

# Ab Initio Study of Structural and Magnetic Properties of Cobalt Doped Zinc Oxide

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## Abstract

In this study, we have investigated the electronic and magnetic properties of Cobalt doped zinc oxide (ZnO) bulk materials using density functional theory (DFT) calculations. The substitution of Co atoms into the ZnO lattice is systematically explored to understand its impact on the electronic band structure, magnetic moments and stability of the material. It is observed that Co doping introduces localized magnetic moments of 3.073  $\mu\text{B}$  associated with Co atoms. The electronic band structure exhibits the semi-metallic nature after the Co doping with a majority spin ( $\uparrow$ ) and a minority spin ( $\downarrow$ ) magnetic configuration hybridization between Co 3d and 2p orbitals of O, indicating the potential for spin-polarized transport in Co-doped ZnO. We have also analyzed the formation energies to assess the thermodynamic stability. It is observed that the binding energy per atom slightly decreased to -3.563 eV, indicating stable Co incorporation. From the obtained results it can be concluded that, through controlled doping strategies the electronic and magnetic properties in ZnO-based materials can be altered for desired properties.

**Keywords:** Band Structure, Magnetic Moment, DFT (Density Functional Theory), Thermodynamic Stability, ZnO

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## Introduction

In recent years, the concept of simultaneously manipulating both electric charge and electrons spin in nanomaterials has generated substantial interest in the domain of spintronics. The primary goal is to create a semiconductor based ferromagnet whose properties can be precisely controlled at room temperature, which in turn will explore possibilities for magnetoelectric and magneto transport related devices [1]. Typically, intrinsic magnetic semiconductors have relatively low Curie temperatures (TC), which restrict their practical utility. However, researchers have proposed a solution by introducing transition metal or rare earth ions into a nonmagnetic semiconductor host lattice [2]. This process results in a dilute magnetic semiconductor (DMS), with the potential to raise TC to levels suitable for room temperature operation [3-4].

In DMS materials, the magnetism is closely linked to the existence of charge carriers, which can take the form of either holes (as seen in materials like GaAs: Mn) or

electrons (as seen in materials like GaN:Gd). However, there is an ongoing debate about the underlying process accounting for the high-temperature magnetic alignment observed in these systems. This debate is further complicated by significant discrepancies between results obtained in experimental and theoretical studies [5-8].

ZnO, an n-type semiconductor with a wide bandgap, has gained significant attention both experimentally as well as theoretically in recent years. This renewed interest stems from the pioneering work of Dietl et al. and Ueda *et al.* [9, 10], who suggested that ZnO doped with transition metals (TMs) could potentially serve as a DMS suitable for spintronic applications at room temperature. This prediction ignited a flurry of experimental efforts to realize room temperature ferromagnetism in transition metals doped ZnO. However, the quest for achieving this ferromagnetism has been met with significant controversy, with the success often hinging on the specific methods employed for sample preparation [11-13]. Recent studies on gallium and cobalt-codoped ZnO have underscored the contribution of gallium

ions situated in octahedral interstitial sites and the presence of oxygen vacancies in enabling ferromagnetism at room temperature [14]. Interestingly, even nonmagnetic Co-doped ZnO has exhibited ferromagnetic behavior when codoped with lithium [15], while co-doping with aluminium has yielded contrasting experimental results [16-17]. The cobalt and copper codoped ZnO system has also demonstrated ferromagnetic properties [18-19].

In particular, we are motivated by the intriguing observations mentioned above, both theoretical and experimental, regarding TMs doped (i.e., Al, Fe, Co) ZnO systems. In this study, we conduct a comprehensive examination of magnetic behaviour of the Co-doped ZnO system. These calculations shows that the critical role of defects in promoting magnetism in the codoped system.

## Methodology

Here we have focused on performing electronic structure calculations using advanced first-principles techniques, particularly within the framework of Density Functional Theory (DFT). To carry out these intricate calculations, we have used the SIESTA (Spanish Initiative for Electronic Simulation with Thousands of Atoms) code [20]. To accurately capture the interactions among electrons within our systems, we employed the GGA-PBE functional, a computational tool that helps in describing these complex electron-electron interactions with threshold less than 0.001 eV/Å per atoms and energy shift of 20 meV. We have used a mesh cutoff energy of 300 Ry to ensure precision and considering the Brillouin zone integration 15 x 15 x 1 Monkhorst pack grid [21].

