First-principles investigations of Zn (Cd) doping effects on the electronic structure and magnetic properties of $CoFe_2O_4$

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(Presented 18 November 2010; received 23 September 2010; accepted 18 October 2010; published online 17 March 2011)

The electronic structures and magnetic properties of spinel Co_{1-x} Zn (Cd)$_x Fe_2O_4$ ($x = 0.0$, 0.25, 0.5, 0.75, and 1.0) have been studied systematically by the first-principles calculation. The optimized structures show that with increasing Zn (Cd) content the crystal lattice parameter increases by 1.47% (5.13%) when the Co ions are completely replaced by Zn (Cd) ions. The results also indicate that the magnetic moment of Co/Fe ion increases and the total spin magnetic moment linearly increases with the Zn (Cd) doping from 3.00 μ_B for $x = 0.0$ up to 10.00 μ_B for $x = 1.0$ per formula unit. The electronic distribution in the Co spin-down subband is highly localized for the crystal field splitting between t_{2g} and e_g levels in the Zn (Cd) doped $CoFe_2O_4$ compounds and the energy band moves downwards while doped with Zn (Cd). Meanwhile, the bandgap decreases with the increase of Zn (Cd) except where $x = 1$ and the spinel structure is half-metal at some degree of doping. © *2011 American Institute of Physics*. [doi:10.1063/1.3535442]

Over the last few years the development of cobalt ferrite ($CoFe_2O_4$) based materials has attracted a great deal of attention due to their cubic magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, electrical insulation, high sensitivity of magnetic induction to applied stress, chemical stability, and low cost.[1–8] Such properties make these materials good candidates for use in magnetoelastic sensors, actuators, and, more recently, as a magnetoelastic component in composite multiferroic.[9] Cobalt ferrites crystallize in an inverse spinel form with space group Fd3m-O^7_h. In spinel ferrites, cations can occupy two types of interstitial site i.e. the tetrahedral (A) site and the octahedral (B) site.

Substitution of nonmagnetic ions at either site alters the A–A or B–B and A–B interactions, which can lead to a significant change in their physical properties. Therefore, by doping the nonmagnetic ion in cobalt ferrites one can tailor or control its properties, including the electrical properties, magnetic properties, etc. A wide range of experimental studies have shown that partial replacement of cobalt by other ions (e.g. Zn and Cd) in cobalt ferrite increases the saturation magnetization to a certain extent.[10–12] However, the magnetic and electronic properties of Co-Zn (Cd) ferrite have rarely been discussed in theoretical studies and few detailed and systematic calculation studies of Co-Zn (Cd) ferrite have been published. In this work, therefore, a systematic investigation of Zn (Cd) doping effects on the electronic structure and magnetic properties of $CoFe_2O_4$ are performed.

The electronic structure calculation and structural optimization are performed using the Vienna *ab initio* Simulation Package[13,14] with the Perdew–Burke-Ernzerh parameterized generalized gradient approximation (GGA)[15] and projector augmented-wave methods.[16,17] A 28-atom unit cell is constructed as a magnetic cell in the present work. To study the effect of concentration in $CoFe_2O_4$, some of the Co^{2+} ions were substituted by Zn $(Cd)^{2+}$ ions in the unit cell. The plane-wave expansion was truncated at a cutoff energy of 450 eV in all of our calculations. The optimizations were performed with a $3 \times 3 \times 3$ k-mesh. The relaxations of lattices were stopped until the forces on each ion converged to less than 10 meV/Å. Then, the total energy, electronic structure, and magnetic properties were calculated using GGA + the on-site Coulomb repulsion energy (U) exchange correlation.[18–20] For the final total energy calculations, the tetrahedron method of a $7 \times 7 \times 7$ k-mesh was used. In both structural optimization and electronic structure calculations, the magnetic moments on tetrahedral and octahedral sites are antiparallel to each other. To explore the effects of the on-site Coulomb energy U on the electronic structures and magnetic moments, specific values for Co ($U = 4.22$ eV and $J = 0.80$ eV), Fe ($U = 4.08$ eV and $J = 0.79$ eV), Zn ($U = 4.76$ eV and $J = 0.80$ eV), and Cd ($U = 3.94$ eV and $J = 0.60$ eV)[20] were chosen in the GGA + U calculation.

