

PACS numbers: 75.50.Pp, 61.72.uj, 81.05.Dz, 71.20.Nr, 75.50.Dd

## ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF COBALT DOPED ZINC OXIDE

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*Using the first principle methods, the electronic structure and magnetic properties of Co doped ZnO are investigated. It is found that Co substitutes Zn site in the host, and this doped configuration favors the ferromagnetic ground state. Electronic structure calculation shows that total magnetic moment for the supercell is 3.03  $\mu_B$ , which is mainly, contributed by Dopant (Co) 2.45  $\mu_B$ . The compound is found to be a semiconductor, where the filled-states are located in the valence bands and the empty ones above the conduction band edge. The filled and empty d-states are also shown to shift downwards and upwards in the valence and the conduction bands, respectively. The total and atom resolved density of states shed light on the evolution of the electronic and magnetic properties.*

**Keywords:** MAGNETIC SEMICONDUCTORS, DENSITY FUNCTIONAL THEORY, II-VI SEMICONDUCTORS, NONMETALLIC FERROMAGNETIC MATERIALS, FIRST PRINCIPLE CALCULATIONS.

(Received 04 February 2011, in final form 29 April 2011)

### 1. INTRODUCTION

Dilute magnetic semiconductors (DMSs), particularly based on III-V and II-VI hosts, have extensively studied due to their potential application in various spintronic devices such as spin-resonant tunneling diodes, spin light emitting diodes [1-2], etc. In particular, ZnO based magnetic semiconductors have been considered as a promising candidate to be used in optoelectronic and piezoelectronic materials [3-5].

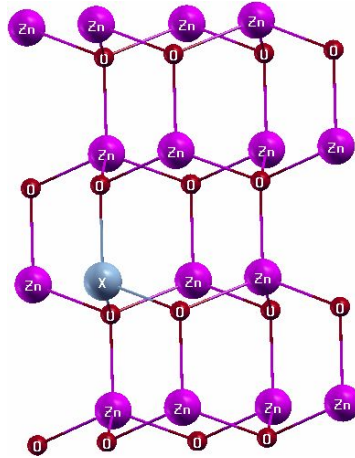
It is found that the experimental studies on transition metal based ZnO have pronounced inconsistent results. Depending on the sample preparation parameters, recent studies on transition metal doped ZnO are reported to exhibit ferromagnetic, paramagnetic or spin glass like behavior [6-15]. It is also speculated that transition metal doped ZnO from clusters or any secondary phases, are detrimental to application of dilute magnetic semiconductors. Therefore, the basic mechanisms responsible for the room temperature ferromagnetism of these magnetic semiconductors have not been stabilized.

Although, several experimental and theoretical studies have been reported on the room temperature ferromagnetism in transition metal doped ZnO [16-30], the origin of ferromagnetism as observed in these compounds as well as if the ground state ferromagnetism is intrinsic or extrinsic, still remains controversial.

Up to now, a considerable work has also been reported on the magnetism of nonmagnetic element doping in the III-V and II-VI compounds based on dilute magnetic semiconductors [31, 32]. It is therefore of interest to investigate the effect of Co doping in ZnO to understand the mechanism of ferromagnetism in transition metal doped ZnO by the means of first principle calculations.

ZnO crystallize in the hexagonal wurtzite (space group =  $P6_3mc$ ) and zincblende phases (space group =  $F43m$ ). The normal phase of ZnO shows a wurtzite structure, which consist of hexagonal Zn and O planes stacking alternatively along the c axis. In the WZ structure, two Zn atoms are placed at  $(2/3, 1/3, 0)$  and  $(1/3, 2/3, 1/2)$  while two O atoms are at  $(2/3, 1/3, 3/8)$  and  $(1/3, 2/3, 1/3)$ , respectively. Each Zn atom is surrounded by four O atoms at the corners of a tetrahedral and vice-versa. This structure is derived from hexagonal-close-packed array of anions.

To study the magnetic properties ZnO doped with Co, we have considered the  $2 \cdot 2 \cdot 2$  supercell and replacing a Zn atom with Co as shown in Fig. 1. The doping concentration is 6.25 %. The formation of a doped system is a process where a certain number of atoms are exchanged between host materials and defect reservoirs. To represent the possibility of forming a defective system, formation energy is calculated. In this calculation, the total energy spin-orbit coupling was excluded.