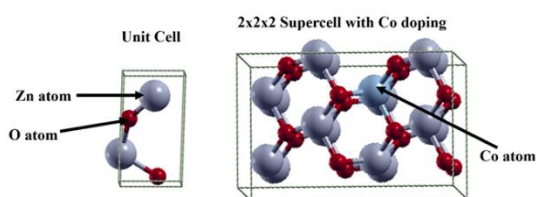


Figure 1: Supercell with 32 atoms

## Results And Discussions

ZnO bulk nanostructure adopts a wurtzite crystal arrangement (Fig. 1), which is a hexagonal analog of the zinc-blende lattice and belongs to the P6<sub>3</sub>mc space group which contains two Zn and O atoms within each unit cell as shown in Fig.1. The optimized lattice constant for pristine bulk is,  $a = 2.903 \text{ \AA}$ ,  $b = 3.085 \text{ \AA}$  and  $c = 5.283 \text{ \AA}$ . For doping of Cobalt, we have employed a 2x2x2 supercell configuration, encompassing 32 atoms (Fig.1). Within this supercell, the replacement of a single Zn atom with a Co atom equates to a dopant concentration of 6.25%. With the doping of Co, the optimized lattice constant is found to increase (Table 1). Moreover, in comparison with pristine,

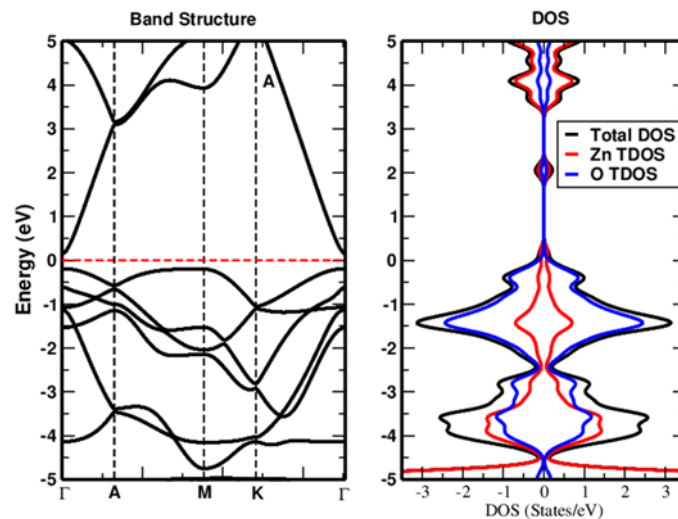
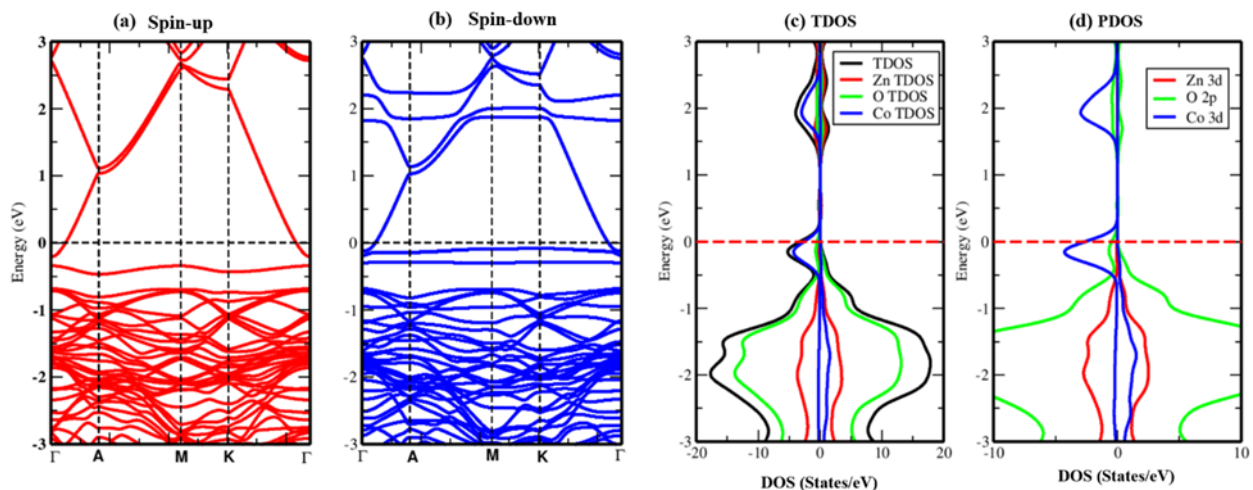
Co doped ZnO supercell resulted in an increase of crystallite size due to the difference in ionic radii of  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ . It suggests that the  $\text{Co}^{2+}$  ions have replaced the  $\text{Zn}^{2+}$  ions within the structure without causing any deformation to the ZnO structure. Such type of behaviour can be understood by considering the  $\text{Co}^{2+}$  ions which tend to naturally adopt an octahedral arrangement within the wurtzite structure. Jayakumar O.D *et.al.* [22] has highlighted that  $\text{Co}^{2+}$  ions possess varying radii depending on their spin state, ranging from 0.65 Å (in the low spin state) to 0.745 Å (in the high spin state). In contrast,  $\text{Zn}^{2+}$  ions typically assume a tetrahedral coordination with an approximate radius of 0.60 Å. As a result, the slight expansion of the Lattice Constants can be attributed to the  $\text{Co}^{2+}$  ions taking up positions within the crystal structure where they form octahedral coordination and effectively replace  $\text{Zn}^{2+}$  ions within the ZnO nanostructures.