Table I lists our calculated structural parameters of Zn (Cd) doped on $CoFe_2O_4$. The lattice constant shows a minimum at $x = 0.5$ and then increases on further dilution for Zn-doping. A linear change in the lattice constant of bulk $Co_{1-x}Zn_xFe_2O_4$ with zinc was observed[21,22] due to the higher ionic size[23] of Zn^{2+} (0.74 Å vs 0.72 Å for Co^{2+}). Nonlinear behavior was reported in Refs. 10, 24, which may be due to the fact that the Co-Zn ferrites are not completely normal or inverse spinel.[25] While our data in Table I reveal a systematic increase of the lattice parameter in the Cd substituted series according to Vegard's law and the result is in good agreement with experiments.[12] The increase of the lattice parameter with increasing Cd content results from the larger ionic size of Cd^{2+} compared to Co^{2+} (0.97 Å vs 0.72 Å).[23]

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TABLE I. Calculated structural parameters and magnetic information for $Co_{1-x}Zn$ $(Cd)_xFe_2O_4$. Experimental measurements are listed for comparison. $\mu_{Fe(Co)}$ is the average spin magnetic moment (μ_B) of Fe and Co.

		Zn doping				Cd doping			
x		a(Å)	$\mu_{Co(B)}$	$\mu_{Fe(A)}$	$\mu_{Fe(B)}$	a(Å)	$\mu_{Co(B)}$	$\mu_{Fe(A)}$	$\mu_{Fe(B)}$
0.00	GGA+U	8.384	2.608	3.972	4.102	8.384	2.608	3.972	4.102
	Expt.	8.420[a]	—	—	—	8.380[c]	—	—	—
		8.385[b]	—	—	—				
0.25	GGA+U	8.400	2.638	3.971	4.144	8.440	2.636	3.965	4.138
	Expt.	8.395[a]	—	—	—	8.460[c]	—	—	—
0.50	GGA+U	8.397	2.697	3.949	4.150	8.540	2.698	3.958	4.176
	Expt.	8.380[a]	—	—	—	8.540[c]	—	—	—
		8.413[b]	—	—	—				
0.75	GGA+U	8.417	2.911	3.985	4.175	8.600	2.755	3.997	4.191
	Expt.	8.437[a]	—	—	—	8.590[c]	—	—	—
1.00	GGA+U	8.507	—	—	4.234	8.810	—	—	4.243
	Expt.	8.491[a]	—	—	—	8.680[c]	—	—	—

[a]From Ref. 10.
[b]From Ref. 21.
[c]From Ref. 12.

The calculated local magnetic moments of Co and Fe (occupying the tetrahedral and octahedral sites, respectively) are also listed in Table I. The results show that all local magnetic moments are suppressed as compared with the ideal values (3.00 μ_B and 5.00 μ_B for Co^{2+} and Fe^{3+}, respectively) due to the *pd* hybridizations. The local moments of Zn and Cd ions are negligibly small. The spin moments on the oxygen ions are also small due to the nearly closed 2p shells. Note that Zn^{2+} and Cd^{2+} have the preferential occupation of tetrahedral sites, thus displacing Fe^{3+} from tetrahedral sites to octahedral sites,[26] which leads to the difference in magnetic properties between the tetrahedral sublattice and the octahedral sublattice in the antiferromagnetic coupling. With increase of x, the absolute magnitude of $\mu_{Co(B)}$ increases from 2.608 to 2.911 μ_B and the $\mu_{Fe(A)}$ ($\mu_{Fe(B)}$) increases from 3.972 μ_B (4.102 μ_B) to 3.985 μ_B (4.235 μ_B) for the Zn doping. The calculated saturation magnetic moment linearly increases with the increase of Zn content 28-atom cell. The magnitude of magnetism is 12.0, 19.0, 26.0, 33.0, and 40 μ_B for $Co_{1-x}Zn_xFe_2O_4$ with compositions $x=0.00$, 0.25, 0.50, 0.75, and 1.00, respectively. For the Cd doping, the absolute magnitude of $\mu_{Co(B)}$ increases from 2.608 to 2.755 μ_B and $\mu_{Fe(A)}$ ($\mu_{Fe(B)}$) increases from 3.972 μ_B (4.102 μ_B) to 3.997 μ_B (4.243 μ_B). The calculated saturation magnetic moments are 12.0, 19.0, 26.0, 32.82, and 40 μ_B for $Co_{1-x}Cd_xFe_2O_4$ with compositions $x=0.00$, 0.25, 0.50, 0.75, and 1.00, respectively. However, the experiments in Refs. 10, 12, 24, 27 reported that saturation magnetization initially increased and then decreased with the increase of x for the Zn (Cd) doped $CoFe_2O_4$. The low magnetization values for large x obtained in the experiments could be ascribed to the Yafet–Kittel type of spin arrangement.[28]

