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Study of Cu-doping effects on magnetic properties of Fe-doped ZnO by first principle calculations

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Abstract. **Using *ab initio* calculations on $Zn_{0.975-x}Fe_{0.025}Cu_xO$ (x = 0, 0·01, 0·02, 0·05), we study the variations of magnetic moments vs Cu concentration. The electronic structure is calculated by using the Korringa–Kohn–Rostoker (KKR) method combined with coherent potential approximation (CPA). We show that the total magnetic moment and magnetic moment of Fe increase on increasing Cu content. From the density of state (DOS) analysis, we show that Cu-induced impurity bands can assure, by two mechanisms, the enhancement of Fe magnetic moment in $Zn_{0.975-x}Fe_{0.025}Cu_xO$.**

Keywords. **(Fe, Cu)-doped ZnO; diluted magnetic semiconductors; DOS.**

1. Introduction

Magnetism and semiconducting properties can coexist in semiconductor materials by introducing a small fraction of magnetic impurity atoms such as Mn, Cr, Co, Ni, Fe and Cu. This category of semiconductors is called diluted magnetic semiconductors (DMSs). Diluted magnetic semiconductors are expected to play an important role in materials science and electronics. In these materials in addition to the charge, the spin degrees of freedom also play an important role in the physical properties. From II–VI compound semiconductors, ZnO has attracted great attention. It has a wide direct bandgap of 3·3 eV (Landolt-Börnstein 2002). ZnO doped with 3*d* transition metal (TM) elements have been studied widely since the calculation model by Dietl *et al* (2008) who have predicted the possibility of ferromagnetism in ZnO with a small amount of Mn as an impurity. Several magnetic, magneto-optical and magneto-transport properties were observed in ZnO systems doped by transition metals, including Mn-added ZnO (Fukumura *et al* 1999; Ando *et al* 2001; Jin *et al* 2001; Wi *et al* 2004; Piamba *et al* 2011; Iqbal *et al* 2011), Fe-added ZnO (Ueda *et al* 2001; Mok Cho *et al* 2002; Piamba *et al* 2011), Co-added ZnO (Ueda *et al* 2001; Lee *et al* 2002; Mok Cho *et al* 2002; Prellier *et al* 2003; Venkatesan *et al* 2004; Wi *et al* 2004) and Ni-added ZnO (Lee *et al* 2002; Prellier *et al* 2003; Ekicibil *et al* 2012).

Moreover, using first-principle calculations, Sato and Katayama-Yoshida (2000) have demonstrated theoretically that a ZnO matrix doped with TM atoms such as V, Cr, Fe, Co and Ni exhibited ferromagnetic ordering. Furthermore, many *ab initio* calculations were performed on two metals co-doped ZnO. For example, He *et al* (2008) showed the origin of ferromagnetism in (Ga, Co)-doped ZnO doped El Amiri *et al* (2012) explained the enhancement of total and Co magnetic moments in (Co, Cu)-doped ZnO.

Recently, many researchers tried to dope other ions into ZnO matrix to obtain two metal ions co-doped ZnO in order to enhance its optical and magnetic properties by introducing additional carriers (Chakraborti *et al* 2007; Li *et al* 2007; Xu *et al* 2008; Brihi *et al* 2010; Dinesha *et al* 2010). Lin *et al* (2004) supposed that a small amount of additional Cu-doping should create additional carriers in Co-doped ZnO, and its magnetization would be greatly enhanced in bulk samples. In this work, we have performed *ab initio* calculations on $Zn_{0.975-x}Fe_{0.025}Cu_xO$. We show that the total moment and magnetic moment per atom of iron increase by increasing Cu concentration.

2. Electronic and magnetic structure calculations

Electronic structure calculations were performed using the Korringa–Kohn–Rostoker (KKR) method within the density functional theory (Akai 1989). To take into account the random distribution of Fe and Cu in Zn sites, we used the coherent potential approximation (CPA). Vosko, Wilk

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and Nusair (VWN) parametrization of the exchange-correlation energy functional was used (Vosko *et al* 1980). The form of crystal potential is approximated by a muffin-tin potential and the wavefunctions in the respective muffin-tin spheres were expanded in real harmonics up to $l = 2$, where l is the quantum angular momentum defined at each site. Spin polarization, relativistic effect and spin–orbit interaction were taken into account. $Zn_{0.975-x}Fe_{0.025}Cu_xO$ is considered to crystallize in wurtzite structure and we assume that Fe and Cu-doping do not affect the experimental lattice constants much (a = 3·25 Å and c = 5·21 Å) for ZnO (Kisi and Elcombe 1989).

