The local magnetic moment and electron transfer of ZnO-based dilute magnetic semiconductors

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Abstract. The electronic structures and magnetic properties of ZnO semiconductors doped with Cu, Co, C, Al and S are studied by first-principles calculation. The electronic transfer among Zn, O and doped atoms, and the differences of the number of electron between spin-up and spin-down, $\Delta s$, $\Delta p$, $\Delta d$ for s, p and d orbits of these atoms, are analyzed in detail. It is found that, the ferromagnetic ground state is stabilized by its half-metallic electronic structure, and the strong local magnetic moments in $\text{Zn}_{1-x}\text{Cu}_x\text{O}$, $\text{Zn}_{1-x}\text{Co}_x\text{O}$ and $\text{ZnO}_{1-x}\text{C}_x$ ($x = 5.55\%$) DMSs originate mainly from the strong hybridizations between Cu-3d and O-2p, Co-3d and O-2p, Zn-3d and C-2p electrons. It is considered that the requirements to give rise to the ferromagnetism in the DMSs are the strong local magnetic moment and the electron transfer. The magnetic coupling in $\text{Zn}_{1-x}\text{Co}_x\text{O}$, $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ and $\text{ZnO}_{1-x}\text{C}_x$ is also considered to be a RKKY interaction.

1. Introduction

Up to now, room-temperature ferromagnetism (FM) has been observed in ZnO doped with V [1], Cr [2], Mn [3], Fe [4], Co [5-6], Ni [7], Cu [8] and C[9]. There are various viewpoints about the mechanism of ferromagnetism in DMSs. First viewpoint considers that the ferromagnetism comes from the secondary phase [10]. The second one suggested that the high-temperature ferromagnetism originates from O-vacancy-stabilized metastable phase rather than through a carrier-induced mechanism between separated and uniformly dispersed Mn atoms in ZnO [11]. The third one is that, the ferromagnetic state is stable due to the double-exchange mechanisms [12]. The fourth one is that, the ferromagnetic state is stable due to the long-range coupling mechanisms [13-15]. Priour et al. considered ferromagnetism in spatially randomly located magnetic moments, as in a diluted magnetic semiconductor, coupled via the carrier-mediated indirect exchange RKKY interaction [13]. The calculated results on the O surfaces of Co-ZnO indicated that substitutional Co ions develop large magnetic moments, and its long-range order depends on their mutual distance [14]. Zhu et al. suggested that Li and Cu atoms tend to segregate toward Mn atoms and strongly promote the ferromagnetic coupling via either RKKY or superexchange interaction [15].

However, up to now, the ferromagnetic coupling mechanism of DMSs is still not quite clear. Is it short range exchange, super-exchange coupling or long-range RKKY exchange? In this paper, the electronic structures and the magnetic properties of ZnO semiconductors doped with Cu, Co, C, Al and S are studied by first-principles calculation.
2. Models and calculation

The electronic structures and magnetic coupling in Zn\textsubscript{1−x}M\textsubscript{x}O or ZnO\textsubscript{1−x}M\textsubscript{x} (x=5.55%, M=Co, Cu, C, Al, S) were calculated based on DFT. The first-principles calculations were performed using PAW method as implemented in VASP. The detailed calculations can be also found in our previous papers [16,17]. A plane-wave energy cutoff of 520 eV was used. The relaxations of lattices were stopped until the forces on each ion are converged to less than 0.01 eV/Å. These parameters ensure a good convergence of 1 meV on the total energies. The experimental lattice constants of ZnO unit cell (a = b = 3.249 Å, c = 5.205 Å) were used. To study the electron transfer, the positions of 72 atoms are labeled in Figure 1 for x=5.55%. Here, both O atoms at the 8\textsuperscript{th} and i\textsuperscript{th} (i=25, 14, 33, 7, 35, 18, 9) sites are replaced by two C or S (grey) atoms; It gives seven distinct pairs of M atoms, such as (8, 25), (8, 14), (8, 33), (8, 7), (8, 35), (8, 18), (8, 9), respectively. Both Zn atoms at the 46\textsuperscript{th} and i\textsuperscript{th} (i=57, 38, 55, 45, 61, 50, 48) sites are substituted with two Co (Cu or Al) atoms. It gives seven distinct pairs of M atoms, such as (46, 57), (46, 38), (46, 55), (46, 45), (46, 61), (46, 50), (46, 48), respectively.

