Computational Materials Science 126 (2017) 344–350

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

# Ferromagnetic orderings in $Co_xCu_yZn_{1-(x+y)}O$ by GGA and GGA+U formalisms within density functional theory

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ARTICLE INFO

*Article history:*
Received 16 March 2016
Received in revised form 27 September 2016
Accepted 30 September 2016
Available online 19 October 2016

*Keywords:*
Semiconductors
Oxide materials
Transition metal impurities
Computer simulations

ABSTRACT

Based on density functional theory within GGA and GGA+U formalisms, first-principles spin-polarized calculations have been performed to study the ferromagnetic orderings in $Co_xCu_{0.042}Zn_{1-(x+0.042)}O$ ($x = 0$ and 0.042). The effect of impurity distances on ferromagnetic and antiferromagnetic ground state in $Cu_{0.042}Zn_{0.958}O$ with GGA scheme has been studied, and compared with the available experimental and theoretical data. Results show that $Cu_{0.042}Zn_{0.958}O$ is ferromagnetic for both the closest and farthest impurity distances, but it is more stable for the closest one. The system is nearly half metallic and room temperature ferromagnetism is expected. When two $Zn^{2+}$ ions are replaced by two $Co^{2+}$ ions in $Cu_{0.042}Zn_{0.958}O$ with GGA and GGA+U formalisms, both the local magnetic moment in 3*d*-Cu and energy difference are reduced. This is in good agreement with the experimental observations, where the room temperature ferromagnetism in $Cu_{0.04}Zn_{0.96}O$ is suppressed when it is doped with Co (4%). When the U parameter for 3*d*-Cu is considered, the ground state for $Cu_{0.042}Zn_{0.958}O$ system remains ferromagnetic. On the other hand, the ferromagnetic ground state found for $Co_{0.042}Cu_{0.042}Zn_{0.916}O$ changes to antiferromagnetic with both GGA and GGA+U schemes. Results with GGA and GGA+U also display a distortion around the impurity-$O_4$ tetrahedron, enhanced antiferromagnetic interaction between Cu—Cu ion and their surrounding atoms, and charge transfer from Co(3*d*) to Cu(3*d*) via O(2*p*) atoms by substitution of $Zn^{2+}$ by $Co^{2+}$ in Cu-doped ZnO. As a result, both the local magnetic moment in 3*d*-Cu and energy difference of $Co_xCu_{0.042}Zn_{1-(x+0.042)}O$ system are reduced.



## 1. Introduction

In recent years, there has been growing interest in studying the magnetic properties of transition metals (TM) doped II-VI and III-V semiconductors due to their potential spintronics applications [1–3]. Among them, TM doped ZnO systems have been focus of great interest [4–7]. ZnO is an excellent semiconductor host for most of the 3*d* TM because $Zn^{2+}$ atom and many 3*d*-TM ions are both divalent. Furthermore, ZnO displays other physical properties that enhance electronic and optoelectronic devices based on TM doped ZnO such as direct and wide band gap, transparency in visual region, crystallization in the wurtzite structure, large piezoelectric constants and high thermal conductivity [8]. Therefore, TM doped ZnO is a highly multifunctional material that can be exploited for manufacturing magneto-optical devices where magnetic, semiconducting, electrochemical, and optical properties coexist [2].

Cu-doped ZnO has been observed to be ferromagnetic both theoretically and experimentally [9–12]. However, Sharma et al. reported that this ferromagnetic order decreases at higher doping concentration due to both the formation of secondary phase and reduction of carrier concentration [13]. On the other hand, it has been found experimentally that doping additional carriers is necessary for enhancing room temperature ferromagnetism in TM-doped ZnO [14–18]. Thus, it could be expected that codoping Cu-doped ZnO with Co ions enhances ferromagnetic properties in Cu-doped ZnO.

Recently, Ashokkumar et al. synthesized successfully $Zn_{0.96-x}Cu_{0.04}Co_xO$ ($0 \leqslant x \leqslant 0.04$) nanoparticles by coprecipitation method [19]. They found that all the samples exhibited a hexagonal wurtzite structure and displayed good optical quality with low scattering or absorption losses. In a later experimental study of $Zn_{0.96-x}Cu_{0.04}Co_xO$ ($0 \leqslant x \leqslant 0.04$), the same author reported that

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http://dx.doi.org/10.1016/j.commatsci.2016.09.045
0927-0256/

magnetization in undoped $Zn_{0.96}Cu_{0.04}O$ sample was suppressed by Co-doping [12]. The authors state that this happened due to the enhanced antiferromagnetic (AFM) interaction between neighboring Cu—Cu ions. This result shows a different behavior in comparison to that presented in $Zn_{0.95-x}Co_{0.05}Cu_xO$ ($0 \leqslant x \leqslant 0.05$) where the magnetic moments appear to be additive for $Zn_{0.95-x}Co_{0.05}Cu_xO$ ($0 \leqslant x \leqslant 0.05$) [20,14].

