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Full Length Research Paper

First principle study of the effect of Co substitution on the magnetic and electronic properties of wz-ZnO

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We have studied the electronic and magnetic properties of $Zn_{0.75}Co_{0.25}O$ compound. The calculations were done by SIESTA and WIEN2K code based on the density functional theory (DFT). We have used a Pseudopotential (PsP) and full potential (FP) approaches in our calculations, as implemented in SIESTA and WIEN2K code respectively. The generalized gradient approximation (GGA) was used for exchange-correlation potential in our two approaches. The result shows that the band structure and total density of state of $Zn_{0.75}Co_{0.25}O$ compound has changed considerably with respect to pure ZnO for spin up and down polarizations. The values of dipole magnetic moment per supercell of $Zn_{0.75}Co_{0.25}O$ compound was obtained about 3.01 and 3.02 μ_B, using PsP and FP approaches respectively.

Key words: Density functional theory, electronic properties, pseudopotential, full potential, zinc oxide.

INTRODUCTION

Magnetism and semiconducting properties can coexist in semiconductors materials with a small fraction of magnetic impurity atoms such as Mn, Cr, Co, Ni, Fe and Cu. This category of semiconductor is then called dilute magnetic semiconductor or (DMSs) (Ohno et al., 1992; Furdyna, 1988). Dilute magnetic semiconductor, are semiconducting materials in which a fraction of the host cations can be replaced by magnetic ions of transition metals or appropriate rare earths. Dilute magnetic semiconductors are expected to play an important role in materials science and electronics. In these materials in addition of the charge, the spin degrees of freedom also play an important role in the physical properties which are related to charge and spin transport. Therefore DMSs have many important applications in magnetic, magneto-optical, magnetoelectronic and spintronic devices (Ohno, 1998; Datta and Das, 1990).

The most interesting dilute magnetic semiconductors are II - VI based materials. In these materials the magnetic impurities ions, which have +2e charge, can easily settle in the place of group II cations. From the II - VI compound semiconductors, ZnO has attracted renewal attention. It has a direct wide band gap about 3.3 eV and due to its wide band gap it has found a lot of applications in the optoelectronic and magneto-optic industry (Look, 2001). The room temperature ferromagnetism was first reported by Dietl et al (2000) in Mn-doped ZnO. After that, many researchers have doped ZnO with 3d transition metal and reported high room temperature ferromagnetism (Sluiter et al., 2005). There have been also a lot of theoretical and computational studies in transition-metal (TM)-doped ZnO (Bruno and Sandratskii, 2006; Pearton et al., 2003).

In this work we have used two different code; SIESTA and WIEN2K code in our calculations. SIESTA uses pseudopotentail (PsP) and WIEN2K uses full potential (FP). We have calculated and compared the band structure and total DOS of the pure and Co-doped zinc oxide by FP and PsP approaches. Although the FP approaches have a better precision, but they take a lot of time when the number of simulated atoms increases. One way for doing calculation for large supercell is using PsP approaches, but the used pseudopotential should check by comparing the result with the result of the more correct

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methods that would be subsequently shown in the study. We have also studied the effect of Co substitution, considering spin-polarized calculations.

METHOD OF CALCULATIONS

In this work we have studied ZnO in wurtzite structure which is a proper host for diluted magnetic semiconductors. Wz-ZnO structure has two Zn atoms and two O atoms in its unit cell and has hexagonal symmetry with $P6_3mc$ space group (Özgür et al., 2005). We used experimental values for our crystal parameters to be a=b= 3.258 Å, c=5.220 Å and u=0.382 (Decremps et al., 2003).

In order to benefit from Bloch theorem in periodic structures, we used supercell approximation (Payne et al., 1992). We made a 1×1×2 supercell of the unit cell which contains 8 atoms and then substituted one of the Zn atoms by one Co atom. In this way we made the cobalt doped wurtzite Zn_{1-x} Co_x O compound with x=0.25, which has been shown in Figure 1. In this new compound the space group was changed to P_3m_1, and the lattice parameters for the supercell after optimization were obtained as A = B = 3.256 Å and *C* = 10.430 Å.

