First principle study of the effect of spin on the electronic and optical properties of Co-doped ZnO

M. R. Benam[1], J. Baedi[2], M. Hezari[1]

[1] Department of Physics, Payame Noor University, P.O.BOX 19395-3697, Tehran, Iran.

[2]Physics Department, Sabzavar Tarbiat Moalem University, Iran

Abstract. We have calculated dielectric constant and refractive index of the Zn15Co1O16 compound, for spin up and spin down polarizations. The calculations were done by SIESTA code based on the Density Functional Theory (DFT) and a pseudopoetntial approach with the Generalized Gradient Approximation (GGA) for the exchange correlation potential. The results show that there is a remarkable difference between the spin up and down states for the mentioned quantities, especially in their static values. One may benefit from these differences in spintronic and magneto-optic devices, where the spin component plays a crucial rule.

Keywords: Spin polarization, Optical properties, Density Functional Theory, Zinc Oxide

1. Introduction.

Semiconductors and magnetic materials have attracted an exceeding interest in the scientific society due to their possible potential applications in the electronic industries[1]. One of the important compounds, which have widely been used in spintronic devices, is Dilution Magnetic Semiconductors (DMS). Dilution Magnetic Semiconductors are materials in which a small fraction of the host cations can be replaced by magnetic ions, like Transition Metal (TM) or rare earth ions[2,3]. In these materials in addition the charge, the spin degree of freedom also plays an important role in transport properties and therefore these materials have found a lot of promising applications in magneto-optic, magneto electronic and widely in spintronic devises [4,5] .

 One of the interesting DMSs materials are the binary II-VI semiconductors. One of the reasons which have made this material more interesting in the scientific society is the easy replacing of the group II cations by impurities magnetic atoms. From the II-VI semiconductors, ZnO compound has been in the central attention of experimental and theoretical researchers. This interest is firstly, due to its wide direct band gap, which is about 3.3 eV [6], and secondly due to the room-temperature ferromagnetism in n-type ZnO-based DMSs[7] . Having wide band gap, makes it a proper material for widespread use in optoelectronics industry [8]. It also has a strong piezoelectricity which can be exploited in a variety of transducer applications and in polarization field effect transistors [9, 10]. The first group which has reported the existing of ferromagnetism in ZnO-based DMSs, was Dietl *et al* group[11]. They found a remarkable room temperature ferromagnetism in Mn-doped ZnO. After that many researchers have doped ZnO with 3d transition metal and reported high room temperature ferromagnetism in TM-doped ZnO [12-13].

 In spite of the existing of a large number of theoretical and experimental works on TM-doped ZnO, there is still less studies about the effect of spin on their optical properties. In this paper , using DFT, we have investigated the effect of spin on the density of state and some optical constants which will be discussed in the following sections.

2. Method of Calculations

We have used a linear scaling, fully self-consistent density functional method for performing first-principles calculations, as implemented in SIESTA code [14]. In our calculations we have used Density Functional Theory (DFT) based on the work by Hohenberg and Kohn [15] and by Kohn and Sham[16] .We have also used the Generalized Gradient Approximation (GGA) [17] for the Exchange-Correlation potential. We

employed the Perdew-Burke-Ernzerhof (PBE) form of the Exchange-Correlation potential in GGA. Troullier-Martins pseudopotentials were used to represent the nuclei plus core electrons [18] .

There is two important parameter in SIESAT code which should be optimized correctly for saving time and also have an acceptable precision in calculations. These parameters are Kgrid-cutoff and Mesh-cutoff energy where their optimized values were chosen, from converging total energy, to be 15 A^0 and 250 Ryd, respectively (Fig 1).
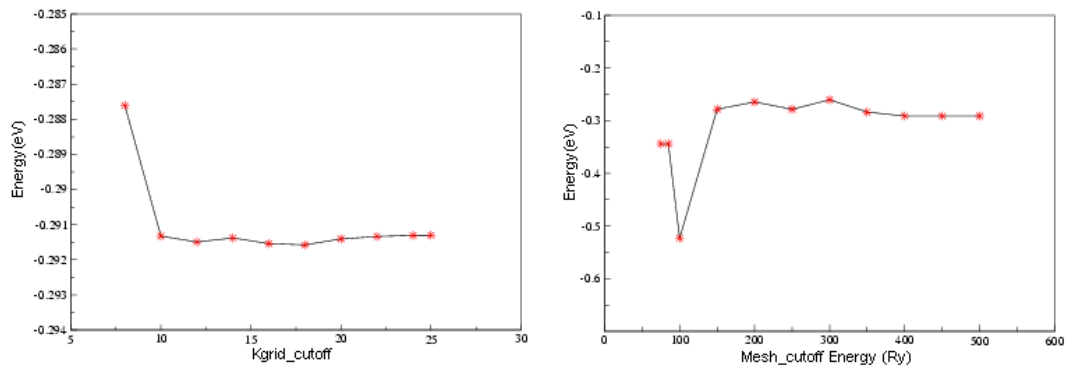