In order to explain the origin of ferromagnetism in co-doping Cu-doped ZnO with Co, in this paper we study the electronic structure and ferromagnetic (FM) orderings in $Co_xCu_{0.042}Zn_{1-(x+0.042)}O$ ($x = 0$ and 0.042), using both GGA and GGA+U formalisms within density functional theory (DFT). Thus, in order to gain physical insight about the magnetic properties of Co-codoped Cu-doped ZnO, the electronic and magnetic properties of Cu-doped ZnO will be first studied, then these results will be compared with previous theoretical and experimental results found for $Cu_{0.042}Zn_{0.958}O$. The effects of distance between Cu impurities on the magnetic properties in Cu-doped ZnO will be also studied. Next, the total energy of the $Co_{0.042}Cu_{0.042}Zn_{0.916}O$ supercell will be calculated with the two spin-polarized Cu (Co) atoms coupled in FM and AFM states. Then, the effect of the Hubbard (U) parameter of impurities on the magnetic properties of $Co_xCu_{0.042}Zn_{1-(x+0.042)}O$ ($x = 0$ and 0.042) will be studied. Finally, in order to provide fundamental insight into the reduction of both the local magnetic moment in 3*d*-Cu and energy difference of $Co_{0.042}Cu_{0.042}Zn_{0.916}O$ as compared to those ones of $Cu_{0.042}Zn_{0.958}O$, a Bader analysis will be applied to $Co_xCu_{0.042}Zn_{1-(x+0.042)}O$ ($x = 0$ and 0.042) system with GGA and GGA+U formalisms.

## 2. Computational methods

The calculations were performed using the first principles pseudo-potential method in the framework of the spin density-functional theory. Exchange and correlation effects were treated with generalized gradient approximation (GGA) implemented in the Perdew-Burke-Ernzerhof functional (PBE) [21]. The core electrons were described by the projector augmented wave (PAW) method [22,23] wherein the *d* states for Cu, Co and Zn were included as valence electrons. The calculations were performed using *vienna ab initio simulation package* (VASP) [24,25]. The electron wave function was expanded in plane waves up to a cutoff energy of 500 eV. A gamma-centered grid of $8 \times 8 \times 8$ *k*-point has been used to sample the irreducible Brillouin zone in the Monkhorst-Pack special scheme for the wurtzite structure with two Zn and two O atoms per primitive cell [26]. Methfessel-Paxton smearing technique with a smearing width of 0.10 eV was adopted [27]. These parameters ensure a convergence better than 1 meV for the total energy. We have also taken into account the correlation effects of the 3*d* orbitals of Cu, Co and Zn within the GGA+U method [28], where the corresponding effective parameter values ($U_{eff}$ = U-J) used in our calculations for 3*d*-Cu, 3*d*-Co and 3*d*-Zn are 1 eV, 1 eV and 0 eV. To compare with other theoretical studies with DFT, we have also considered different effective parameter values ($U_{eff}$ = U-J) for 3*d*-Cu, 3*d*-Co and 3*d*-Zn [11,16,28,29].

In order to investigate the magnetism of $Co_xCu_{0.042}Zn_{1-(x+0.042)}O$ ($x = 0$ and 0.042), we first studied the electronic and magnetic properties of $Cu_{0.042}Zn_{0.958}O$ using a 96-atom $3a \times 2a \times 4c$ supercell, based on a conventional ZnO wurtzite unit cell with the common lattice parameters *a* and *c*. A $3 \times 4 \times 2$ *k*-point grid was first used for testing the total energy calculations corresponding to both FM and AFM phases of $Cu_{0.042}Zn_{0.958}O$ in a $3a \times 2a \times 4c$ supercell. The energy cutoff was set to 500 eV. We found that $Cu_{0.042}Zn_{0.958}O$ is a Γ-Γ direct semiconductor, as the pure ZnO semiconductor case. We also compared our results with those ones reported by previous theoretical and experimental studies of $Cu_{0.042}Zn_{0.958}O$ and found similar qualitative results, as will be shown in Section 3.1. Then we carried out the total energy calculations for $Co_xCu_{0.042}Zn_{1-(x+0.042)}O$ ($x = 0.042$) using a 96-atom $3a \times 2a \times 4c$ supercell and $3 \times 4 \times 2$ *k*-point grid. The energy cutoff was set to 500 eV.