The calculations were performed in the framework of density functional theory (DFT) within the independent-particle approximation using Kohn-Sham Eigen states and Eigen values (Hohenberg and Kohn, 1964; Kohn and Sham, 1965). The generalized gradiant approximation (GGA) (Perdew et al., 1996) was used for the exchange-correlation energy. In addition we used a PsP and FP approaches in our calculations as implemented in SIESTA (Ordejon et al., 1996) and WIEN2K (Blaha et al., 2001; Schwarz (2003) codes respectively. In both approaches we have performed ferromagnetic spin-polarized calculations that are we considered the effect of spin in the Kohn-Sham Hamiltonian of the system.

In SIESTA code, core electrons which have not considerable effect in chemical and electronic properties are replaced by efficient Troullier-Martins pseudopotentials (Troullier and Martins (1990, 1991) in their fully separable form. In this code, pseudo atomic orbitals (PAO's) basis set (Sankey and Niklewski, 1989) have been used for the expansion of the wave functions of valence electrons. These orbitals are constructed from multiplying of a numerical radius function by an angular function with a definite *m* and *l* quantum numbers. From the three kind of basis set in the code, double zeta plus polarization (DZP) was chosen. There are two important parameters in SIESAT code which should be optimized correctly for saving time and also to have an acceptable precision in calculations. These parameters are Kgrid-cutoff and Mesh-cutoff energy where their optimized values obtained from converging total energy to be 20 Å and 250 Ryd, respectively. The WIEN2K code uses Full Potential Linearized Augmented Plane Wave (FP-LAPW) method. Besides, the wave functions are expanded into spherical harmonics within atomic muffin-tin (MT) spheres and in the form of plane waves in the remaining space. The MT spheres are supposed not to overlap with each other. The chosen radii of MT spheres for atoms were R_{MT} (Zn) =1.97 Å and R_{MT} (O) = 1.75 Å. The cut-off energy, which defines the separation of the valence and core state, was chosen to be about -6.5 Ry. The convergence criteria was chosen to be the total energy and set at 10^{-4}eV.

RESULTS AND DISCUSSION

Band structure and DOS of ZnO

First brillion zone (BZ) and the band structures of ZnO calculated by the FP and PsP methods, as shown in Figure 2. It should be noticed that the energies have been shifted so that the Fermi energy is located at the top of the valence band as zero energy. We see that the ZnO has a direct band gap at the Γ point with an energy gap about 0.8 and 0.7 eV, obtained from FP and PsP methods, respectively. We see also that there is a remarkable similarity between the calculated band structures around the Fermi energy by these methods.

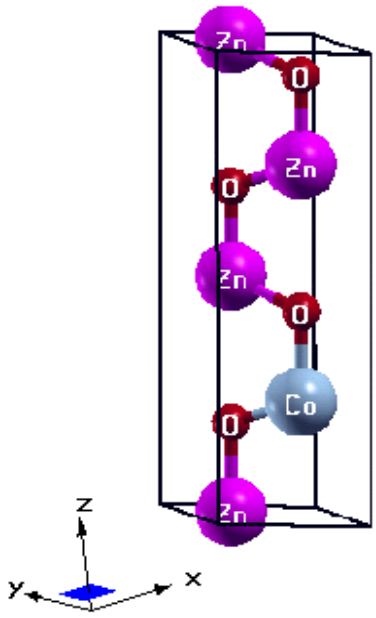

Figure 1. Structure and atomic positions of a 1×1×2 supercell of $Zn_{0.75}Co_{0.25}O$ compound.

