

# Half-metallic ferromagnetism in Cu-doped zinc-blende ZnO from first principles study

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## ABSTRACT

Electronic structures and magnetism of Cu-doped zinc-blende ZnO have been investigated by the first-principle method based on density functional theory (DFT). The results show that Cu can induce stable ferromagnetic ground state. The magnetic moment of supercell including single Cu atom is  $1.0 \mu_B$ . Electronic structure shows that Cu-doped zinc-blende ZnO is a p-type half-metallic ferromagnet. The half-metal property is mainly attribute to the crystal field splitting of Cu 3d orbital, and the ferromagnetism is dominated by the hole-mediated double exchange mechanism. Therefore, Cu-doped zinc-blende ZnO should be useful in semiconductor spintronics and other applications.

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## 1. Introduction

Diluted magnetic semiconductors (DMSs) have been studied extensively because of their potential usage of both charge and spin of freedom of carriers in the spintronics [1–4]. In order to make use of these materials/devices at room temperature, a chief goal of current research is to fabricate DMSs with Curie temperature  $T_C$  as high as possible for the spintronic applications. During the past years, a number of transition metal (TM) doped semiconductors with room temperature ferromagnetism have been reported, such as Mn-doped ZnSnAs<sub>2</sub> [5], Ni and Cu doped wurtzite ZnO [6–8], Co doped anatase TiO<sub>2</sub> [9], Cr doped AlN [10] and CdTe [11]. Since Dietl et al. [12] predicted that ZnO and GaN-based DMSs could exhibit ferromagnetism above room temperature when doped with sufficient carriers and magnetic atoms, the wide band gap semiconductors ZnO and GaN have attracted considerable attention in searching for high  $T_C$  ferromagnetic DMS materials. Dietl's work motivated intensive studies on the structural and physical properties of ZnO and GaN. Studies on electronic structure and magnetism of wurtzite ZnO-doped by transition metals (TM) have also been widely performed [13–17]. We know that ZnO has three different crystal structures: the normal low-pressure phase hexagonal wurtzite (B4) structure, the rocksalt (NaCl or B1) structure and the cubic zinc-blende (ZB or B3) structure [18–20]. Generally, most researches of TM-doped ZnO have been concentrated on the wurtzite structure;

even so, in fact many studies have found only low temperature ferromagnetism or paramagnetism. Until now, as far as we know, the electronic structures and magnetism of the TM-doped zinc-blende ZnO have not been widely reached.

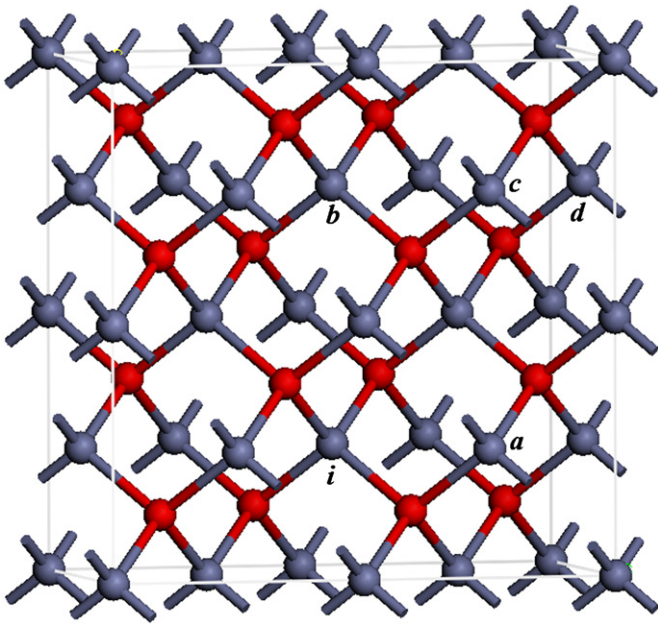
Although the two structures, wurtzite ( $C_{6v}^4, P63mc$ ) and zinc-blende ( $T_d^2, F43m$ ), of ZnO have different space groups, they have the same local tetrahedral environment and become different only in their third-nearest-neighbor atomic arrangement. Therefore, the structures of the wurtzite and zinc-blende ZnO are very similar. Dalpian et al. [21] proposed a new method to stabilize the cubic zinc blende phase by impurity doping for compounds that are usually more stable in the hexagonal phase. They showed that this can be achieved by injecting holes into GaN using 3d-containing acceptors. According to Dalpian and Wei's idea, we have investigated the electronic structures and magnetism of Cu-doped zinc blende ZnO by means of the first principles method based on density functional theory (DFT).