3. Results and discussion

We focus on the magnetic moments of $Zn_{0.975-x}Fe_{0.025}Cu_xO$, ($x$ = 0, 0·02, 0·05). Using *ab initio* calculations, we found that both the total magnetic moment and magnetic moment of Fe increase by increasing Cu concentration. Figure 1 presents variation of the total moment and Fe moment per atom. These results show that the increase of Cu-doping concentration from 0 to 0·05, leads to an increase of both the total moment and iron moment from 0·22 to 0·27 μ_B and from 3·47 to 3·61 μ_B, respectively. Recently, Zhang *et al* (2007) have shown that saturation magnetizations (M_s) are 1·8 μ_B/Fe^{2+} and 2·7 μ_B/Fe^{2+} for $Zn_{0.975}Fe_{0.025}O$ and $Zn_{0.97}Fe_{0.025}Cu_{0.005}O$, respectively. In order to explain this trend of the magnetic moment, we analyse the electron density of states (DOS). First, the valence–electron configurations of Zn and substituting Fe and Cu atoms are $3d^{10}4s^2$, $3d^64s^2$ and $3d^{10}4s^1$, respectively. According to the first hand's rule, the minimum of the total energy of an isolated 3*d* atom corresponds to the occupation of the 3*d* orbitals that gives the highest spin moment. Therefore, the minority 3*d* states of Fe must be partially occupied whereas those of Cu are almost fully occupied. Indeed, the calculated electronic structures of 3*d*-states of Zn, Fe and Cu in $Zn_{0.975-x}Fe_{0.025}Cu_xO$ DOS are in agreement with this assumption (see figure 2(a and b)). Secondly, in figure 3, the total DOS of $Zn_{0.975-x}Fe_{0.025}Cu_xO$ (x = 0, 0·02, 0·05) are reported. In particular, in figure 3(a), the region where DOS is zero presents the bandgap of the host matrix with a value almost equal to 2 eV. Moreover, in figure 3(a–c), we note that the region between 0 and –1·36 eV opens as Cu concentration increases, indicating that the local density of states nearing to left of the Fermi level becomes slightly important. This can be explained by the creation of shallow donor levels caused by Cu introduction. Indeed, as observed in figures 2(a and b), these levels are mainly originating from Cu-3*d* bands. Moreover, Cu-3*d* bands lie exactly in such region (–1·36–0 eV) existing in the bandgap of $Zn_{0.975}Fe_{0.025}O$ DOS (see figure 3(a)), so Cu-introduction creates donor impurity bands. According to our band structure calculations, we can observe the overlap between Fe-3*d* and Cu-induced impurity band states for the spin-down around the Fermi level (figure 2(a and b)) which leads to significant DOS at Fermi level and contributes to the enhancement of the total moment. This overlap also leads to

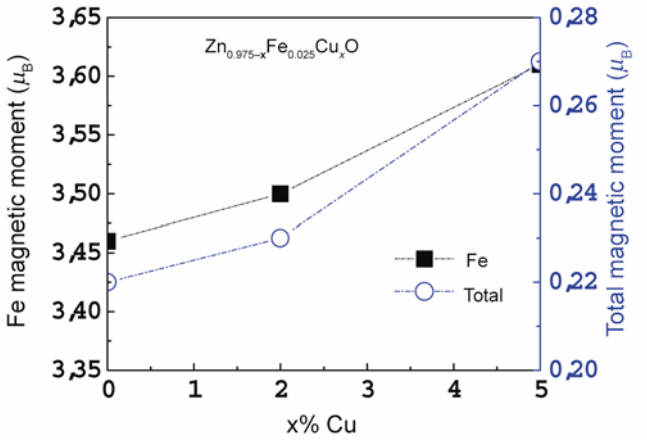

Figure 1. Variation of total and Fe magnetic moments in $Zn_{0.975-x}Fe_{0.025}Cu_xO$ (x = 0, 0·02, 0·05) samples.

