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# Effect on Defect in N or F-Doped Ferromagnetic $Zn_{1-x}Cu_xO$: First-Principles Study

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## Abstract

**We investigated the electronic and magnetic properties for O or Zn defect of (Cu, N) or (Cu, F)-co-doped ZnO with the concentration of 2.77% - 8.33% by using the first-principles calculations. The ferromagnetic coupling of Cu atoms in (Cu, N)-codoped ZnO can be attributed to the hole-mediated double-exchange through the strong 2*p*-3*d* coupling between Cu and neighboring O (or N) atoms. The ferromagnetism in Cu-doped ZnO is controllable by changing the carrier density. The Cu magnetic moment in low Cu concentration (2.77%) is increased by the N-doping, while for the F-doping it decreases. For two Cu atoms of $Zn_{0.9445}Cu_{0.0555}O$ with O vacancy, the antiferromagnetic state is more energetically favorable than the ferromagnetic state.**

## Keywords

**The *p*-Type ZnO: Cu, Carrier Doping, Ferromagnetic, Half-Metallic, First-Principles**

## 1. Introduction

The semiconductors in which captions partially are replaced by transition-metal ions are called diluted magnetic semiconductors (DMSs) [1] [2]. DMSs have attracted a great deal of attention because of the possibility of incorporating magnetic degrees of freedom in traditional semiconductors. However, it is one of the primary challenges to create the ferromagnetic (FM) semiconductors due to the difficulty in the spin-injection into the semiconductors to form DMSs at room temperature or above room temperature. The charge from the *s* and *p* elec-

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trons of II-VI compound semiconductor, and the spin from the magnetic impurity, can be used in the magnetoelectronics (spintronics). Since ZnO is a direct wide-band gap (3.4 eV) semiconductor which is piezoelectric, ZnO-based DMS would be useful for transparent thin film transistors, blue and UV light-emitting diodes and laser diodes. For instance, the epitaxial ZnO thin films doped with all the 3d transition-metal ions by using a pulsed-laser deposition method were fabricated [3]. Ferromagnetic orderings in ZnO-based DMSs are theoretically predicted in Ref. [4]-[6]. They [4] propose Zener's *p-d* exchange model to describe the carrier-induced ferromagnetism.

The dopant materials can be segregated to form precipitates of clusters, which are actually responsible for the FM properties. The effect of such FM clusters must be examined more carefully before the usefulness of such materials for spintronics applications can be determined. The Cu-doped ZnO has the possibility of being free of magnetic precipitates and hence to form the unambiguous DMSs. Therefore, the Cu atom has been attracted as candidates for useful dopants in both theoretical and experimental attention. First-principles calculations based on density functional theory have showed that Cu dopants in ZnO favor a spin polarization and a FM ground state [6]-[9]. In our work, the stability of FM state in (Zn, Cu)O DMSs with a Cu concentration of 2.77%, 5.55%, and 8.33% has been investigated systematically by first-principles calculations. We have considered the effects of carrier doping separately from the concentration of Cu dopant. The effects on the electronic states by Nitrogen (hole) or Fluorine (electron) doping have been investigated in (Zn, Cu)O DMSs. Analyzing calculated density of states, the mechanism to stabilize the FM state in the (Cu, N)-codoped ZnO and (Cu, F)-codoped ZnO has been discussed.

## 2. Computational Methodology

The first-principles simulations were performed using the full-potential linear muffin-tin orbital (FPLMTO) method based on the framework of the density-functional theory (DFT) [10]. The muffin-tin radii of Cu, Zn, and O were chosen to be 2.2, 2.1, and 1.6 a.u., respectively. The final set of energies was computed with the plane-wave cutoff energy of 913 eV. The convergence tests of the total energy with respect to the plane-wave energy cutoff and k-point sampling had been carefully examined. Brillouin zone integrations were performed with the special k-point method over a gamma-centered $4 \times 4 \times 4$ mesh. It is corresponding to 64 k-points. It insured that the total energies and the magnetic moments were converged on a better 10 meV/cell and 0.01 $\mu_B$/atom scale, respectively. The exchange-correlation energy of the electrons was described in the generalized gradient approximation (GGA) as proposed in Perdew-Burke-Ernzerh of functional [11].