Figure 1 shows the atom-projected density of states (DOS) for $Co_{1-x}Zn_xFe_2O_4$ ($x=0$, 0.25, 0.5, 0.75, and 1.0). The calculation for both undoped and doped structures shows that the ground state has changes from insulating to half-metallic character except where $x=1.0$ with increasing zinc concentration. The DOS of nonmagnetic ions (Zn^{2+}) is dominant in the range of 9–8 eV below E_F and has little effect on the electronic structure at E_F. In fact, the projected DOS of Co and Fe ions in the octahedral sites plays an important role in the electronic structure around E_F. When the zinc content increases (x increases from 0.0 to 0.75) the DOS above E_F decreases. There is a sharp band shift of the Co^{2+} levels when doped with Zn in the $CoFe_2O_4$ structure. The crystal field splitting between

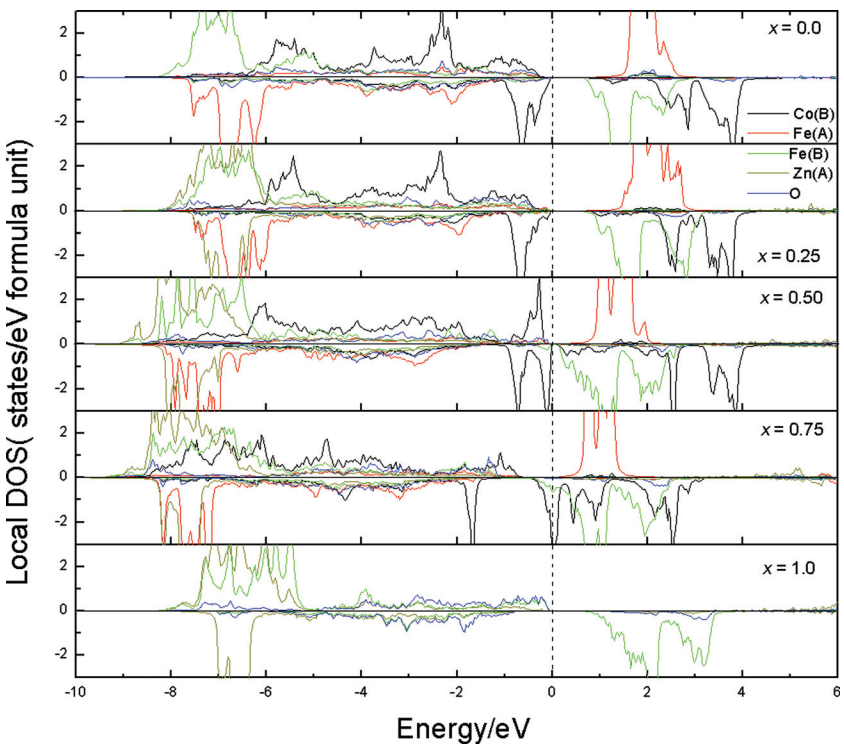

FIG. 1. (Color online) The atom-projected DOS of $Co_{1-x}Zn_xFe_2O_4$ ($x=0.0$, 0.25, 0.5, 0.75, and 1.0) from GGA + U calculations. The spin-up and/or spin-down DOS is shown above and/or below the abscissa axis. The Fermi level is at zero energy.

