistry Group, University of Turin, Torino, Italy, 1999).
- ¹³A. D. Becke, *J. Chem. Phys.* **93**, 5648 (1993).
- ¹⁴H. Ohnishi and T. Teranishi, *J. Phys. Soc. Jpn.* **16**, 35 (1961).
- ¹⁵K. P. Sinha and A. P. B. Sinha, *J. Phys. Chem.* **61**, 758 (1957).
- ¹⁶X. Zuo, Y. He, A. Yang, B. Barbiellini, V. G. Harris, and C. Vittoria, *J. Appl. Phys.* **97**, 10F104 (2005).