International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 19 (2018) pp. 14341-14344

Magnetic properties induced by Mn atom in ZnO from theoretical study

Miguel J. Espitia R[1*], Juan M. Oviedo C[2], Luis C. Sánchez P[2]

[1]GEFEM Group, Universidad Distrital Francisco José de Caldas, Bogotá, Colombia.

[1,2]GAMASCO Group, Universidad de Córdoba, Montería, Colombia.

**Corresponding autor*

Abstract

Ab *initio* calculations using full-potential linearized augmented plane wave (FP-LAPW) method within density functional theory were performed in order study the effects of the incorporation of one Mn-atom in the structural, electronic and magnetic properties on ZnO compound. The calculation was carry out in the structure wurtzite employing the computational Wien2k code. Specifically, we investigate the $Zn_{0.75}Mn_{0.25}O$ concentration. We found that due to the one Mn incorporation the ZnO losses the semiconductor behavior, the new $Zn_{0.75}Mn_{0.25}O$ acquire a half-metallic ferromagnetic character with a magnetic spin polarization of 100% of the conduction carriers and a magnetic moment of 5.0 μ_β/cell. This electronic and ferromagnetic behavior come from the strong hybridization of the Mn-3d and O-2p orbitals. The new $Zn_{0.75}Mn_{0.25}O$ is a good candidate for applications in the spintronic field.

Keywords: Density Functional Theory, electronic and magnetic properties.

INTRODUCTIÓN

ZnO is very important material in several areas condensed material devices, including photocatalysis, transparent conductive electrodes in solar cells, laser diodes [1, 2], optoelectronic [3], and piezoelectric applications in surface acoustic wave devices [4, 5], cosmetic products [6]. Recently, ZnO doped a very low concentration with nonmagnetic and magnetic metal transition atoms have attracted considerable attention due to potential application in diluted magnetic semiconductor. Additionally, in recent years ferromagnetism at room temperature was recently reported. [7] in Fe-doped ZnO synthetized by the chemical pyrophoric reaction method. Simultaneously, density functional theory calculations within pseudopotential method (DFT) [8] has been found ferromagnetism at room temperature in Mn- and Co-doped ZnO. In addition, Mera J. et al. [9] by means experimental technique pulsed-laser deposition, grown epitaxially and observed magnetic behavior attributed to Mn in $Zn_{1-x}Mn_xO$ thin films. The magnetic properties of ZnO doped with transition metals make it one of the most promising materials for applications in spintronic devices, because ZnO is very abundance, environment friendly nature direct and due to is a semiconductor material with a wide band gap 3.3 eV. Finally, the devices based on spintronics have several advantages over their conventional electronic counterparts, faster data processing speed, such as non-volatility, greater integration density and low energy consumption [10]. For these superior properties of the ZnO, in this work we investigated the structural, electronic and magnetic properties of the $Zn_{0.75}Mn_{0.25}O$ compound due to potential applications spintronics.

COMPUTATIONAL METHOD

The optimization structural and electronic structure calculations were performed using density functional theory [10, 11] with the full-potential linearized augmented-plane-wave (FL-LAPW) method. The computational calculation were made using the WIEN2k code [12]. The correlation and exchange effects between electrons are included using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [13]. In the FL-LAPW method, the cell is divided into two types of regions, the atomic spheres centered at the nuclear sites and the interstitial region between non-overlapping spheres. Inside of the atomic spheres, the wave functions are replaced by atomic functions, whereas in the interstitial region, the function is expanded in plane waves. The charge density and the potentials are expanded in spherical harmonics up to $l_{max} = 10$ inside of the atomic spheres, and the wave function in the interstitial region is expanded in plane waves with a cutoff parameter of $K_{max} = 8/R_{mt}$, where R_{mt} is the smallest radius of the atomic sphere in the unit cell, and K_{max} is the magnitude of the largest *k*-vector of the reciprocal lattice. To ensure convergence in the integration of the first Brillouin zone, 1.600 points were used, which corresponds to 144 *k*-points at the irreducible part of the first Brillouin zone for the wurtzite phase, which obtained with the Monkhorst-Pack method [14]. The integrals over the Brillouin zone are solved using the special approximation of *k*-points of Monkhorst-Pack. For the expansion of the potential in the interstitial region, it is considered that $G_{max} = 12$. The *Muffin-tin* radii were of 1.6 bohr for N, 1.85 bohr for Mn, and 2.0 bohr for Zn. All calculations were carried out with spin polarization, in order to determine the presence of magnetic properties in the compound. The calculation process ended when the forces became smaller than 10^{-4} eV/Å. The convergence threshold for self-consistent field iteration was 10^{-5} eV.

