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# Effect of (Co, N) co-doping of p-type ZnO on electronic and magnetic properties by DFT+$U$ studies

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ABSTRACT

This study presents the calculation of (Co-N) co-doped ZnO in the wurtzite structure of 32 atoms, a density functional calculation and a theoretical analysis of the electronic and magnetic properties are investigated using the Full-Potential Linearized Augmented Plane Wave (FPLAPW) method, implemented in WIEN2k package. We have used two approaches LSDA and LSDA+$U$ to analyze and correct the density of state, and to understand the Co and N influence on $p$-type ZnO at different concentrations, i.e., their bonding with nitrogen is also determined. The results prove that ZnO doped with two N concentrations of 6.25% and 12.5% is $p$-type, semi-metallic and ferromagnetic caused by the strong hybridization effect between N *2p* and O *2p* states, with a full magnetic moment of $1\mu_B$ and $0.31\mu_B$, respectively. As for co-doped ZnO with Co and two concentrations of N, the LSDA+$U$ approximation shows that the total magnetic moment increases with the N concentration from 3.92 to $4.51\mu_B$ due to hybridization effects between Co *3d* and N *2p* states.

## 1. Introduction

Since the late 1970s, studies on diluted magnetic semiconductors (DMS) [1,2] have been widespread. Compounds II-VI (CdTe, ZnTe, HgTe, ZnS, CdS, ZnO, etc.) in which they randomly substitute magnetic dopants (Mn, Fe, Co, Cr, etc.) and non-magnetic dopants (N, P, Al, As, etc.) in our case zinc oxide (ZnO) is part of the wide-band gap semiconductors (Eg = 3.37 eV at room temperature) with a hexagonal wurtzite crystalline structure [3–5]. While zinc oxide doped with one of the above transition metals (TM) becomes mainly diluted magnetic semiconductor (DMS) materials; and produce interesting magnetic properties in the Curie high temperature (CT) as well as in the ambient temperature (ferromagnetic DMS) [7,8]. According to a theoretical study of Dietl [6], for example, with an almost ambient temperature CT (280–300 K) [9,10]. The origin of ferromagnetism in these materials remains controversial and could come from metallic clusters present in the matrix [11]. The cobalt doping of ZnO by laser ablation gaves us a low ferromagnetic coupling as Particularly in Co-doped ZnO [12] there are reports of giant magnetic moments (≈6.1 $\mu_B$/Co) [13], and high ferromagnetic-ordering temperatures with moments of 1–3 $\mu_B$ [14,15] ], and in some cases there is no ferromagnetic behavior [16–18]. In this paper, we investigated the electronic and magnetic properties of co-doped ZnO (used simultaneously with two different cobalt and nitrogen impurities (Co, N) suitably chosen to give another route in order to achieve the ferromagnetism system compound or alloy using density functional theory (DFT) because the structure of the ionic Co (Co2 + = 0.58 Å) is extremely close to zinc (Zn2 + = 0.6 Å) [19], which makes Co a potential candidate, so Co is chosen in order to have a better understanding of the magnetic properties of these materials. In identifying the electronic states, we first calculate the electronic structures and the total energy, which contribute to the ferromagnetic coupling (FM) and antiferromagnetic (AFM) of ZnO: Co with co-dopants on the one hand with 1N and on the other hand with 2N, then we compare the total energies calculated with the presence of a impurity N and 2N in the FM and AFM states. To determine their

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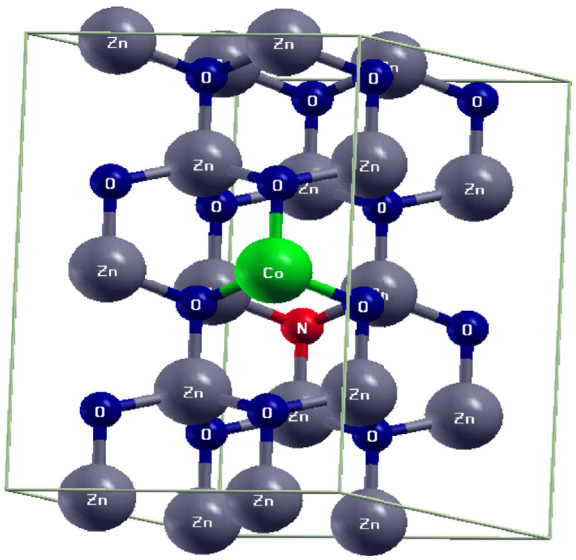


**Fig. 1.** Wurtzite structure of ZnO with impurities Cobalt and Nitrogen.

magnetic moment, we used the local spin density approximation (LSDA) and the Hubbard potential LSDA + $U$ [20].