The experimental and theoretical band gap energies of this crystal have been compared in Table 1. We see that our results are in agreement with other DFT-GGA calculations (Schleife et al., 2006; Topsakal et al., 2009). Although it is clear that GGA underestimates the band gap with respect to experiment, which our calculations also shows it, the remarkable difference between experiment and theory may also be due to the fact that we have not considered the localization nature of d and f orbitals in our calculations.

The total density of states (t-DOS) by PsP and FP have been shown in Figure 3, zero energy has been set at the Fermi level. The conduction band mostly contains Zn-4s orbitals and the bottom of the valence band is constructed from O-2p and Zn-3d orbitals. Excellent consistency between calculated (DOS) by two method is observed.

In order to show that the wz-ZnO crystal has no any magnetic moment, we performed a spin-polarized calculation where the t-DOS for spin up and down states has been shown in Figure 4. We see that the total populations of the electrons with spin up and down are the same and therefore the net magnetic moment per cell is zero.

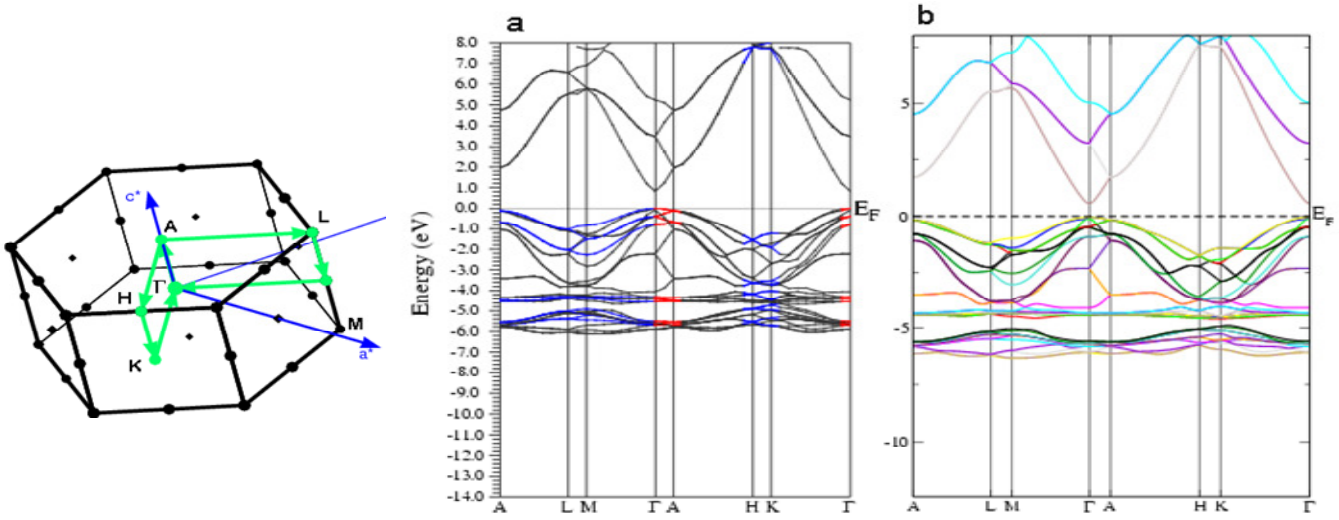

Figure 2. Band structure of wz-ZnO along the lines with high symmetry by (a) FP and (b) PSP approaches.

Table 1. Band gap in experimental and theory method.

Energy (eV)	Method
3.3 (Look, 2001)	Exp.
0.70 (This work- PsP)	GGA+SIESTA
0.80 (This work- FP)	GGA+WIEN2K
0.73 (Schleife et al. 2006) (VASP)	GGA+VASP
0.75 (Topsakal et al. 2009) (VASP)	GGA+VASP