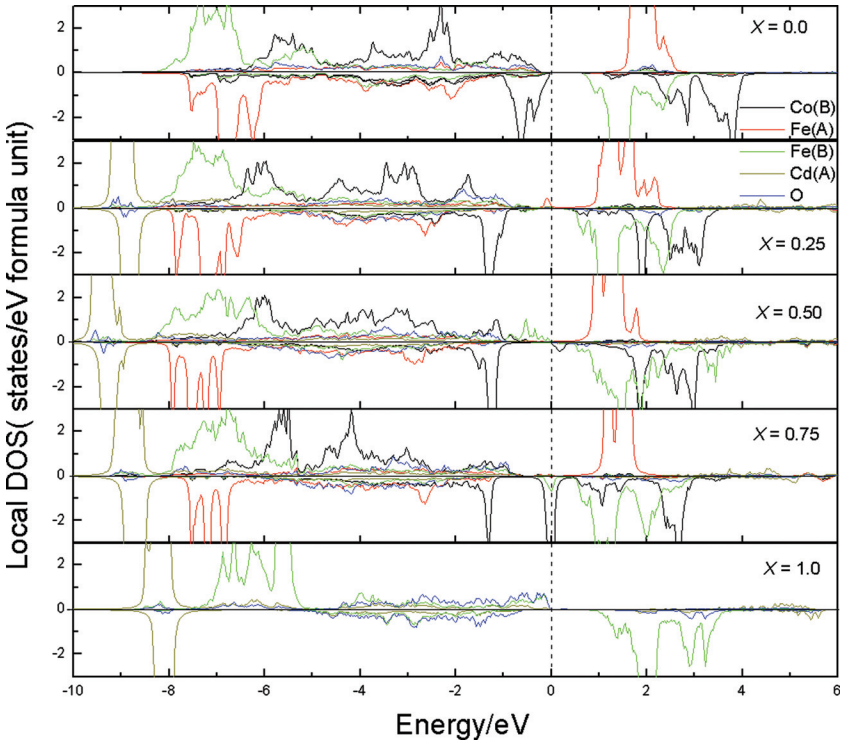

FIG. 2. (Color online) The atom-projected DOS of $Co_{1-x}Cd_xFe_2O_4$ ($x=0.0$, 0.25, 0.5, 0.75, and 1.0) from GGA + U calculations. The spin-up and/or spin-down DOS is shown above and/or below the abscissa axis. The Fermi level is at zero energy.

Co t_{2g} and Co e_g levels in Zn doped $CoFe_2O_4$ compounds is larger than that of the $CoFe_2O_4$ compound. The band of Fe^{3+} in the tetrahedral site becomes more polarized with increasing zinc content while the case is opposite for Fe^{3+} in the octahedral site.

Figure 2 shows the atom-projected DOS for $Co_{1-x}Cd_xFe_2O_4$ ($x=0$, 0.25, 0.5, 0.75, and 1.0), which reveals a change from insulating to metallic character except where $x=1.0$ with increasing cadmium concentration. The DOS of nonmagnetic ions (Cd^{2+}) is far below E_F and has little impact on the electronic structure at E_F. Similar to Zn doped $CoFe_2O_4$, the crystal field splitting between Co t_{2g} and Co e_g levels strengthen in the Cd doped $CoFe_2O_4$ compounds. In addition, as Zn^{2+} and Cd^{2+} have a strong preference for the A sites, the displacement of Fe^{3+} to the B sites due to the substitution of Zn^{2+} and Cd^{2+} reduces the A–B interaction, as clearly shown in Figs. 1 and 2.

In conclusion, we have investigated the effects of Zn (Cd) doping on the electronic structure and magnetic properties of $CoFe_2O_4$ by density function calculations. The results show that the crystal lattice parameters increases as Zn (Cd) concentration increases except where $x=0.5$ for Zn doping. The total spin moment of the compound linearly increases with Zn (Cd) doping from 3 μ_B for $x=0.0$ up to 10 μ_B for $x=1.0$ per formula unit. The result is not in agreement with the existing experimental results, which shows that the spin moment initially increased then decreased. This could be due to the Yafet-Kittel type of spin arrangement in real system. It is also found that the Co/Fe ion magnetic moment increases with Zn (Cd) doping and the DOS is sensitive to the concentration of Zn (Cd) doped $CoFe_2O_4$. The A–B superexchange interaction is weakened as the Zn (Cd) content increases.

We acknowledge the computer time at the High Performance Grid Computer Center of the South China University of Technology (SCUTGrid). This work was supported by the National Natural Science Foundation of China (Grant Nos. U0734001 and 50874050), the Natural Science Foundation of Guangdong Province (Grant No. 8151064101000084), and the Fundamental Research Funds for the Central Universities, SCUT (Grant Nos. 2009ZZ0025, 2009ZM0291, and 2009ZM0247).

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