![Figure 1](image)

Figure 1. The 3 × 3 × 2 supercell of wurtzite ZnO containing 36 Zn (blue) and 36 O (red) atoms with the labeled doped atomic sites.

3. Results and discussions

The typical total density of states (DOSs) and projected density of states (PDOSs) for Zn\textsubscript{0.9445}Cu\textsubscript{0.0555}O, have been calculated. From the calculated results, it is found that the their electronic structures have a half-metallic character, and most of the spin polarization states are found to originate from Cu 3d electrons. Also, the majority of the peaks at the Fermi level is contributed by Cu-3d electrons. Moreover, the ferromagnetism is a consequence of overlap between Cu 3d and O 2p states in the vicinity of the Fermi level, namely hybridization between Cu 3d electron and O 2p electron. For Zn\textsubscript{0.9445}Co\textsubscript{0.0555}O and ZnO\textsubscript{0.9445}C\textsubscript{0.0555}, the similar DOSs, PDOSs and ferromagnetism have been found in our previous studies [5, 17]. The total magnetic moments for the Zn\textsubscript{1−x}Co\textsubscript{x}O, Zn\textsubscript{1−x}Cu\textsubscript{x}O and ZnO\textsubscript{0.9445}C\textsubscript{0.0555} supercells are nearly 6.05μ\textsubscript{B}, 2.0μ\textsubscript{B} and 4.0μ\textsubscript{B} respectively. The results above are coincident with Akai’s theory in which it is suggested that DMS with half-metallic character has a ferromagnetic ground state [12]. So the nearly half-metallic electronic structures should favor the ferromagnetic ground state. The typical DOSs and PDOSs for Zn\textsubscript{0.9445}Al\textsubscript{0.0555}O and ZnO\textsubscript{0.9445}S\textsubscript{0.0555} have also been calculated. The calculated results indicate that the DOSs and PDOSs of spin-up and spin-down are almost symmetrical, which means that ZnO DMSs doped with Al or S are not magnetic.

For each configuration in Figure 1, the total energy difference $J=E_{\text{AFM}}-E_{\text{FM}}$ between the ferromagnetic ($E_{\text{FM}}$) and antiferromagnetic ($E_{\text{AFM}}$) spin configurations for various doped concentrations are calculated. In the simulation, the value of $J$ is considered as the magnetic coupling strength for the pair of Co, Cu or C atoms. If the value of $J$ is negative, the AFM configuration is more stable, and if it...
is positive, the FM configuration is more stable. Figure 2 shows the magnetic coupling strength $J$ of Zn$_{0.945}$Co$_{0.055}$O, Zn$_{0.945}$Cu$_{0.055}$O and ZnO$_{0.945}$C$_{0.055}$ for seven Co-Co, Cu-Cu and C-C configurations. From the figure, it is found that most of the configurations of Zn$_{0.945}$Co$_{0.055}$O, Zn$_{0.945}$Cu$_{0.055}$O and ZnO$_{0.945}$C$_{0.055}$ DMSs have FM ground state except configuration 1 of ZnO$_{0.945}$C$_{0.055}$. This trend is consistent with the results obtained by Sluiter et al. [18] and Park et al.[19].

**Figure 2.** Magnetic coupling strength $J$ for seven Co-Co, Cu-Cu and C-C configurations for Zn$_{0.945}$Co$_{0.055}$O, Zn$_{0.945}$Cu$_{0.055}$O and ZnO$_{0.945}$C$_{0.055}$.