## 2. Computational details

To study the electronic structure of ZnO:(Co,N), we use a supercell containing 32 atoms in wurtzite structure. The un-doped material corresponds to $Zn_{16}O_{16}$ and to study the Cobalt doping and Nitrogen co-doping we substitute one of the Zinc ions by one Cobalt ion and Oxygen ions by Nitrogen. (Fig. 1). Our calculations are based on the density functional theory (DFT) in the LSDA, with additional Hubbard correlation terms describing on-site electron–electron repulsion associated with the 3d narrow bands in (LSDA+$U$ approach) [21], using the FP-LAPW method [22]. The system is performed with ($3 \times 3 \times 2$) supercell associated with fundamental lattice constants $a = 3.0249$ Å and $c = 5.206$ Å, and the dimensions 9.747 Å and 10.412 Å parallel to $a$ and $c$ axes, respectively. Which are in agreement with the experimental and other theoretical work [17]. The valence-electron configurations for the elements discussed in this paper trial are Zn: $3d^{10}4s^2$, O: $2s^22p^4$, N: $2s^22p^3$, Co: $3d^74s^2$, respectively. The value of the Hubbard $U$ parameter for ZnO: Co is already roughly known from previous theoretical studies [23]. We varied them between 4 and 8 eV but we present most of the results for a value of $U = 6$ eV. The muffin-tin (MT) radii of Zn,Co, N, and O were

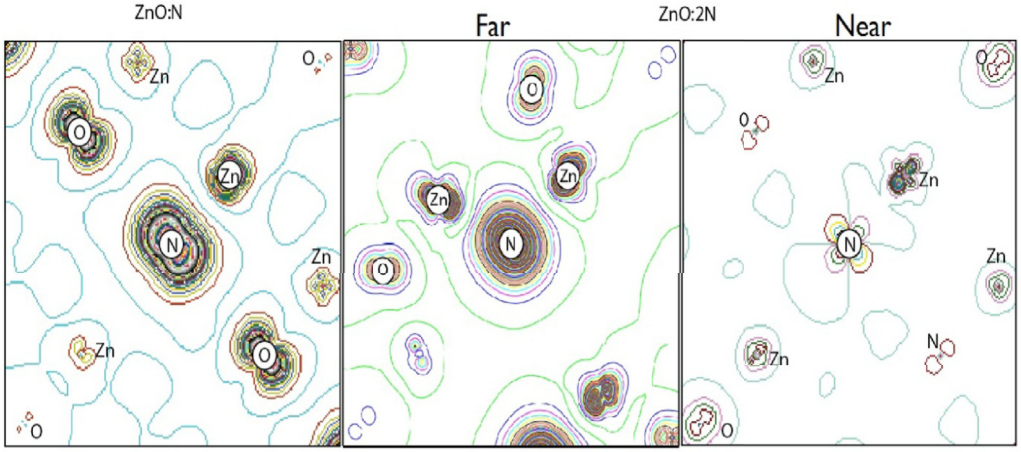


**Fig. 2.** Spin density of ZnO with (from left to right)N, 2N far and 2N near.

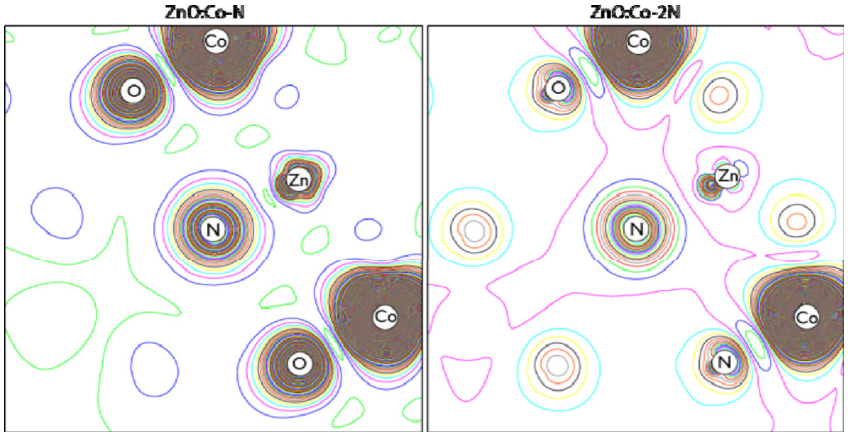


**Fig. 3.** Spin density of co-doped ZnO Co with N (left) and 2N (right).