# FIRST-PRINCIPLES STUDY OF INTRINSIC POINT DEFECTS AND Cu DOPED IN ZnO

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This article presents ab initio calculations of the electronic and magnetic properties of copper-doped ZnO supercells. In hexagonal structures of the wurtzite type based on ZnO, changes in the density of electronic states in the presence of point defects in zinc or oxygen atoms are considered. Within the framework of the density functional theory, using various pseudopotentials, the magnetic moments and band gap is calculated for doping with a Cu structure with ZnO and for different charge states of defects.

**Keywords:** ZnO, ab initio calculations, density functional theory, point defect, Cu-doped
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## INTRODUCTION

ZnO is a wide-band-gap semiconductor, which has attracted a considerable attention during the past years due to its potential technological applications. Doping can cause dramatic changes in electronic, optical, and magnetic properties by changing the electronic structure of ZnO [1-3]. ZnO-based magnetic semiconductors such as ZnO:P [4], ZnO:C [5] and ZnO:Zn, Al, Pt, Ag, and Au [6] have attracted attention in recent years. In particular, it was shown in [6] that Zn, Al, Pt / ZnO films after vacuum annealing exhibit ferromagnetism at room temperature.

In the work [7] it is shown that the magnetic the moment of the defective supercell has a strong dependence on the impurity concentration and the presence of vacancies. The introduction of an oxygen atom increases the likelihood of zinc vacancy formation. Theoretically the electronic and magnetic properties of different point defects in ZnO, which are Zinc interstitials ($Zn_i$), Zinc antisites ($Zn_O$), Oxygen interstitials ($O_i$) and Oxygen antisites ($O_{Zn}$) defects in ZnO were [8] studied.

In [9] the character of conduction band and valence band in ZnO nanoparticles was investigated. The band gap energy of 3.3eV is obtained from the absorption emission spectrum. In the ZnO system doped with atoms of 3d-transition metals Mn, V, Cr, Fe, Co, and Ni, ferromagnetic ordering of the magnetic moments was found [10]. It is shown that the V, Cr, Fe, Co, and Ni atoms exhibit ferromagnetic ordering of their magnetic moments in ZnO without additional processing. The calculated [11] band gaps using Hubbard *U* semiempirical corrections are in agreement with previous experimental works and shows both the valence band maximum and conduction band minimum located at the *Γ* point of the Brillouin zone.

In this work, vacancies of the different nanostructures of ZnO and electronic and magnetic states of the structure in the presence of Zn and O atoms point defects were studied. The effects of Cu doping on the electronic structure and magnetic properties of ZnO was also investigated.

## COMPUTATIONAL DETAILS AND THEORETICAL METHODS

The crystal structure of wurtzite ZnO belongs to the hexagonal system, the space group is P63mc. In the crystal structure the unit cell parameters are a=3.2495A$^0$, b=5.2069A$^0$, Space group 186. The calculations were performed using density functional theory (DFT), as implemented in the Atomistix Tool Kit program software. The exchange-related energy can describe the selected potential as a super soft potential with the Perdew–Burke–Ernzerhof (PBE) functional (Figure 1).

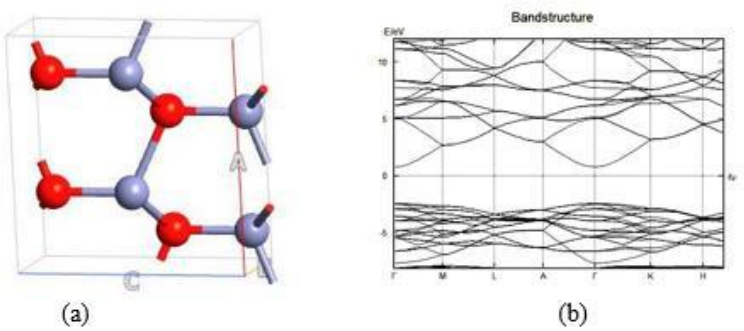


*Fig. 1.* The atom structure (a) ZnO containing 8 atoms (b) bandstructure ZnO.