RESULTS AND DISCUSSIONS

Structural properties

Due to the wurtzite structure is the ground state of the ZnO, All the calculation was carry out in the same structure. To reach the $Zn_{0.75}Mn_{0.25}O$ concentration we replaced one Zn atom with a one Mn atom in the supercell of eight atoms. We found that $Zn_{0.75}Mn_{0.25}O$ compound crystalize in the hexagonal structure belonging to space group 156 (*P3m1*) as show in the figure 1. To evaluate the main structural parameters as equilibrium lattice constant and bulk modullus, the calculated values of energy-volume of the binary ZnO compound and the $Zn_{0.75}Mn_{0.25}O$ concentration were fitted to equations state of Murnaghan [15]. Which is defined by equation 1.

$$E(V) = E_0 + \frac{B_0 V}{B_0'}\left[\frac{\left(V_0/V\right)^{B'}}{B_0'-1} + 1\right] - \frac{B_0 V_0}{B_0'-1} \qquad (1)$$

where B_0 is the bulk modulus and its first derivative is B'_0, V_0 is the equilibrium volume of the cell, and E_0 is the binding energy. The lattice constant and bulk modulus are listed in the table 1.

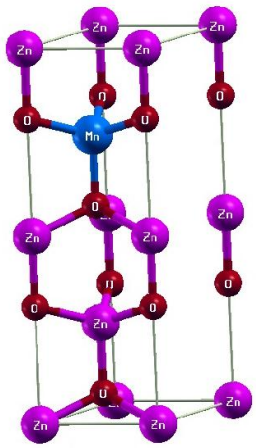

Figure 1. Conventional unit cell for $Zn_{0.25}Mn_{0.75}O$ obtained after relaxation process. Source authors

Table 1. Lattice constant and bulk modullus of the ZnO and $Zn_{0.25}Mn_{0.75}O$ in the wurtzite structure.

Compound	a_0 (Å)	B_0 (GPa)
ZnO	3.260	142.98
	3.283[a]	146.48[d]
	3.246[c]	142.60[d]
$Zn_{0.25}Mn_{0.75}O$	3.322	141.40

[a]ref. [16], [b]ref. [17], [c]ref. [18], [d]ref. [19],

The lattices constant and bulk modullus of ZnO in the wurtzite structure calculated in this work, are compared with experimental and theoretical data available in the literature. The calculated values of lattice constant and bulk modullus were 3.260 Å and 142.98 GPa, respectively. These results agree well with the theoretical reports 3.283 Å [16], 146.48 GPa [17] and are also in good agreement with experimental results 3.246 Å [18] and 142.60 GPa [19], being the maximum discrepancies of ~ 0.7% and ~ 2.4%, respectively. On the other hand, the calculated values of the lattices constant and bulk modullus of $Zn_{0.75}Mn_{0.25}O$ compound was 3.332 Å and 141.40 GPa, respectively. We note that the incorporation of the one Mn atom in the ZnO supercell not change the rigidity of the new compound, because the bulk modulus of the $Zn_{0.75}Mn_{0.25}O$ compound (141.40 GPa) is very close to bulk modullus of ZnO (142.98 GPa). Additionally, the lattice constant of $Zn_{0.75}Mn_{0.25}O$ (3.332 Å) greater than lattice constant of ZnO (3.260 Å). This happen because the unit supercell of the new compound have three Zn atoms while the unit cell of the ZnO have two Zn atoms.

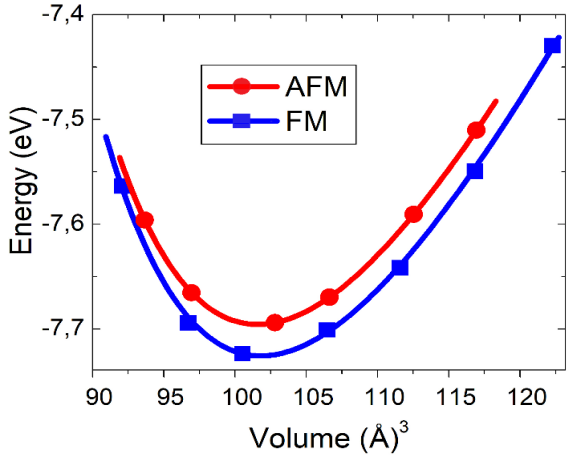

Figure 2. Energy vs volume of the $Zn_{0.75}Mn_{0.25}O$ compound in the ferromagnetic phase FM (blue color) and antiferromagnetic phase (red color). Data calculated are points and adjust is the continues curve. Source authors

In order to investigate the magnetic phase most stable for the $Zn_{0.75}Mn_{0.25}O$ compound, we calculated the variation of the total energy as a function of the volume in the ferromagnetic (FM) and the antiferromagnetic phase (AFM) were fitted to Murnaghan. The results are show in the figure 2. We can see in the figure 2, for the compound the most stable magnetic phase corresponds to the ferromagnetic (FM). The difference of energy between total energy of FM and AFM states, which is defined as ($\Delta E = E_{FM} - E_{AFM}$) is -220 meV. Therefore, the $Zn_{0.75}Mn_{0.25}O$ compound has a ferromagnetic behavior.

