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First-Principles Investigation of the Electronic Structure and Magnetic Properties for Co-Doped Fe_3O_4

Yuhua Hou[1,a], Yujun Zhao[2,b], Dechang Zeng*[,1,c], Zhongwu Liu[1,d], Lishi Wen[1,e]

[1]School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, P.R.China
[2]Department of Physics, South China University of Technology, Guangzhou 510640, P.R. China

[a]houyuhua@tom.com, [b]zhaoyj@scut.edu.cn，[c]medczeng@scut.edu.cn,
[d]zwliu@scut.edu.cn, [e]lsw2303@163.net

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Abstract: The electronic structure and magnetic properties of the $(Co_{1-x}Fe_x)_{Tet}(Co_xFe_{2-x})_{Oct}O_4$ spinels (x is defined as the degree of inversion) scenario are investigated theoretically from first-principles, using generalized gradient approximation (GGA) method for the systems with strong coulomb correlations, which gives a correct description of the electronic structure. The GGA+U method gives an improved qualitative result compared with the GGA not only for the excited-state properties such as energy gaps but also for the ground-state properties such as magnetic moments and crystal parameters. The nominal valence of the transition metal elements and the ground state structure have been established based on the study of variation of the cation distribution (x=0.0, 0.25, 0.5, 0.75 and 1.0) over the tetrahedral and octahedral sites. The site-preference calculation on bulk systems indicates that Co^{2+} ions strongly prefer the octahedral B sites, and the electronic structure and magnetic properties of cobalt ferrites highly depend on the cation distributions even though the chemical composition of the compound does not change. The results are in good agreement with the available experimental data and most of the other theoretical results.

Introduction

Spinel ferrites [1] have been studied for many years both on their magnetic behavior and on their correlated nature according to their structural properties to improve their performance in high-frequency devices. Especially the spinel cobalt ferrite is a very important magnetic material, which has covered a wide range of applications including electronic devices, magnetic delivery microwave devices and high density information storage [2-4].

The spinels AB_2O_4 constitute one of the most interesting and important families of crystalline compounds, the *A* and *B* cations can occupy two different sites in the spinel structure, *e.g.* octahedral (O_h) and tetrahedral (T_d) sites within an fcc oxygen sublattice. Studies of cation distributions in spinels are of considerable interest for a better understanding of correlation between structure and properties such as magnetic properties, conductivity, catalytic activity, *etc*, which are dependent on the relative O_h and T_d occupancy by metals [5-7]. The cation distribution can be characterized by the fraction of the divalent metal cations in octahedral sites, such as: $(Co_{1-x}Fe_x)_{Tet}[Co_xFe_{2-x}]_{Oct}O_4$. In this formula, the parentheses and square brackets denote the tetrahedral and octahedral surroundings, respectively. Temperature and heat treatment process [8-11] have an important effect on the cation distributions and thus it is difficult to synthesize spinels in a wide range of cation distributions experimentally.

Recently, many theoretical studies [4, 12-14]have been dedicated to $CoFe_2O_4$. Some approaches (LSD,LMTO) [4,12]usually describe these materials to be half-metallic, and the reason is that the transition metal(TM)d electrons in oxides are strongly correlated and cannot be adequately described within the standard band theory framework which places them too high in energy around the fermi level. The DFT+U [12] and SIC-LSD [14] considering the strong correlations for the transition metal (TM) *d* electrons have correctly described $CoFe_2O_4$ as insulators. In this work, the GGA+U approximation was employed to systematically study the magnetic structures of the transition metal oxides $(Co_{1-x}Fe_x)_{Tet}[Co_xFe_{2-x}]_{Oct}O_4$($x$=0.0,0.25,0.50,0.75 and 1.0) in terms of local and microscopic properties derived from quantum-mechanical calculations.

Spinel Structures

The conventional unit cell of the $CoFe_2O_4$ spinel structure contains eight formula units, and it is cubic and belongs to the Fd3m space group (227). Cations occupy 8a and 16d special wyckoff positions of T_d and O_h symmetries at (0,0,0) and (5/8,5/8,5/8), respectively, whereas oxygen occupy the 32e general position at (u, u, u), u being the positional parameter of oxygen[15]. It should be noted that the spinel is a relatively open structure since the cations only occupy around 33% of the octahedral and tetrahedral voids [16].

In this work, The smallest irreducible cell instead of the conventional unit cell was used to solve the electronic structure of the crystal, and the advantage of using this primitive cell is to decrease computational time while keeping the physics of the system unaltered. The primitive unit cell of the normal and inverse spinel structure consists of a hexagonal cell (see Fig.1) with two $CoFe_2O_4$ formula units. In the case of x=0.25, 0.5 and 0.75, a supercell containing four $CoFe_2O_4$ formula units has been used to model these spinel structures.

Computational Methods

Every geometry optimization and minimization of the total energy have been performed using the Vienna ab initio Simulation Package (VASP)[17,18]which has been successfully applied to calculate many complex systems. In the density functional theory (DFT) framework used, the Kohn-Sham equations have been solved by the generalized gradient approximation(GGA-PBE) proposed by Perdew-Burke-Ernzher[19]. The electron-ion interaction was described by the Projector Augmented-Wave method (PAW)[20,21]. The plane-wave expansion was truncated at a cutoff energy of 450 eV. For the Brillouin-zone integration, a 7×7×7 Monkhorst-Pack special k-points grid has been used. In the present work, we thus pursue GGA+U approach, setting U=4.22eV and J=0.80eV for Co ion and U=4.08eV and J=0.79eV for Fe ion, which can result in a reasonable result.