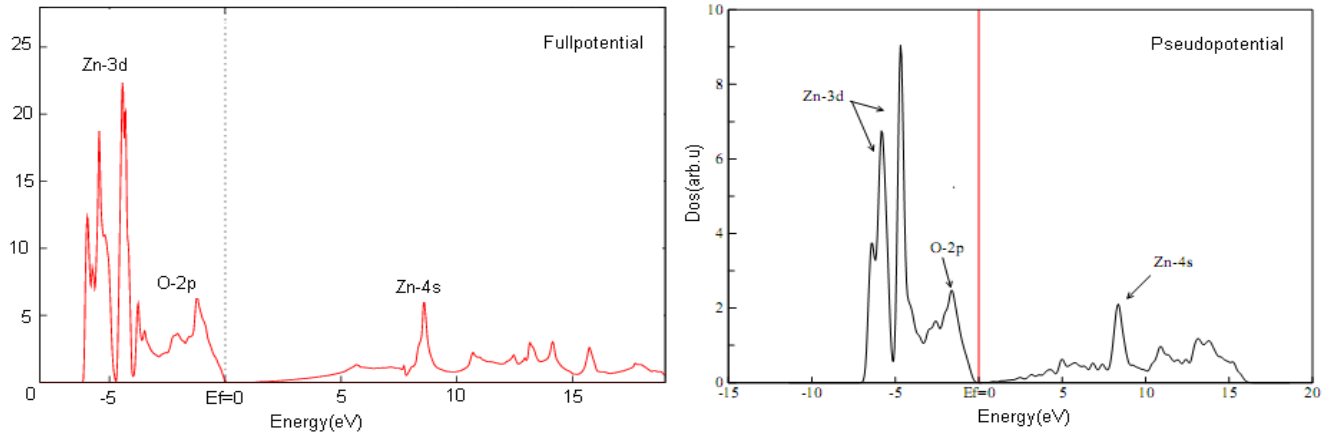

Figure 3. Total DOS of ZnO compound by FP and PSP approaches.

Band structure and DOS of Zn0.75Co0.25O

Band structure of $Zn_{0.75}Co_{0.25}O$ compound has been calculated by PsP and FP methods and the result for spin up and down situations have been shown in Figure 5. The calculated band structure by the PsP method for spin up and down has been shown in one diagram. Regarding this fact, one can see that there is a good similarity between the results of the two mentioned methods. Comparing the band structures for Co-doped and undoped ZnO, we see that the band structure has changed and the Fermi energy passes through the bands with substituting Co atoms. The change in the band structure may be due to the mixing of Co-3d orbitals with the valance band of the host, which is mainly originated from the O-2p orbitals.

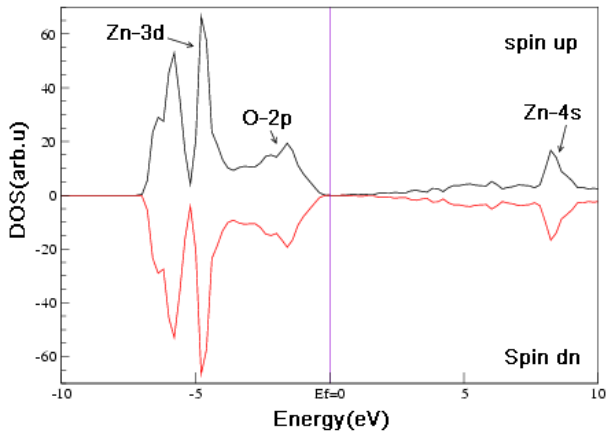

Figure 4. Total density of state for the spin up and down situations of undoped wz-ZnO.