**Fig. 1** – Crystal structure of ZnO employed to define Co doped ZnO (wurtzite structure, space group =  $P6_3mc$ ). Blue (X) atom shows the position of substituted Co

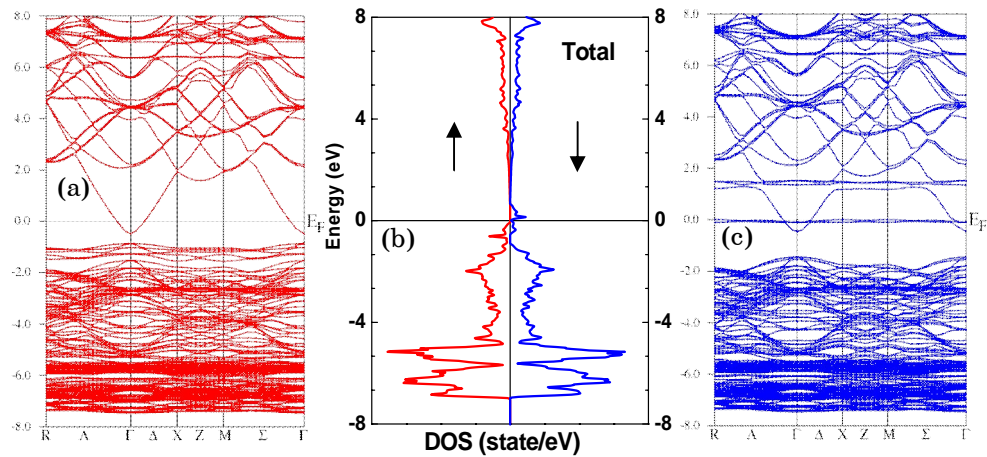
## 2. COMPUTATIONAL DETAILS

The first principle calculations are carried out by using full potential linear augmented plane wave (FP-LAPW) method as implemented in WIEN2k code [33]. In this method, the electronic wave functions, charge densities and crystal potential are expanded in spherical harmonic inside the

nonoverlapping spheres centered at each nuclear position, while plane waves in rest of space (interstitial region). Generalized gradient approximation based exchange and correlation functional are treated as proposed by Wu and Cohen [34]. The partial waves were expanded up to  $l_{\max}=10$ , inside the atomic sphere. While the number of plane waves in the interstitial was limited by cutoff at  $K_{\max}=7/R_{\text{MT}}$ . The charge density was Fourier expanded up to  $G_{\max}=13$ . The self-consistency is achieved when the energy difference between succeeding iterations is less than  $1.0 \cdot 10^{-4} R_y$ . A  $12 \cdot 12 \cdot 6$  special  $k$ -point mesh, resulting 436  $k$ -points, is used for first Brillouin zone integration. Using this energy eigenvalues and eigenvectors at these points, the density of states (DOS) are determined by the tetrahedral integration method. The atomic radii  $R_{\text{MT}}$  used are, 1.94 a.u for Zn, 1.72 a.u for O and 1.94 a.u for Co.