Fig.1 Converging total energy with respect to Kgrid_cut off (left) and Mesh_cutoff Energy (Right).

Zinc oxide compound is crystallized in wurtzite, zincblende and rocksalt structure [19]. Among this structure the wurtzite structure is more stable which was used in our simulations. Its unit cell consists of two Zn and two O atoms which belong to two interpenetrating hexagonal closed packed lattices. It has hexagonal symmetry with P63mc space group [20]. We used experimental value for our crystal parameters to be a=b= 3.258 Å, c=5.220 Å and u=0.382 [21].

In order to benefit from Bloch theorem in periodic structures, we used supercell approximation [22] . We made a   supercell of the unit cell which contain 32 atoms and then replaced one of the Zn atoms by one Co atom. In this way we made the cobalt doped wurtzite Zn15Co1O16 compound which has been shown in Figure 2. We then performed spin-polarized calculation for both doped and undoped compounds which the result has been shown in the following sections
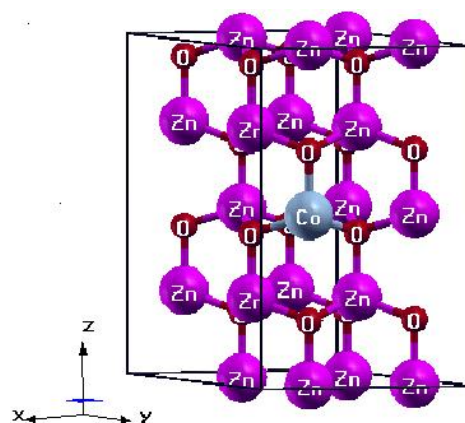

Fig. 2. The supercell of co-doped wurtsiz $Zn_{15}Co_1O_{16}$

3. Results and discussions

3.1. Electronic Properties

The total density of state for the spin up and down situations of Undoped $Zn_{16}O_{16}$ compound has been show in Figure 3. The valance band is mainly constructed from the O-2p and Zn-3d orbitals which has been extended nearly from zero to -4.5 eV and from -4.5 to -6 eV, respectively. The population of electrons in the majority and minority spins, in pure state are equal which means that pure Zinc oxide is a non magnetic semiconductor material.
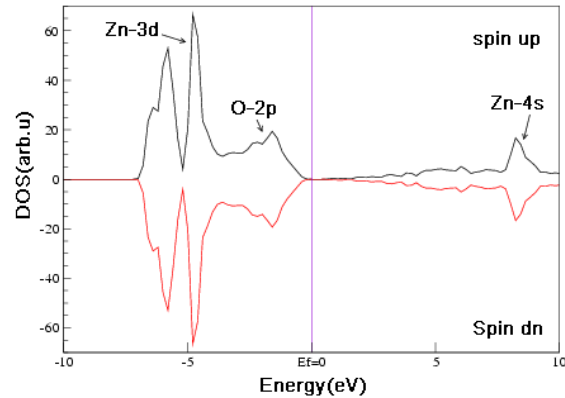
Fig. 3 Total density of state for the spin up and down situations of undoped $Zn_{16}O_{16}$