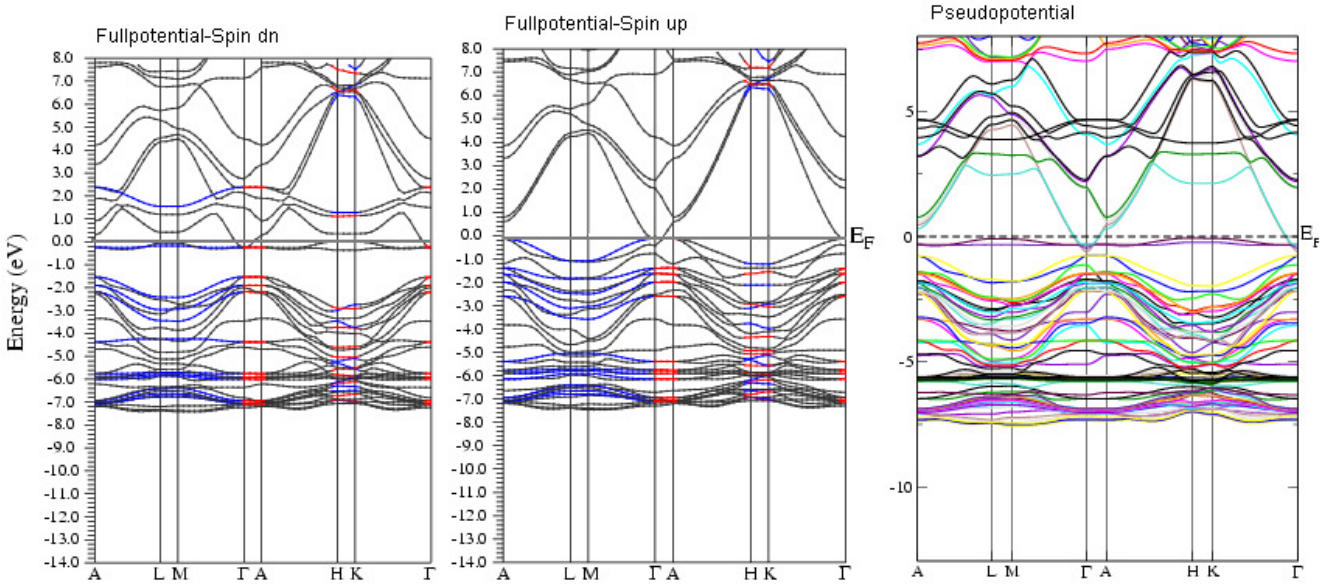

Figure 5. Band structure of $Zn_{0.75}Co_{0.25}O$ compound by both methods.

There is a remarkable difference between the populations of spin up and down electrons in the corresponding band structures which means that the $Zn_{0.75}Co_{0.25}O$ compound should be a ferromagnetic. The important characteristic of a ferromagnetic material is its spontaneous magnetization. The difference in the number of spin-up and spin-down electrons gives rise to the observed spontaneous magnetic moment. In fact, in this situation, Co atoms are the responsible of the exhibition of magnetic behavior in $Zn_{0.75}Co_{0.25}O$. It means that the delocalized conduction band electrons and valence band holes in ZnO, interact with the localized magnetic moment associated with the localized partially filled d state of Co atoms, and therefore there would be a strong hybridization of the 3d orbitals of the Co ion and p orbitals of the host anions. This hybridization will shift the state with spin up and down around the Fermi energy and will result a net localized magnetic moment.

The calculated values of the dipole magnetic moment per super cell (here per Co atom, because there is one Co atom in the super cell) by FP and PsP approaches was obtained about 3.02 and 3.01 μB, respectively. This results show that the value of magnetic moment by two mentioned method are nearly the same.

Our calculated magnetic moment is in excellent agreement to the expected magnetic moment of a Co^{2+}