Further, we have calculated the binding energy using [23], in order to investigate the structural stability. The calculated binding energy for Pristine ZnO is found to be -3.462 eV/atoms while it increases to -3.563 eV/atoms when Cobalt is doped, resulting into further stability of Co doped crystal as compared to pristine ZnO. The computed band structure of pristine ZnO, with the reference point designating the Fermi level as zero (red dotted line in Fig. 2 (band structure)), reveals two critical regions; the conduction band above and the valence band below (Fig. 2). These bands intersect at the same k-point, marked as  $\Gamma$ , indicating that ZnO possesses the characteristic of being a direct gap semiconductor. The calculated value of band gap for pure ZnO is found to be 0.342 eV which is in agreement the literature [24]. However, it is worth noting that this computed value is significantly smaller than the experimental measurement of 3.2 eV, such deviations may be due to the calculations using the LDA or GGA methods [25]. Our calculations yielded a significantly lower band gap which can be attributed to certain limitations of the Density Functional Theory (DFT) within the Generalized Gradient Approximation (GGA), especially when applied to transition metal oxides like ZnO [21].

In Fig. 3 (c) & (d), a comprehensive view of the total Density of States (DOS) and the Partial Density of States of Co doped ZnO, specifically focusing on the Zn-d and Co-d orbitals which encompass Ferrimagnetic (FI) configurations. In the absence of any structural defects within the pristine ZnO system, the d orbitals associated with Co, which are separated by 3.25 Å in a crystal field characterized by tetrahedral symmetry, undergoes a process called orbital splitting [23]. This splitting leads to the emergence of two distinct sets of states spin-up and spin-down. It is expected that the transition metal (TM) ions exclusively occupy substitutional positions at the Zn site, leading to an expected oxidation state of 2<sup>+</sup> for Co. Under a spin-polarized condition, the system exhibits a preference

**Table 1:** Optimized parameter of pristine ZnO and Cobalt doped ZnO

Structure	Lattice Constant (Å)	Binding Energy (eV/atom)	Magnetic Moment ( $\mu\text{B}$ )	Band Gap (eV)	Bond Length (Å)
ZnO pristine (Unit Cell)	a = 2.903 b = 3.085 c = 5.283	-3.462	0.000	0.342	Zn-O = 2.06
Co doped ZnO at Zn Site (2x2x2)	a = 5.861 b = 6.006 c = 10.577	-3.563	3.073	Half metal	Zn-O = 2.09 Co-O = 2.11

**Figure 2:** Band structure and total density of states (TDOS) of pristine ZnO**Figure 3:** Band structure of Co doped ZnO (a) Spin-up, (b) Spin-down, (c) TDOS and (d) PDOS of each atom

for a high-spin configuration. The Co doing, which possesses a  $d^7$  configuration, the majority spins (spin-up), is completely filled with  $d\downarrow 5$  electrons (Fig. 3 (c) & (d) shown as blue coloured lines), while the minority spin channel (spin-down), is only half-filled. The total Density of States (DOS) and Partial DOS presented in Fig.3 (c) & (d) accurately depict the distribution of electrons as described above. As expected, the Ferrimagnetic (FI) state introduces a reversal in the occupancies of Co in both the up and down spin channels and adopts the configuration of  $d\downarrow 5$ , aligning with the electron distribution characteristic of

the Ferrimagnetic state. For our study, the primary focus was to explore the influence of cobalt (Co) content on the band structure of Co-doped ZnO.

## Conclusions

In this work, the primary focus was to explore the influence of cobalt (Co) content on the band structure of ZnO. We observed that pristine ZnO is a direct band gap semiconductor with energy band gap of 0.342 eV. With the Cobalt doping the structure becomes more stable with a

binding energy of -3.563 eV as compared to pristine ZnO. Moreover, the doping of Co enhanced the spin polarized states by removing the spin degeneracy near Fermi energy. Band structure and total density of states of Co doped ZnO exhibit both spin up and spin down states near Fermi energy. Partial DOS of both spin up and spin down states shows that the contribution of down spin states to the magnetic behavior is more. Therefore, Cobalt doped ZnO is promising material for spintronics.

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