The LMTO basis set and charge density were expanded in terms of the spherical harmonics up to $l = 6$ inside each muffin-tin sphere. The LMTO basis functions in the valence energy region were chosen as 4*s* and 3*d* for Cu, and 4*s*, 4*p*, and 3*d* for Zn. The basis function of Zn (or Cu) for the 4*s*, 4*p*, and 3*d* is generated with cut-off energy of 223.04 eV (or 210.80), 323.68 eV, and 474.64 eV (or 448.80), respectively. The valence electrons were not assumed to have the spin-orbital coupling but had generated the self-consistent super cell potential by considering the scalar relativistic effects. The atomic potentials were approximated by spherically symmetric potential. However, the full charge-density, including all non-spherical terms, was evaluated in Fourier series in the interstitial region on the FPLMTO method.

## 3. Results and Discussion

### 3.1. Structural and Magnetic Properties

The equilibrium lattice parameters of $a = 3.246$ Å, $c = 5.202$ Å, and internal parameters $u = 0.3819$ in the perfect ZnO were obtained from the FPLMTO-PW (plane-wave) calculations. The crystalline structure is a wurtzite, which consists of Zn and O plane stacked alternatively along *c*-axis. The calculated parameters are in agreement with the experimental ones [12] [13]. The electronic structure and magnetic properties on the (Cu, N)- or (Cu, F)-codoped ZnO with the concentration of 2.77%, 5.55%, and 8.33% had been investigated for a supercell of 72 atoms with one, two, and three Zn atoms substituted by Cu. The Cu magnetic moment shows nearly constant value by 0.56 $\mu_B$ as increasing the Cu concentration. The magnitude of magnetic moment is not affected by changing the doping concentrations, while the band-gap is decreased as Cu concentration increases. The band gaps in Cu-doped ZnO are 0.65, 0.22, and 0.08 eV for the Cu concentration of 2.77%, 5.55%, and 8.33%, respectively. The total magnetic moment in a supercell increases with respect to the Cu dopant increases. The

nearest four surrounding O atoms from Cu dopant are polarized with the magnetic moment by 0.13 $\mu_B$ in parallel direction to the Cu atom. In comparison with the experimental result [14], the Cu magnetic moment in ZnO thin films decreases linearly with the increase of Cu concentration. They had reported that the results of the measured magnetization of Cu-doped films grown in the $N_2O$ atmosphere give evidence of FM behavior. For the ZnO:Cu film doped with 1%, a clear indication of a Curie temperature around 390K with the magnetic moment of 0.4$\mu_B$ per Cu atom had been reported.

We performed the calculations for various Cu-O-Cu angles in order to verify whether the atomic relaxation by O vacancy ($V_O$) or by Cu is responsible for the magnetic moments. The atomic coordinates of two Cu sites (1 and 2 site in the **Figure 1**) were allowed to relax, and the coordinate of site 4 was fixed. Therefore, the Cu-O-Cu angle and the Cu-O bond lengths of 1 - 4, 2 - 4, and 3 - 4 are different in each other. The Cu-O-Cu angle was varied between 105˚ and 113˚ (109˚ for unrelaxed lattice). **Figure 2** shows the magnetic moment per cell by the relaxation of Cu atoms. As a consequence of the relaxation by Cu, the magnetic moments on both Cu and O atoms are not change nearly. It is noticeable that it does not undergo a Jahn-Teller distortion by Cu in the region around $V_O$ defect in ZnO.

## 3.2. Effects of O or Zn Vacancy and Electronic Properties

When the $V_O$ is induced in Cu-doped ZnO, the Cu-3*d* states are not change nearly, while the O-2*p* states shift downward energy. The hybridization between Cu-3*d* and O-2*p* states is reduced. The interaction between these two sites becomes very weak. The magnetic moment in a supercell becomes low due to the spin-polarization is weak. For 2.77% Cu-doped ZnO with $V_O$ of 2.77%, the magnetic moments for Cu and O atoms are 0.34 $\mu_B$ and 0.02 $\mu_B$, respectively. For a Zn vacancy ($V_{Zn}$), the magnetic moments for Cu and O atoms are 0.65 $\mu_B$ and 0.25 $\mu_B$, respectively. In the case of the concentration of 2.77% Cu, the magnetic properties with (without) $V_O$ or $V_{Zn}$ are consistent with the previous theoretical and experimental results [9] [14] [15]. However, for the concentration of 5.55% Cu, we obtained the different result as compared with the other previous works. The antiferromagnetic (AFM) state for $Zn_{0.9445}Cu_{0.0555}O$ with $V_O$ of 2.77% is more energetically favorable than the FM state. The difference in total energy between AFM and FM states is −25.80 meV. The magnetism is close to the ferrimagnetic state. This result is listed in **Table 1**. The Cu magnetic moment in ZnO with $V_O$ becomes lower than that with $V_{Zn}$. In the case of low Cu concentration, even though the magnetic moment is low, it shows that the FM state in Cu-doped ZnO is more energetically favorable.