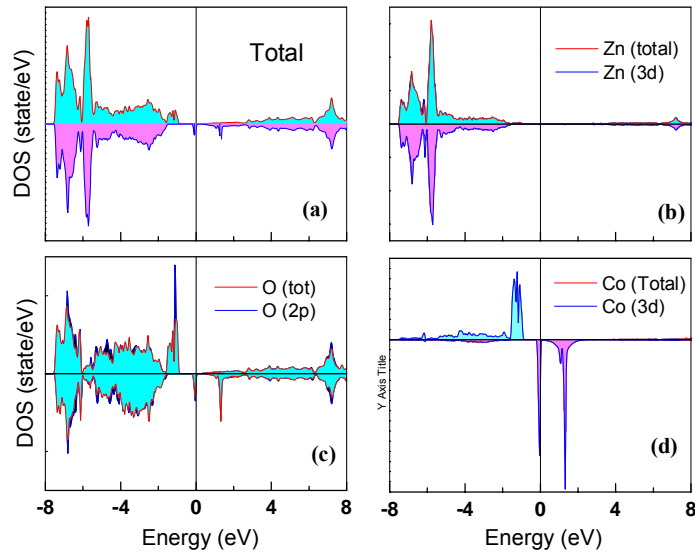
### 3. RESULTS AND DISCUSSION

In the present study, single Co was substituted at the position of Zn atom in the respective 32 atom supercell, which is correspond to 6.25% doping concentration as shown in Fig. 1. The Co doping in ZnO, results to a total magnetic moment of 3.03  $\mu_B$ , which is mainly contributed by the  $3d$  electrons of Co (2.45  $\mu_B$ ). It is also observed that besides Co, the first neighboring Zn (with 0.002  $\mu_B$ ), O (with 0.08  $\mu_B$ ) atoms and the second neighboring O atom (with 0.04  $\mu_B$ ) are also spin polarized in the same spin direction. Having the same direction of magnetic moments shows there is ferromagnetic (FM) coupling between the dopant and the neighboring host atoms. Calculated spin-polarized band structures of Co doped ZnO along with the total DOS are displayed in Figs. 2 a-c. Fig. 2 shows a prominent energy gap at the Fermi level in one spin direction while the other direction show the metallic character.



**Fig. 2** – Spin polarized energy bands and total density of states of Co-doped ZnO. Energy bands for spin up (a) total DOS for spin up and down (b), energy bands for spin down states (c)

For a detail illustration of the electronic and magnetic properties, in Figure 3 a-d the calculated total and partial DOS of the system are shown. Total and partial DOS depict that, near the Fermi level most of the states are dominant by  $2p$  states of O and  $3d$  states of Co. It is found the Zn states dominates in the region ( $-4$  to  $-8$  eV) below the Fermi level. On the other hand the O states are found below the Fermi level in the region ( $-2$  to  $-8$  eV) as well as show significant contribution above the Fermi level. It is also seen that near the Fermi level, the  $3d$  states of Co hybrid with the  $2p$  states of O atoms. This hybridization results to  $p-d$  and  $s-d$  exchange splitting of the energy levels near the Fermi level. This splitting shifts the majority spin states downward, minority spin states upward, and show 100 % spin polarization.



**Fig. 3** – Spin polarized total and atom resolved density of states of Total (a) host atom Zn (b) host atom O (c) dopant Co (d), respectively

From the projected densities of states in Fig. 3(b-d), major hybridizations occurred between Co- $3d$  and O- $2p$  orbitals, forming bonding ( $t_b$ ) and antibonding ( $t_a$ ) states, with a nonbonding ( $e$ ) state lying between the two states. For majority spins, the  $e$  and  $t_a$  states were located at about  $-1.12$  and  $-1.45$  eV, respectively, while in case of minority spins, the  $e$  and  $t_a$  states appear in the conduction band at about  $0$  and  $1.32$  eV, respectively. It is worthwhile to mention here that the position of  $e$  and  $t_a$  states considered after fixing the Fermi level ( $E_F$ ) to  $0$  eV. Majority spin  $3d$  states are fully occupied, hybridize strongly with O  $2p$  states, and do not appear as a sharp feature in the density of states. The spin-up states are fully occupied but the spin down states is partially filled. The Co dopant has four O atoms as a first nearest neighbors. Due to the hybridization between dopant and its nearest neighbors (NN) atoms, hole states arise which are extended up to 2 NN.

#### 4. CONCLUSIONS

In summary, we have performed a detailed first-principles study on the Co doping in ZnO. The total magnetic moments for the 32 atom supercell is found to be 3.03  $\mu\text{B}$ , which is mainly, contributed by Dopant (Co) 2.45  $\mu\text{B}$ . Although, nearest neighbour host atoms also show magnetism and have the same spin direction which advocates the ferromagnetism coupling in such magnetic semiconductors. The exchange splitting of the energy levels near the Fermi level observed which is responsible for the shifting of the majority spin states downward and minority spin states upward and results 100 % spin polarization, and warrants the applicability of these compounds in the spintronic devices.

This work is supported by (VS and OUK) the DST/NRF Centre of Excellence in Strong Materials, University of the Witwatersrand, Johannesburg, South Africa. GS acknowledge the financial support provided by DST, New Delhi for the project “Banasthali Centre for Education and Research in Basic Sciences” under their CURIE programme. We are also thankful to Prof. Blaha and Prof. Schwarz for providing the WIEN2k code.

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