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The atomic structure and bandstructure of wurtzite ZnO is shown in Figure1. Have calculated the energy gap for ZnO ($E_g$=3.22eV). The k points in the Brillouin zone are set to 2×2×2 (2×2×1 supercell), 2×2×2 (3×3×1 supercell). In order to correspond with the experimental results, the model constructed in this paper is a pure ZnO unit cell model; $Cu_{0.125}$ $Zn_{0.875}O$ (2×2×1) with a Cu atom replacing Zn atom (corresponding doping amount is 12.5%), $Cu_{0.056}Zn_{0.944}O$ (3×3×1) with a Cu atom replacing Zn atom (corresponding doping amount 5.6%); and the crystal structure is shown in Figure 2.

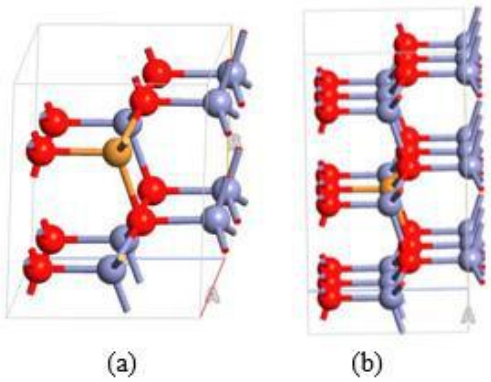


*Fig. 2.* The models of: (a) $Cu_{0.125}$ $Zn_{0.875}O$ supercell, (b) $Cu_{0.056}Zn_{0.944}O$ supercell.

## RESULTS AND DISCUSSION

In ZnO supercells is used the LDA or GGA calculation by introducing a strong correlation term between atoms, which is described in the model by the Hubbard parameter. In all calculations the 5d state of Zn and the 4p state of O was taken. The band gap of ZnO is 3.22eV which is close to the thoretical values. To simulate the doping and vacancy effects have studied 16 and 36 (Figure2) atomic supercells.

The following shares in the total magnetic moment are derived from Mulliken popilation analysis in the case of the Cu doped 16 atoms ZnO and Cu doped 36 ZnO with Zn vacancy: 0.998 $\mu B$ (magnetic moment of Cu is 0.54 μB, 7$^{th}$ O near to Cu atom is 0.157 μB) and 3.004 $\mu B$ (magnetic moment of Cu is 0.561 μB, 14$^{th}$ and 18$^{th}$ O around to Cu atom is 0.98 and 0.81 μB), (Figure 3) respectively.

The calculated (Table1) values of the magnetic moments per one dopant Cu atom for various supercells with Cu(Zn) substitution.

*Table 1*

| ZnO supercell doped Cu (O 4p, Zn 5d, Cu 3d) | Method | $\mu$/Cu, ($\mu B$) |
|---|---|---|
| (2×2×1) | SGGA | 1 |
| (2×2×1) | LSDA+U | 0.898 |
| (2×2×1) | SGGA+U | 0.998 |
| (3×3×1) with Zn vacancy | SGGA+U | 3.004 |

In a given table 1 SGGA is spin-polarized GGA-PBE method, and SGGA+U is spin-polarized GGA-PBE method with Hubbard U approximation.

The LSDA+U interaction term usually enhances spin magnetic moments and local spin density approximation method with Hubbard U.

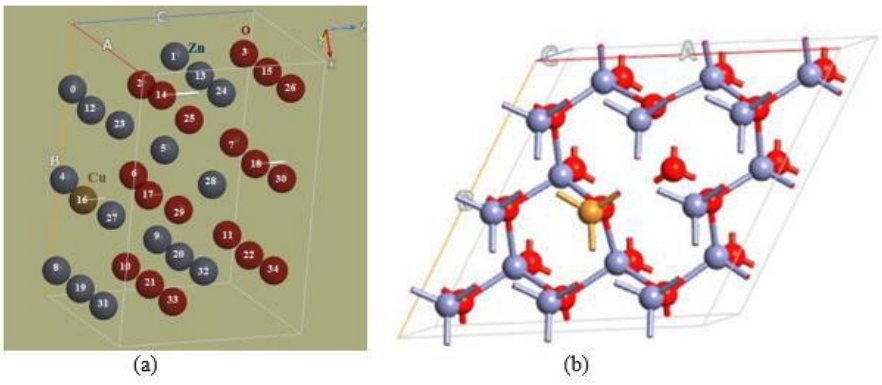


*Fig. 3.* The atom structure $Zn_{16}O_{18}Cu$ with Zn (a),(b) vacancy.