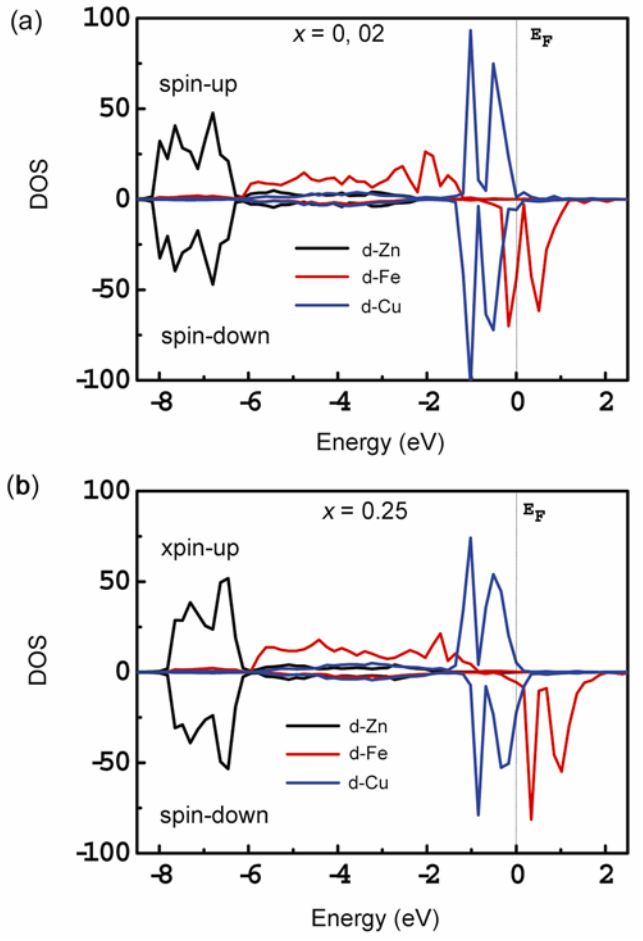

Figure 2. (**a**–**b**) Partial DOS of Zn, Fe and Cu in $Zn_{0.975-x}Fe_{0.025}Cu_xO$ (x = 0·02, 0·05) samples.

hybridization between the involved spin-down states. Such hybridization facilitates mutual charge transfer between Cu and Fe atoms which favours interaction between the localized moments of Fe atoms. This interaction tends to align Fe moments and contributes to increase the charge polarization (spin-up–spin-down) for Fe atoms which explains the results listed in table 1 and consequently the increase of magnetic moment of iron. So, we can conclude that there is a superexchange interaction between Fe atoms caused by Cu-induced donor impurity bands. This interaction is expected to enhance the ferromagnetic ordering between Fe atoms. This assumption is also confirmed by our calculations listed in table 2, where we have reported the difference between the energies of antiferromagnetic (AFM) and ferromagnetic (FM) configurations $\Delta E = E_{AFM} - E_{FM}$. Positive value of ΔE means that Fe atoms prefer FM spin order. Also the exchange parameter J (see table 2) was derived from ΔE by using the following equation.

$$\frac{\Delta E}{2} = -JS(S+1), \tag{1}$$

where S is the Fe magnetic moment and J the exchange parameters of exchange between Fe atoms. We find that without Cu and Fe, atoms choose the AFM spin-order. Soumahoro *et al* (2010) reported that the anti-ferromagnetic contribution increases with iron concentration in Fe-doped ZnO films. As seen in table 2, we note also, that ΔE and J become positive and increase with Cu concentration. So Cu incorporation in Fe-doped ZnO enforce the ferromagnetic coupling between Fe atoms. This can be explained by the fact that the copper atoms are logged between Fe atoms and consequently favours super exchange interaction between Fe atoms. Working on similar components, Fengchun *et al* (2011) reported that activation of the ferromagnetism of (Co, Cu)-doped ZnO relative to Co-doped ZnO is due to the effective hybridization between Co-3*d* states and the Cu-induced donor impurity band at the Fermi level which is consistent with our results. Another possible explanation of the enhancement of magnetic moment of iron is the role of donor impurity bands on the magnetic couplings. Recently, Coey *et al* (2005) proposed that the ferromagnetic exchange couplings mediated by shallow donor electrons that formed bound magnetic polarons (BMP) in oxide DMSs (Venkatesan *et al* 2004; Coey *et al* 2005). In our work, the Cu cation substitution for Zn^{2+} ions introduces easily shallow donor levels in the bandgap and therefore, contributes to BMP formation which favours a