**Figure 3** shows the spin-projected density of states (DOS) for $Zn_{0.9445}Cu_{0.0555}O$ with $V_O$ or $V_{Zn}$. The interact-

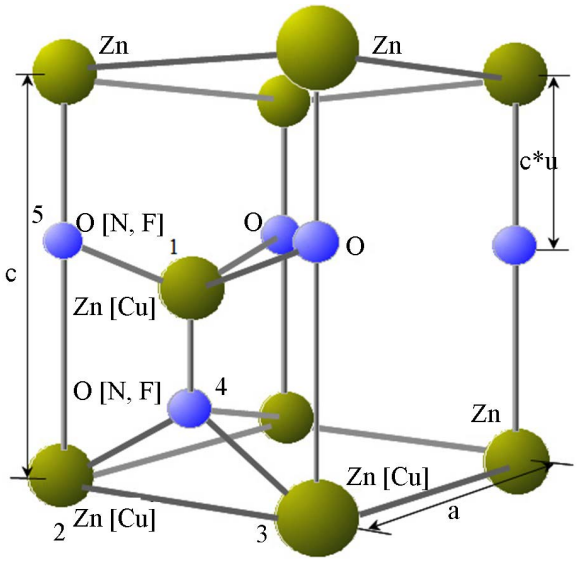


**Figure 1.** Wurtzite unit cell of ZnO with three Cu sites and two N or F sites. The Cu dopant and N (or F) site are re-presented in the parentheses. The 3 and 4 sites denote the vacancies of Zn and O, respectively (2.77%).

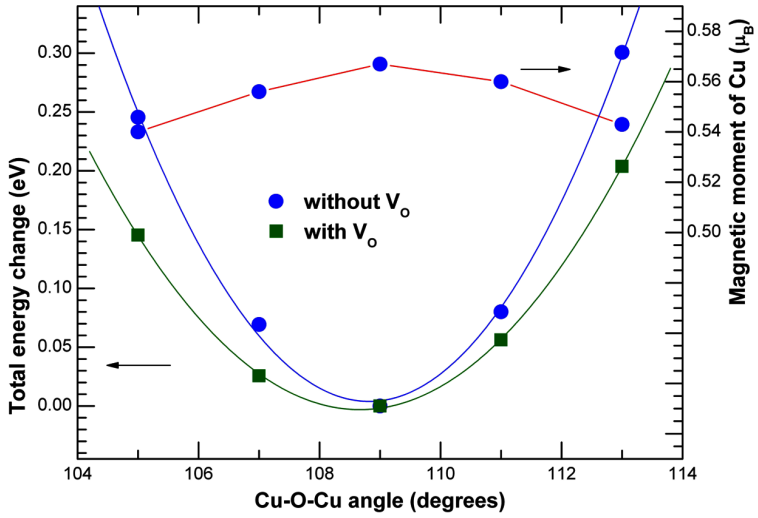


**Figure 2.** Total energy changes with respect to unrelaxed lattice, total magnetic moment per supercell as a function of the Cu-O-Cu angle in Cu-doped ZnO. The Cu concentration is 5.55%.

**Table 1.** The magnetic moments ($\mu_B$) of Cu and O (inside the parentheses) for $Zn_{1-x}[V_{Zn}]Cu_xO_{1-y}[V_O]F_y$ with $V_O$ and $V_{Zn}$ (the concentration of each vacancy is 2.77%) in the $CuO_4$ tetrahedron, total energy differences between AFM and FM states for each systems ($\Delta E = E_{total}(AFM) - E_{total}(FM)$, in meV), and the Cu and O magnetic moments by electron (F) doping.