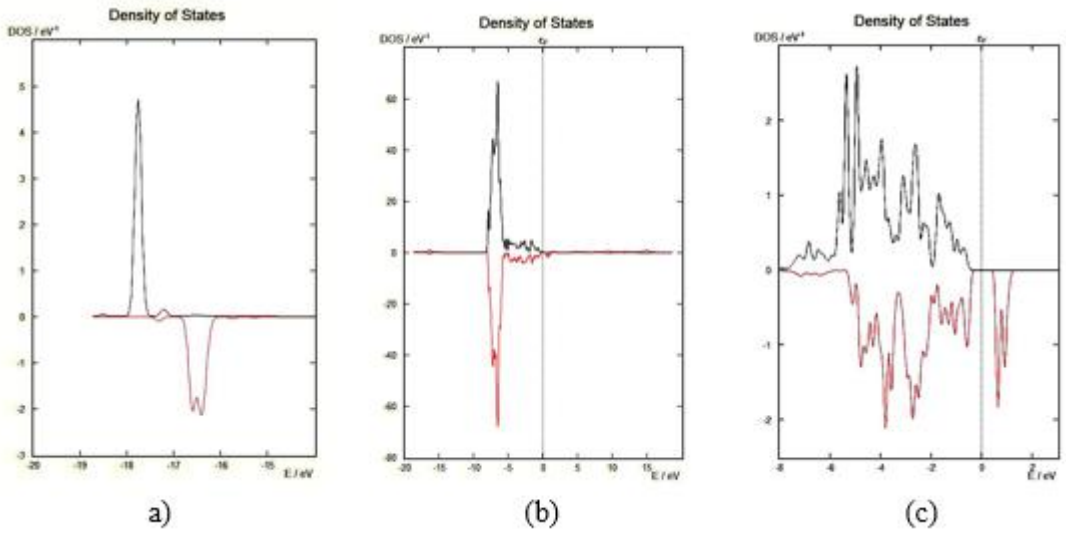


*Fig. 4.* Partial densities of states of a) s state-18th oxygen atom near of vacancy, b) d-state- Cu atom, c) density of states of $CuZn_{17}O_{18}$

The electron-ion interaction of particles in ZnO is calculated using the Hubbard model. In this case, the d-electrons of Zn were considered as valence electrons. The results are shown in Table 2. The electron density gradient in unoccupied orbitals was calculated in the frame of the generalized gradient approximation (GGA). As can be seen, with a change in the charge of the defect, the value of the band gap changes noticeably.

*Table 2*

| **Hexoqonal (2×2×1) ZnO supercell** | **$E_{total}$(eV)** | **$E_g$(eV)** | **GGA +U** | **q (charge state)** |
|---|---|---|---|---|
| O point defect | -15375.84187 | 4.10 | Zn-5d, O-4p | 2 |
| O point defect | -15387.42573 | 4.02 | Zn-5d, O-4p | 1 |
| O point defect | -14270.56442 | 4.10 | Zn-5d, O-4p | 0 |
| O point defect | -15387.42573 | 1.85 | Zn-5d, O-4p | -1 |
| O point defect | -15675.73909 | 1.55 | Zn-5d, O-4p | -2 |
| Zn point defect | -14270.56442 | 3.01 | Zn-5d, O-4p | -1 |
| Zn point defect | -14273.14449 | 2.86 | Zn-5d, O-4p | 0 |
| Zn point defect | -14513.37432 | 3.32 | Zn-5d, O-4p | 1 |

## CONCLUSIONS

Ab initio calculations of intrinsic point defects (Zn and O) in supercells containing 16 and 36 wurtzite ZnO and ZnO atoms doped with Cu showed the following. The magnetic moment in the structures $Cu_{0.125}Zn_{0.875}O$ (2 × 2 × 1) and $Cu_{0.056}Zn_{0.944}O$ (3 × 3 × 1) based on ZnO was calculated using the Mulliken population analysis. The participation of defects in structures based on ZnO containing nonmagnetic Cu impurities noticeably changes the physical properties. It was found that in ZnO, the Cu-doped magnetic moment changes in the range 1-0.998μB. And, the introduction of zinc vacancy into this structure increases the magnetic moment to 3.004μB. In the case of a Zn point defect with a charge q = 0, the band gap is 2.86 eV. Whereas the participation of an oxygen defect with a charge q = 0 increases the band gap to 4.10 eV.

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