## 2. Method

In this paper, we use the WIEN2K [22] package, which is based on the FP-LAPW+local orbital (lo) method, one among the most accurate schemes for band structure calculations. We investigate magnetic coupling via the density of states (DOS) and the electronic band structure. These results will help us to further understand the origin of magnetism in Zn<sub>1-x</sub>Cu<sub>x</sub>O. In our calculations, the radii of atom spheres are 2.1, 2.3 and 1.5 a.u. for Zn, Cu and O atoms, respectively. The cutoff parameter  $R_{MT}K_{MAX}$  is taken as 7.0, where  $R_{MT}$  is the smallest radius of atoms and  $K_{MAX}$  is the maximum value

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**Fig. 1.** The crystal structure of  $1 \times 2 \times 2$  supercell of zinc-blende ZnO. Gray and red balls indicate Zn and O, respectively. The positions of Zn substituted by Cu are denoted by i and a–d. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the reciprocal lattice vectors used in the plane wave expansion. Generalized gradient approximation (GGA) [23,24] is used to treat the exchange correlation potential, and relativistic effects are taken into account. For the Brillouin zone integration, we used 200  $k$ -points in the first Brillouin, and the  $k$ -point meshes are  $9 \times 4 \times 4$  for the 32 atoms in the reciprocal space. The self-consistent calculations are considered to be converged only when the integrated charge difference per formula unit,  $\int |\rho_n - \rho_{n-1}| dr$ , between input charge density  $[\rho_{n-1}]$  and output  $[\rho_n]$  is less than  $0.0001e$ .

According to Ref. [18], the zinc-blende ZnO has a cubic crystal system (space group  $F\bar{4}3m$ ,  $a=b=c=4.60 \text{ \AA}$  and  $\alpha=\beta=\gamma=90^\circ$ ). The doping configurations of  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$  are based on the  $1 \times 2 \times 2$  supercell containing 16 ZnO. Two doping levels are investigated: for  $x=0.0625$ , one Zn atom is substituted by Cu; for  $x=0.125$ , two Zn atoms are substituted by Cu atoms. For the latter, we consider the four different configurations (from nearest-neighboring to fourth neighboring,  $d(i, j)$  with  $j=a-d$ ) of the two Zn atoms replaced by two Cu atoms (Fig. 1). First, based on the different configurations, we carry out both geometric optimization and atomic relaxation to find the equilibrium configuration. To examine the energetics between the ferromagnetism (FM) and antiferromagnetism (AFM) spin-polarized electronic configurations of the Cu ions, we have performed the energy calculations for zinc-blende  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$  ( $x=0.125$ ). In FM and AFM states with GGA, we considered two parallel and antiparallel Cu atoms, respectively.

### 3. Results and discussion

As a defective system, the formation energy of Cu-doped zinc-blende ZnO can be obtained by a process in which a certain number of atoms are exchanged between host materials and defect reservoirs. The corresponding formation energy [25–28] can be calculated as follows:

$$E^f = E_d - E_h \pm n_\alpha \mu_\alpha \quad (1)$$

where  $E_d$  and  $E_h$  are the total energy of a system with and without defects, respectively;  $n_\alpha$  is the number of atoms removed (+) or