The total density of state for the spin up and down situations of doped $Zn_{15}Co_1O_{16}$ compound has been shown in Figure 4. In this figure we see that the population of electrons in the majority and minority spin are not equal and differ a little bit which means that the Co-doped Zinc oxide should be a ferromagnetic semiconductor material. In fact the Fermi energy passes through the t-DOS of spin down, where it mainly comes from the contribution of Co-3d orbitals. This different spin dependence character of electrons around the Fermi energy causes different physical behavior, like different optical properties for spin up and down situations, which will be discussed in the following section.
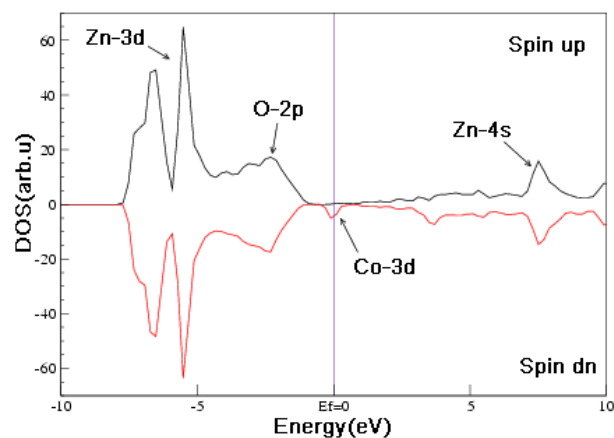
Fig. 4 Total density of state for the spin up and down situations of doped $Zn_{15}Co_1O_{16}$ compound

One of the reason of the changing band structure and t-DOS of Co-doped Zinc oxide may be the exchange interaction between the localized $3d$ spins of the Co ions with the carriers in the valence band (O-2p). In fact, there is a strong hybridization between the Co-3d orbitals in the conduction and O-2p orbitals in the valance band which causes these changes.

3.2.   Optical Properties

The frequency dependence of real and imaginary part of dielectric constant of $Zn_{15}Co_1O_{16}$ compound has been calculated for spin up and spin-down polarizations (Figure 5). We see that there is a sharp change in spin down situation in low photon frequency. This difference in response at low frequency may be due to the mentioned metallic characteristic in spin down polarization. The imaginary part of spin up start to increase from the energies about 0.7 eV which is nearly equal to the energy gap or to the threshold energy for direct interband transitions, which means that the absorption of incident photons should start at this energies. There is other remarkable peaks in the imaginary part of dielectric constant at the energies of about 2.5, 11.5 and 14.0 eV which is nearly the same for the spin up and down.
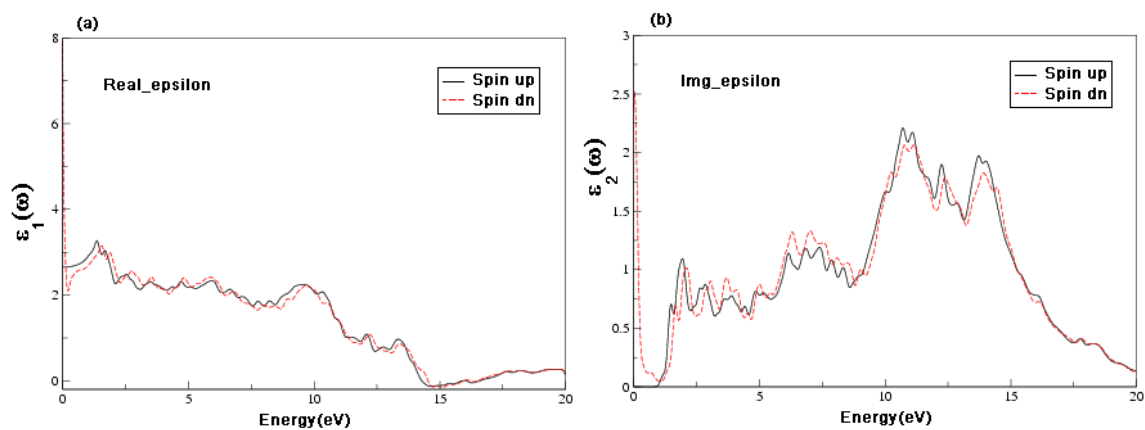

Fig. 5 (a) Real part and (b) Imaginary part of dielectric constant of $Zn_{15}Co_1O_{16}$ compound for spin up(continues line) and spin down (dash line).