| | $Zn_{1-x}Cu_xO[V_O]$ ($V_O$) | $Zn_{1-x}Cu_xO$ (Perfect) | $Zn_{1-x}[V_{Zn}]Cu_xO$ ($V_{Zn}$) | $Zn_{1-x}Cu_xO_{1-y}F_y$ ($y$ = 0.0277/0.0555) |
|---|---|---|---|---|
| 0.0277 | 0.34 | 0.56 | 0.65 | 0.17/0.11 |
| | (0.02) | (0.05) | (0.25) | (0.0)/(0.0) |
| 0.0555 | 0.20/−0.04 | 0.56 | 0.58/−0.22 | 0.37/0.19 |
| | (0.0) | (0.09) | (0.38) | (0.0)/(0.0) |
| 0.0833 | - | 0.57 (0.13) | - | - |
| ΔE | −25.80 | 76.10 | 154.36 | - |

tion between Zn and O (or Cu) sites is very weak due to the electronic state of Zn is a little at the near the Fermi level ($E_F$). The O-2*p* states just near the $E_F$ induce the localized bands of occupied and unoccupied states by Cu dopant. The energy gap below the $E_F$ by the $V_O$ is nearly same with 0.20 eV. The half-metallic character disappears due to upward shift of the dopant band. For $V_{Zn}$, the $E_F$ moves toward the top of valence band, thus it shows the half-metallic character. The Cu-O bond in Cu-doped ZnO has largely covalent because of the strong hybridization between the Cu-3*d* and O-2*p* states.

When the $V_O$ presents in ZnO, it introduces shallow donor states. These donor states are largely composed of the *4s* electrons of four Zn atoms surrounding the $V_O$. Each $V_O$ generates four dangling bonds localized at four Zn atoms surrounding the vacancy site. The defect band through the $E_F$ is mainly arising from Zn 4*s* states with a little contribution of Zn 4*s* and O *sp* states. When introducing one $V_O$, the charge of Zn atoms near $V_O$ spreads toward the defect site through the dangling bonds, and the spin polarized interaction is so weak that opposing induced spins are created diffusely in a large space around the vacancy. The change of magnetic moment for the variance of Cu concentration is little due to the direct 3*d*-3*d* correlation between Cu atoms is very small. As can be seen in **Table 1**, when the $V_O$ or $V_{Zn}$ introduces in Cu-doped ZnO, the magnetic coupling of Cu may be understood in the result of an indirect double-exchange interaction through the site of $V_O$ or $V_{Zn}$.

**Figure 4** illustrates spin-projected DOS for 5.55% Cu-doped $ZnO_{1-y}N_y$ and $ZnO_{1-y}F_y$ of FM state with $y$ = 0.0555 (N; nitrogen, F; Fluorine). The energy-band by N-doping shifts a little toward lower-energy as compared to that of Cu-doped ZnO. The energy band of (Cu, N)-codoped ZnO is similar to that of Cu-doped ZnO with $V_{Zn}$. There exist the unoccupied N-2*p* states in the minority-band. The spin alignments of the Cu and N atoms can be

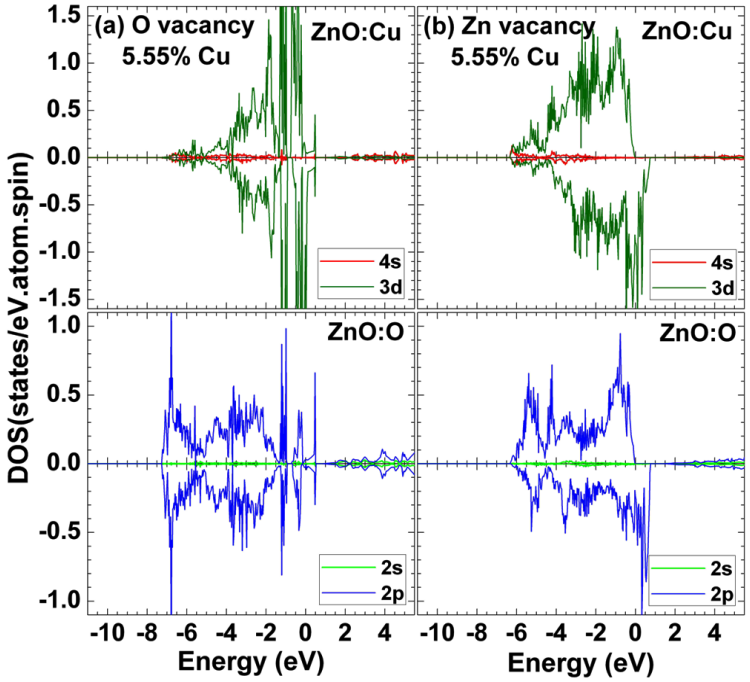


**Figure 3.** DOS for Cu and O sites of 5.55% Cu-doped ZnO (a) with an O vacancy in the AFM state, (b) with a Zn vacancy in the FM state. The Fermi level is set to zero.