Figures 3 (a) (b) (c) show the electron transfer structures of configurations 2, 5 and 7 for Zn$_{0.945}$Cu$_{0.055}$O, and pure ZnO. As seen in Figure 2, the configurations 2, 5 and 7 have all stable ferromagnetism. For the pure ZnO, every O atom gains 1.25 electrons, and every Zn atom loses 1.25 electrons. When Cu atoms are doped, the electron transfer resulting from the doped Cu atoms is evident, and the charge redistribution appears. The electrons of doped local Cu atom are transferred not only to the nearest O atoms but also to O atoms being far away the local Cu atom, which means that the transfer electrons above are itinerant. Similar electron transfer structures have been obtained in Zn$_{0.945}$Co$_{0.055}$O and ZnO$_{0.945}$C$_{0.055}$. Comparing to the electron transfer structures of three samples, we can find that the itinerant electron number in Zn$_{0.945}$Co$_{0.055}$O is minimum, and one in Zn$_{0.945}$Cu$_{0.055}$O is second, and one in ZnO$_{0.945}$C$_{0.055}$ is largest.

In order to investigate further the exchange coupling mechanism in DMSs, we choose the atom plane containing first doped atom, which is named as “both atom layers”. Figures 4(a) and (b) show the typical space distributions of the atoms in the both atom layers above for the configuration 1 of ZnO$_{0.945}$C$_{0.055}$ and the configuration 2 of Zn$_{0.945}$Co$_{0.055}$O (or Zn$_{0.945}$Cu$_{0.055}$O), respectively. Moreover, the difference of spin-up and spin-down electrons in $s$, $p$, and $d$ orbits of those Zn,O and Co(or Cu, C) in both atom layers above have been calculated. Figure 5 (a) shows the differences of spin-up and spin-down electrons, $\Delta s$, $\Delta p$, $\Delta d$ in $s$, $p$, and $d$ orbits of Co, Zn and O in the “both atom layers” of configuration 4 for Zn$_{0.945}$Co$_{0.055}$O. Figure 6 (b) shows ones of Cu, Zn and O in the “both atom layers” of configuration 2 for Zn$_{0.945}$Cu$_{0.055}$O. Figure 5 (c) shows ones of C, Zn and O in the “both atom layers” of configuration 7 for ZnO$_{0.945}$C$_{0.055}$. From Figure 5(a), it is found that the local magnetic moment of the doped Co atoms in Zn$_{0.945}$Co$_{0.055}$O is largest, and the local doped Co atoms induce the strong 3d moment of Zn and 2s (2p) moments of O, which gives rise to the largest total moment with 6.05$\mu_B$. From Figure 5(c), one notices that, although the local 2p moment of the doped C atoms in ZnO$_{0.945}$C$_{0.055}$ is minimum, the doped C atoms induce the considerable 3d moment of Zn and 2s moments of O, which results in the secondary total moment with 4.00$\mu_B$. From Figure 5(b), we can observe that, the local magnetic moment of the doped Cu atoms in Zn$_{0.945}$Cu$_{0.055}$O is moderate, but the doped Cu atoms induce the least 3d moment of Zn and 2s moments of O, which leads to the minimum total moment with 2.00$\mu_B$. 

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**Figure 3** shows the electron transfer structures of configurations 2, 5 and 7 for Zn$_{0.945}$Cu$_{0.055}$O, and pure ZnO. As seen in Figure 2, the configurations 2, 5 and 7 have all stable ferromagnetism. For the pure ZnO, every O atom gains 1.25 electrons, and every Zn atom loses 1.25 electrons. When Cu atoms are doped, the electron transfer resulting from the doped Cu atoms is evident, and the charge redistribution appears. The electrons of doped local Cu atom are transferred not only to the nearest O atoms but also to O atoms being far away the local Cu atom, which means that the transfer electrons above are itinerant. Similar electron transfer structures have been obtained in Zn$_{0.945}$Co$_{0.055}$O and ZnO$_{0.945}$C$_{0.055}$. Comparing to the electron transfer structures of three samples, we can find that the itinerant electron number in Zn$_{0.945}$Co$_{0.055}$O is minimum, and one in Zn$_{0.945}$Cu$_{0.055}$O is second, and one in ZnO$_{0.945}$C$_{0.055}$ is largest.
Figure 3. The electron transfer structures of configurations 2, 5 and 7 for \( \text{Zn}_{0.945}\text{Cu}_{0.055}\text{O} \) DMSs, and pure \( \text{ZnO} \).