The magnetic coupling between the doped Cu atoms and the stable ground state of $Cu_{0.042}Zn_{0.958}O$ was studied by performing the total energy calculations corresponding to FM and AFM phases for both short and far Cu—Cu distances. The short and far Cu—Cu distances for $Cu_{0.042}Zn_{0.958}O$ are, approximately, 3.3 Å and 11.0 Å, respectively, as shown in Table 1. Then, two Zn atoms were replaced in the most stable configuration (short Cu—Cu distances) of $Cu_{0.042}Zn_{0.958}O$ supercell with two Co ions to represent a concentration of $x = 0.042$ in $Co_xCu_{0.042}Zn_{1-(x+0.042)}O$, as shown in Fig. 1. Next, the total energy of the $Co_{0.042}Cu_{0.042}Zn_{0.916}O$ supercell was calculated with the two spin-polarized Cu (Co) atoms coupled in FM and AFM states. The Co—Co and the shortest Cu-Co distances are 10.7 Å and ~3.3 Å, respectively, for $Co_{0.042}Cu_{0.042}Zn_{0.916}O$ supercell. In all cases, the atomic positions were optimized.

## 3. Results and discussion

### 3.1. $Cu_xZn_{1-x}O$ ($x = 0$ and 0.042) with GGA and GGA+U formalisms

At ambient conditions, ZnO crystallizes in the hexagonal close-packed wurtzite structure (space group $P6_3mc$). In this primitive cell there are two units of ZnO, tetrahedrally coordinated each, where four atoms of oxygen surround each atom of zinc. The experimental lattice parameters $a, c/a$ and $u$ of wurtzite ZnO are, respectively, $a = 3.253$ Å, $c/a = 1.603$ Å and $u = 0.382c$ [30]. Our PBE results overestimate both *a* and *c* quantities by 1.107% and 1.497%, respectively, and underestimate the *u* parameter by 0.523%. In contrast, our GGA(PBE)+U results underestimate the lattice parameters $a, c/a$ and $u$ by 0.553%, 0.125% and 0.785%, respectively. These results are in good agreement with those ones of previous study of ZnO by GGA+U method [31]. GGA+U gives smaller values than GGA. It is well known that DFT-GGA does not describe correctly the hybridization between Zn-*d* and O-*p* orbitals below the Fermi energy. Instead, it has been proven that GGA+U improves it [8]. The GGA calculations for $Cu_{0.042}Zn_{0.958}O$, tabulated in Table 1, show that the system prefers the FM state for both short and far Cu—Cu distances. It is also displayed that the total magnetic moment is almost constant, with a value of ~1.00 $\mu_B$ per Cu atom. Furthermore, it is shown that the nearest Cu—Cu distance displays the most stable FM ground state and the highest FM energy difference ($\Delta E = E_{AFM}$-$E_{FM}$ in meV).

To study the stable configuration for Cu substitution in ZnO bulk, we calculated the formation energy for $Cu_xZn_{1-x}O$ ($x = 0.042$). The formation energy ($E_f$) can be defined as:

$$E_f = E[Cu_xZn_{1-x}O] - E[ZnO] - \eta_{Cu}E[Cu] + \eta_{Zn}E[Zn]$$

where $\eta_{Cu}$ and $\eta_{Zn}$ are the numbers of Cu added and Zn removed to the ZnO semiconductor host, respectively. E[$Cu_xZn_{1-x}O$], E[ZnO], E[Cu], E[Zn] are the total energies of the supercell with Cu impurity, pure ZnO without impurity, Cu and Zn atoms, respectively. The results of the calculated formation energies for $Cu_{0.042}Zn_{0.958}O$ are listed in Table 1. The formation energy ($E_f$) for the FM ground state and $\Delta E$ found for $Cu_{0.042}Zn_{0.958}O$ are ~4.9 eV and ~112 meV, respectively. The results above are in agreement with previous theoretical and experimental studies of Cu-doped ZnO [9–12]. Huang et al. studied the FM stability in $Cu_xZn_{1-x}O$ ($x = 0.037$, 0.083, 0.056 and 0.125) for the short and far Cu—Cu distances by GGA approach [11]. The authors reported a half-metallic ground state and high ferromagnetic stability for all the calculated Cu concentrations.