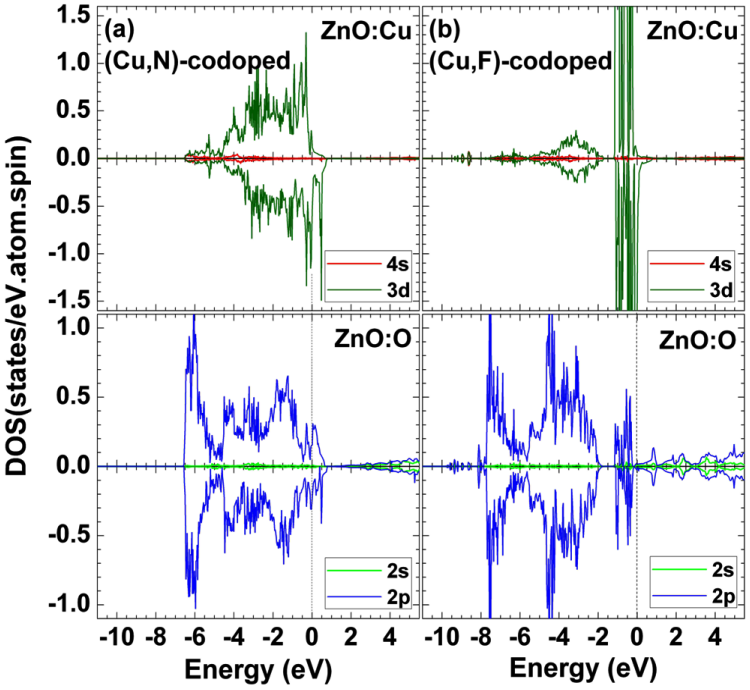


**Figure 4.** DOS for Cu and O sites of 5.55% Cu-doped ZnO in the FM state (a) with 5.55% N-doping, (b) with 5.55% F-doping. The Fermi level is set to zero.

shown as Cu(↑)-N(↑)-Cu(↑), indicating that ferromagnetism is mediated through the *p-d* exchange interaction between the hole carriers and Cu atoms. The N magnetic moment is a 0.4 $\mu_B$/N. The half-metallic character

is disappeared with respect to the change of N concentration. As is compared with the other work by Liu and co-workers, the (Mn, N)-codoped ZnO system shows a half-metallic character [16]. On the contrary to the $V_O$ or $V_{Zn}$, the crystal field splitting between $t_2$ and $e$ states with N or F doping is weak. The bands of Cu $t_2$ (or $d_{xy}$) and Cu $e$ (or $d_{x2-y2}$) are located at below the $E_F$. For the F doping, the Cu magnetic moment is smaller than that of N-doping. As increasing the F concentration, the FM state is disappeared. The Cu magnetic moment is nearly zero. The interaction between Cu-3*d* and O-2*p* states becomes very weak because of the Cu-3*d* band is localized at just below the $E_F$.

## 4. Conclusion

In conclusion, the Cu magnetic moment with respect to the Cu concentration is not change nearly. The direct *3d-3d* correlation between Cu atoms in wurtzite ZnO is small. When it is the substitution of Zn by Cu, the Cu and O atoms form the O-Cu-O bond within the $CuO_4$ tetrahedron. The O(2*p*)-Cu(3*d*)-O(2*p*) bond is formed through the 2*p*-3*d* coupling. The *p-d* interaction chain is responsible for FM in Cu-doped ZnO. For (Cu, N)-codoped ZnO, the FM coupling between Cu and O (or N) atoms shows the spin alignment of Cu(↑)-O(or N)(↑)-Cu(↑). Therefore, the FM coupling of Cu atoms in (Cu,N)-codoped ZnO can be attributed to the hole-mediated double-exchange through the strong *p-d* coupling between Cu and neighboring O atoms. The Cu-3*d* and O-2*p* states in ZnO with $V_{Zn}$ are strongly correlated; the Cu magnetic moment increases. While, when the $V_O$ exists in Cu-doped ZnO, the Cu magnetic moment is strongly reduced due to the interactions between the Cu-3*d* and neighboring O-2*p* states is disappeared. Thus we note that the Cu dopants may show an indirect double-exchange interaction by introducing O or Zn vacancy site.

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