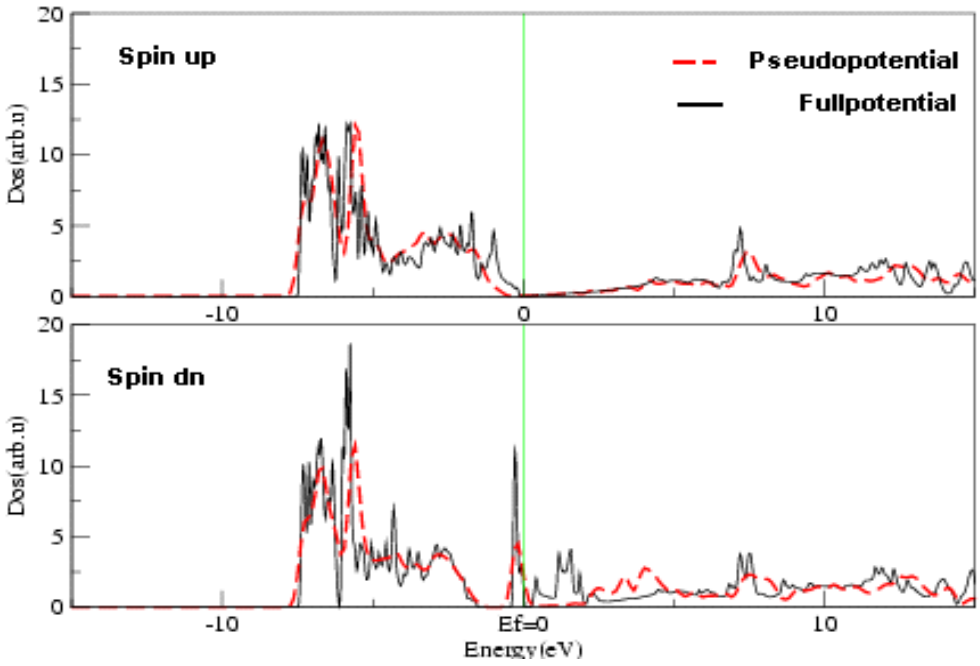

Figure 6. Total DOS of $Zn_{0.75}Co_{0.25}O$ compound which compared in both methods.

ions in a tetrahedral crystal field that is 3.0 μB/Co atom. There has been a lot of experimental works for magnetic moment of ZnO:Co system. The results obtained by different groups with different experimental conditions are different or even it is not shown any reasonable relation between the concentration of Co and the measured magnetization. In fact the experimental value of magnetic moment is depend on the preparation methods, the kind of substrate, annealing temperatures, oxygen vacancy, Co concentration and etc (Pan et al., 2008). Rode et al. (2003) have growned $Zn_{0.75}Co_{0.25}O$ thin films on Al_2O_3 substrate and reported 1.0 μB/Co atom for its magnetic moment while Dinia et al. (2005) have reported 0.8±0.1 μB/Co atom for the $Zn_{0.75}Co_{0.25}O$ thin film grown at 400°C on Al_2O_3 substrate and 0.5±0.1 μB/Co atom for the same system but grown at 600°C. This result shows that the experimental values of the magnetic moment for ZnO:Co systems extremely depend on the experimental conditions.

Total densities of state of $Zn_{0.75}Co_{0.25}O$ compound for the spin up and down situations were calculated by pseudo- and full-potential approaches and have been shown in Figure 6. The figures also show that the population of electron with spin down are more than the population with spin up and therefore support the last results obtained by band structure calculations. The t-DOS by the two approaches for the spin up situation is nearly the same but for the spin down it differ slightly, especially in the 1- 2 eV energy range above the Fermi energy which is also can be seen in the band structures diagrams.

CONCLUSIONS

In conclusion, we have calculated and compared the band structure, t-DOS and the dipole magnetic moment of the pure and Co-doped zinc oxide by a FP and PSP approaches. The energy gap of the pure and the $Zn_{0.75}Co_{0.25}O$ compound by the two methods was nearly the same and comparable to experiment considering the well-known underestimation of the band gap by DFT.

We showed that substituting Co instead of Zn atoms will change it to a ferromagnetic. The calculated dipole magnetic moment of the Co-doped zinc oxide by two approaches was nearly the same. We showed also that there is an excellent consistency between the calculated quantities by PsP and FP approaches which manifest that the used pseudopotentials are proper and efficient and can be used for calculations with more atoms in the supercell.

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