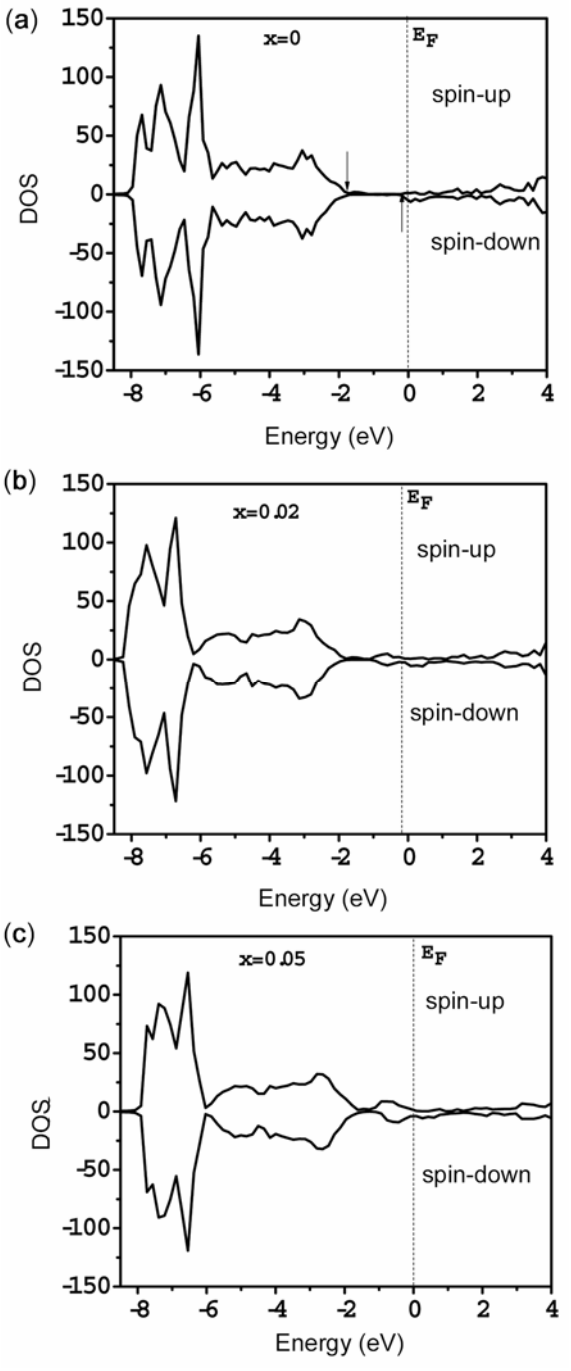

Figure 3. (**a**–**c**) Total DOS of $Zn_{0.975-x}Fe_{0.025}Cu_xO$ (x = 0, 0·02, 0·05) samples.

Table 1. Valence charge of Fe.

	Up	Down	Up/Down
0	4, 33	0, 86	3, 47
2	4, 34	0, 84	3, 5
5	4, 38	0, 77	3, 61

Table 2. Variation of ΔE and J vs content of Cu.

x (% Cu)	$E_{AFM} - E_{FM}$ (meV)	J (meV)
0	–0·3	$-9{\cdot}52 \times 10^{-3}$
2	1·35	$4{\cdot}28 \times 10^{-2}$
5	5·3	0·16

ferromagnetic exchange coupling between Fe ions and consequently increase of Fe magnetic moment. Both interpretations are well confirmed by our DOS calculations, so we can conclude that both mechanisms can contribute to the enhancement of ferromagnetism in Cu–Co doped ZnO.

4. Conclusions

In this work, we have performed *ab initio* calculations on $Zn_{0·975-x}Fe_{0·025}Cu_xO$ (x = 0, 0·01, 0·02, 0·05). We have reported that the magnetic moment per Fe atom increases with increasing Cu content. Also, using total and partial DOS, we are able to show that Cu-induced impurity bands ensure by two mechanisms, the enhancement of Fe magnetic moment in $Zn_{0·975-x}Fe_{0·025}Cu_xO$ systems.

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