The frequency dependence refraction index of $Zn_{15}Co_1O_{16}$ compound has been calculated for spin up and down polarizations and has been shown in Figure 6. There is again a remarkable difference between the refraction indexes in spin up and down situations, especially in low frequencies. The static refraction index for spin up is about 1.6 while for spin down is about 2.75. In fact the refractive indexes related to spin down starts to decrease from its static value and reach below the static value of spin up and then goes up and then behaves like spin up in other frequencies.
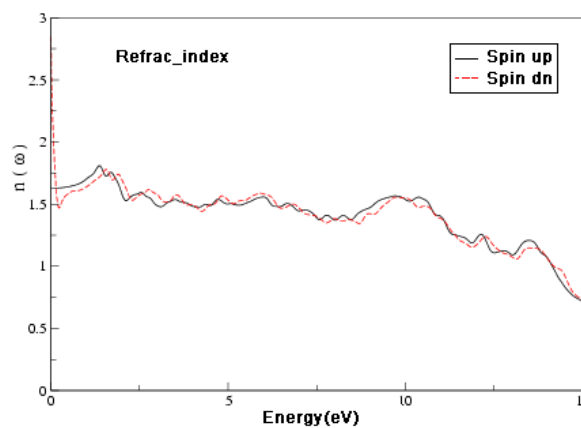

Fig. 6 The refraction index of $Zn_{15}Co_1O_{16}$ compound for spin up (continues line) and spin down (dash line).

4. Conclusions

In conclusion, the density of state of undoped $Zn_{16}O_{16}$ and doped $Zn_{15}Co_1O_{16}$ compounds for spin up and down polarization were calculated and compared with each other. We saw that the spin down and up situations show a metallic and semiconductor characteristic, respectively. The dielectric constant and refractive index of doped $Zn_{15}Co_1O_{16}$ compound were calculated for spin up and down polarizations. There was a remarkable difference between the two spin situations, especially in low frequency and their static values. We may benefit from these differences in spintronic and magneto-optic devices, which the spin component plays a crucial rule in them.

5. Acknowledgements

6. References

[1]   M. Tanaka, *J. Vac. Sci. & Technol*. 1998, **B16** : 2267 .

[2]   H. Ohno, H. Munekata, S. von Molnár and L. L. Chang, *Phys. Rev. let*. 1992, **68**,:2664.

[3]   J. K. Furdyna, *J. Appl. Phys.* 1988. **64**: R29-R64.

[4]   T. Mizokawa, T. Namba, A. Fujimori, T. Fukumura and M. Kawasaki, *Phys. Rev*. 2002, **B65**: 85209.

[5]   H. Ohno, *Science*. 1998. **281**:951-956.

[6]   L. Börnstein , Group III Condensed Matter 36A (Springer Verlag Heidelberg) (2002).

[7]   S. Ghosh , V. Sih, W.H. Lau , D. D. Awschalom, S. Y. Bae, S. Wang, S. Vaidya and G. Chapline *, Appl. Phys. Lett.* 2005, **86**:232507.

[8]   D.P. Norton, Y.W. Heo, M.P. Ivill, K. Ip, S.J. Pearton, M.F. Chisholm, T. Steiner, *Materials Today* 2004, **7** (6): 34-40.

[9]   V.E. Wood and A.E. Austin, *Magnetoelectric interaction phenomena in crystal* , Gordon and Breach , New York, 1975.

[10] P. Gopal and N. A. Spaldin, J. Electron. Mater. 2006, **35**: 538 .

[11] T. Dietl, H. Ohno, F. Matsukara, J. Cibert, and D. Ferrand, *Science* 2000, **287**1019 .

[12] E.C. Lee and K.J. Chang, Phys. Rev. 2004, **B69**:85205.

[13] M. H. F. Sluiter, Y. Kawazoe, P. Sharma, A. Inoue, A. R. Raju, C. Rout and U. V. Waghmare , *Phys. Rev. Lett*. 2005, **94**:187204 .

[14]   P. Ordejon, E. Artacho & J. M. Soler , *Phys. Rev*. 1996, **B53**:R10441.

[15] P. Hohenberg and W. Kohn, *Phys. Rev*. 1964, **136**:B64 .

[16]   W. Kohn and L. J. Sham, *Phys. Rev*. 1965, **140**:A1133.

[17] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett*. 1996, **77**:386.

[18]   N. Troullier, J. Martins , *Phys. Rev*. 1991, **B4** :1993.

[19] A. Ashrafi and C. Jagadish. *J. Appl. Phys*. 2007, **102**.

[20] Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Doğan, V. Avrutin, S . J. Cho, and H. Morkoç, *J. Appl. Phys.* 2005, **98**:41301.

[21] F. Decremps , F. Datchi , A.M . Saitta, A. Polian , S. Pascarelli , A. DiCicco , J.P. Itiˊe and F. Baudelet *, Phys. Rev*. 2003, **B68**,:104101 .

[22] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys*. 1992, **64**:1045-1097.