added (–) to the hosts and  $\mu_\alpha$  is the chemical potential, which depends on the growth conditions of a material. In order to calculate the corresponding quantities, we adopt the relation  $\mu_{\text{Zn}} + \mu_{\text{O}} = \mu_{\text{ZnO}}$ . In addition, the chemical potentials must satisfy the boundary conditions  $\mu_{\text{O}} \leq (1/2)\mu_{\text{O}_2}$  and  $\mu_{\text{Zn}} \leq \mu_{\text{Zn}}(\text{bulk})$ . Considering the  $\text{Zn}_{15}\text{CuO}_{16}$  supercell with the corresponding concentration of 0.0625, the formation energy of a Cu substitution for Zn is calculated by the expression  $E^f = E[\text{Zn}_{15}\text{CuO}_{16}] - E[\text{Zn}_{16}\text{O}_{16}] - \mu_{\text{Cu}} + \mu_{\text{Zn}}$ , where  $E[\text{Zn}_{15}\text{CuO}_{16}]$  and  $E[\text{Zn}_{16}\text{O}_{16}]$  are the total energies of the supercell including a Cu dopant and the pure host, respectively;  $\mu_{\text{Cu}}$  and  $\mu_{\text{Zn}}$  are the chemical potential of bulk Cu and Zn, respectively (optimized zinc-blende structure). The obtained formation energy of  $\text{Zn}_{0.9375}\text{Cu}_{0.0625}\text{O}$  is 2.59 eV, which may suggest that Cu-doped zinc blende ZnO can be fabricated in experiments.

In order to determine the ground state of  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$ , we adopt four different configurations with the same doping concentration of 12.5 at% (Fig. 1). The total energy and energy differences of ferromagnetic (FM) and antiferromagnetic (AFM) phases in above configurations are calculated. We present the optimized Cu–Cu bonds in  $d(i, j)$  ( $j=a-d$ ), total energies and relative energy difference between FM and AFM states ( $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ ) in  $\text{Zn}_{1-x}\text{Cu}_x\text{O}$  ( $x=0.125$ ) in Table 1. According to the calculated results, it is found that the above four doped configurations all favor the ferromagnetic ground state, which means that the long range ferromagnetic interactions exist between the well-separated Cu atoms. In addition, it is obvious that the energy differences between FM and AFM phases decrease along with the increase of the length of the nearest Cu–Cu bonds. The largest energy difference between FM and AFM phases of the four different configurations is 0.2379 eV; such large energy differences imply that the above room temperature ferromagnetism for Cu-doped ZnO can be expected.

Considering the effect of the different doping concentrations, we have calculated the electronic structures of Cu-doped zinc-blende ZnO for  $x=0.0625$  and  $x=0.125$ . For  $x=0.0625$ , in order to satisfy the doping limit, we adopt the fourth-neighboring distance of Cu–Cu atoms in the  $d(i, d)$  configuration. In Fig. 2(a) and (b), we present the spin-polarized energy band structures of FM Cu-doped zinc-blende  $\text{Zn}_{15}\text{CuO}_{16}$  ( $x=0.0625$ ). For the spin-up component, in the vicinity of the Fermi level, it is found that the top of the valence band (VB) and the bottom of the conduction band (CB) of spin-up electrons are both located at  $G(0, 0, 0)$ , and the spin-up component is a semiconductor with a direct-band-gap of about 0.5 eV; however, the spin-down component is metallic with two bands crossing the Fermi level. For  $x=0.0625$ , the result shows that the total magnetic moment per Cu is  $1.0 \mu_B$ , and this doping system also shows half-metallic character [29]. Cu-doped wurtzite ZnO based on DFT has been studied by Ye et al. [8]; their results showed that this system has a FM ground state with half-metallicity. Their calculated results are as follows: the half-metal band gap Cu-doped wurtzite ZnO is 0.3 eV; total magnetic moments are  $1.0 \mu_B$  per Cu and the Cu atom is polarized with a

**Table 1**

The calculated total energies and optimized length of the Cu–Cu bonds  $d(i, j)$  for the four different configurations of the  $\text{Zn}_{14}\text{Cu}_2\text{O}_{16}$  supercell.  $\Delta E$  is the FM stabilization energy between the FM and AFM states ( $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ ) for each configuration.

| Configurations | $d_{\text{Cu-Cu}}$<br>( $\text{\AA}$ ) | $E_{\text{FM}}$ (eV) | $E_{\text{AFM}}$ (eV) | $\Delta E$ (eV) | Coupling |
|----------------|--|----------------------|-----------------------|-----------------|----------|
| I (i, a)       | 3.055                                  | –33624.6978          | –33624.4599           | 0.2379          | FM       |
| II (i, b)      | 4.665                                  | –33624.6958          | –33624.6590           | 0.0368          | FM       |
| III (i, c)     | 5.738                                  | –33624.2516          | –33624.2478           | 0.0038          | FM       |
| IV (i, d)      | 6.537                                  | –33624.6323          | –33624.6198           | 0.0125          | FM       |

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