The electron transfer structures for \( \text{Zn}_{0.945}\text{Al}_{0.055}\text{O} \) and \( \text{ZnO}_{0.945}\text{S}_{0.055} \) indicate that, after two O atoms are replaced by two Al and S atoms in \( \text{ZnO} \), the charge distributions of Zn and O atoms have the evident change, which means that the doped Al or S atoms give rise to the obvious electron transfer. However, it is observed that the values of \( \Delta s, \Delta p, \Delta d \) are almost near zero, which means that there does hardly exist the localized magnetic moment in \( \text{Zn}_{0.945}\text{Al}_{0.055}\text{O} \) and \( \text{ZnO}_{0.945}\text{S}_{0.055} \).

From the discussions above, it is found that the requirements to give rise to the ferromagnetism in the DMSs are the strong local magnetic moment and the electron transfer between the doped atoms.

Figure 5. The differences of spin-up and spin-down electrons in s, p, and d orbit of Co, Zn and O for “both atom layers”: (a) confi. 4 of \( \text{Zn}_{0.945}\text{Co}_{0.055}\text{O} \); (b) confi. 2 of \( \text{Zn}_{0.945}\text{Cu}_{0.055}\text{O} \); (c) confi. 7 of \( \text{ZnO}_{0.945}\text{C}_{0.055} \).
Figure 4. Atom array structure of the both atom layers (a) for the confi. 1 of ZnO$_{0.945}$C$_{0.055}$, and (b) for the confi. 2 of Zn$_{0.945}$Co$_{0.055}$O (or Zn$_{0.945}$Cu$_{0.055}$O).

such as Co, Cu and C. The locale moments result from the strong hybridization between the Cu-3d and O-2p electrons, Co-3d and O-2p electrons, Zn-3d and C-2p electrons, respectively. Moreover, in Zn$_{1-x}$(Co,Cu)$_x$O and ZnO$_{1-x}$C$_x$, there exists the electron transfer not only among the doped atoms and the nearest neighbor atoms, but also among the doped atoms and the long-range atoms. That is, the magnetic coupling among the doped atoms (the local magnetic moments) is implemented by the interaction between the local magnetic moments and the transferred itinerant electrons. Therefore, the $p$-$d$ hybridization and the itinerant $d$ carriers are suggested to mediate the long range ferromagnetic exchange between Co, Cu and C atoms. The magnetic coupling in Zn$_{1-x}$(Co,Cu)$_x$O and ZnO$_{1-x}$C$_x$ is considered to be a RKKY interaction. Although there exists the obvious electron transfer in Zn$_{1-x}$Al$_x$O and ZnO$_{1-x}$S$_x$, there is not local moment. As a result, Zn$_{1-x}$Al$_x$O and ZnO$_{1-x}$S$_x$ have not ferromagnetism.

4. Conclusion

The electronic structures and magnetic properties of Zn$_{1-x}$M$_x$O (M=Co, Cu, Al, C, S) ($x = 5.55\%$) DMSs have been studied. The requirements to give rise to the ferromagnetism in the DMSs are the strong local magnetic moment and the electron transfer between the doped atoms. The magnetic coupling in Zn$_{1-x}$Co$_x$O, Zn$_{1-x}$Cu$_x$O and ZnO$_{1-x}$C$_x$ is considered to be RKKY interaction.

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