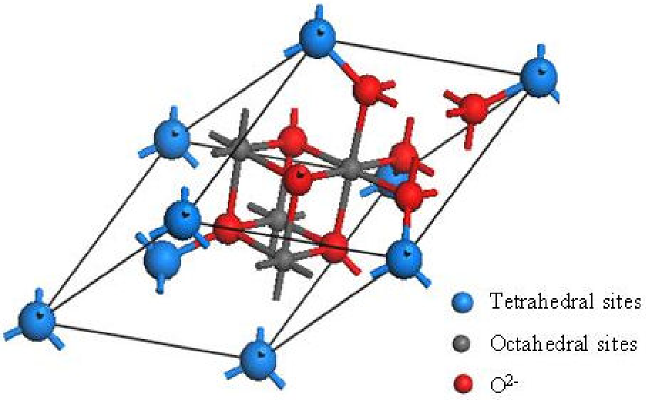

Fig.1 Hexagonal cell used in the calculation

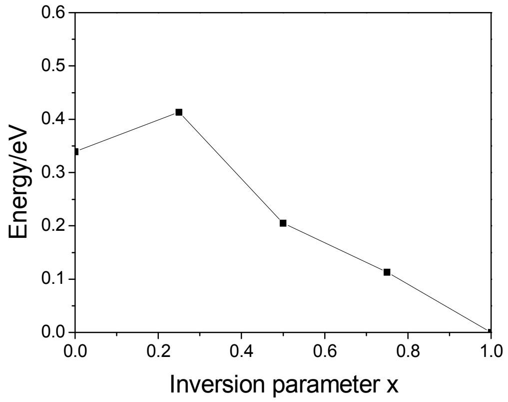

Fig.2 Calculated total energies of $CoFe_2O_4$ spinels at static condition for x=0,0.25,0.50,0.75 and 1.0

Results and Discussion

Structure trends. Fig.2 plots the total energy at the calculated equilibrium static geometries of all the $CoFe_2O_4$ spinels considered in this work versus the degree of inversion x. According to our total energy calculations, the most stable structure is the inverse spinel structure, which is in agreement with the experimental findings [9-11] and other theoretical results [13, 14]. A spinel $CoFe_2O_4$ with a lower degree of inversion x could not be synthesized experimentally due to its instability, but in the present theoretical study, we could investigate cell models with selected x values covering the whole range between 0 and 1, which can supplement the information required in some experimental studies. The static equilibrium configuration of $CoFe_2O_4$ in the inverse spinel configuration (x=1) is found at a=8.384Å and u=0.378, which is in very good agreement with the experimental values [9, 15] and other theoretical results [14].

Table1 Theoretical and experimental cohesive properties of bulk $CoFe_2O_4$ for different values of the inversion parameter x (△E being defined as relative value to the inverse spinel)

Inversion parameter x	u	a(Å)	△E(eV)
x=0.0	0.380	8.308	0.339
x=0.25	0.380	8.270	0.413
x=0.5	0.379	8.337	0.205
x=0.75	0.375	8.355	0.113
x=1.0	0.378	8.384	0
Others theoretical: x=1.0[14]		8.379	
Exp:x=1.0[15]	0.380	8.390	
Exp:x=0.75[9]	0.381	8.381	

Magnetic structure. An investigation of the spin states from the different spinel configurations (x=0 to x=1) has been carried out to illustrate the nature of the magnetic properties of the $CoFe_2O_4$ spinel. Since the spinels contain Fe^{3+} and Co^{2+} in different environments, the electron distribution depends on the strength of the crystal field, so both high spin(weak field) and low spin(strong field) states are possible[5].

Table2.Calculated magnetic moments (μ_B) for Co, Fe and total magnetic moment for per formula unit for different x values

Inversion parameter x	Co_{tet}	Co_{oct}	Fe_{tet}	Fe_{oct}	M_{total}
x=0.0	-2.42			4.12	7
x=0.25	-2.43	2.75	-3.97	4.12	6
x=0.5	-2.45	2.63	-3.95	4.12	5
x=0.75	-2.43	2.62	-3.97	4.11	4
x=1.0		2.61	-3.97	4.10	3
x=1.0[14]		2.58	-4.11	4.11	3
x=1.0[12]		2.58	-3.93	4.08	3
Exp: x=0.69[22]		3.21	-3.08	3.21	3.34
Exp: x=0.96[11]					3.16
Exp: x=0.79[11]					3.84

Table2 lists magnetic moments (μ_B) of Co, Fe and total magnetic moment for per formula unit for the spinels considered. The analysis of the results show that total net magnetic moment decreases, and the tetrahedral Co^{2+} and Fe^{3+} ions always present the high spin configuration state with x increasing, and the spin in the tetrahedral environment is lower than that in the octahedral environment, which show the tetrahedral crystal field (T_d) is stronger than the octahedral crystal field (O_h). The results are in agreement with most theoretical and experimental results.

Conclusion

In this study, the $CoFe_2O_4$ spinel was systematically investigated for the first time by density functional theory with GGA+U method. The calculations show the inverse spinel structure (x=1) to be the most stable, which is in agreement with available experimental and other theoretical results. The influence of x over its whole range (0-1) for Co^{2+}in the octahedral sites on the magnetic properties of $CoFe_2O_4$ was studied. The results show that Co^{2+}ions and Fe^{3+}ions always present the high spin states (three unpaired electrons and five unpaired electrons per ion), and the tetrahedral crystal field (T_d) is stronger than the octahedral crystal field (O_h). The total net magnetic moment decreases with the increasing x, so a small degree of inversion can be expected in an unconventional environment.

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