Electronic Properties

The band structure and density of states (DOS) were calculated using the equilibrium lattice constant listed in the table 1. The band structure and DOS were calculated along high symmetry path. The band structure of $Zn_{0.75}Mn_{0.25}O$ compound in the wurtzite structure is shows figure 3, we take the Fermi Level as zero of energy. The band structure shows the compound have a half-metallic ferromagnetic character, because around to the Fermi level, the spin up (left) are metallic and spin down (right)

are semiconductors. The spin down has an energy gap of ~ 2.20 eV. The compound have a spin polarization of 100% of the conduction carriers. Therefore, the compound satisfies the first requirement to be a spin injector [20-22]. Hence, the compound is a good candidate for potential application in the spintronic field.

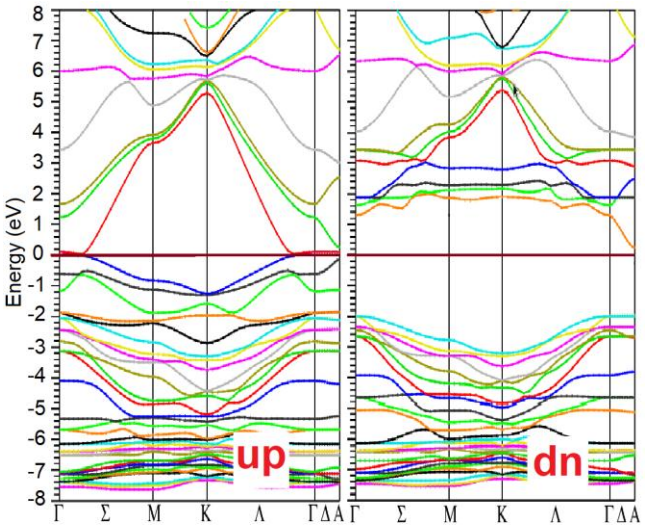

Figure 3. Band structure of $Zn_{0.75}Mn_{0.25}O$ compound in the wurtzite structure. Source: Authors.

The DOS of $Zn_{0.75}Mn_{0.25}O$ compound is ilustrated in the figure 4. The DOS confirm once again that compound have a half-metallic behavor. Because the majority spin (up) are metallic and minority spin (down) are semicontor. We can see that near the Fermi Level the DOS is main contribution come from Mn-3d states and O-2p states in minor contribution, which cross the Fermi level.

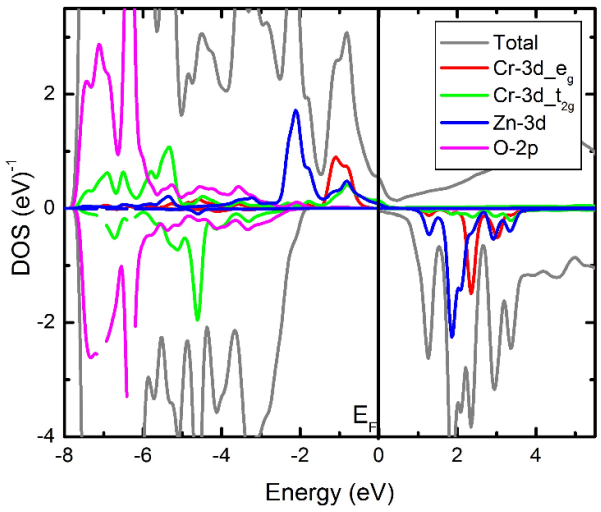

Figure 4. Band structure of $Zn_{0.75}Mn_{0.25}O$ compound in the wurtzite structure. Source: Authors

Additionally, according to the crystal field theory, when a Mn atom replaces a Zn atom, the Mn atom is situated in tetrahedral crystal field formed by the four O ion, as shown in figure 5(a). The tetrahedral symmetry splits the five energy levels of the Mn-3d atom into three high-energy degenerate states, t_{2g} (d_{xy}, $d_{xz,}$ and d_{yz}), and two low-energy degenerate states, e_g(d_{z^2} and $d_{x^2-y^2}$) [23], as shown in figure 5(b). Remembering that electronic configuration of the Mn atom in the $Zn_{0.75}Mn_{0.25}O$ compound, is attributed to the Mn^{2+} [24, 25]. In the figure 5(b) no spins-down are shown because according to the density of states, DOS, (Figure 4), there is no spin-down contribution near Fermi level. The attribution of the Mn^{2+} electronic configuration to the $Zn_{0.75}Mn_{0.25}O$ compound can be understood as follows. The Mn^{2+}atom has five valence electrons {[Ar]$3d^5$}; when Mn occupies the Zn site, it gives off two electrons (staying in the Mn^{2+} configuration). Of the five electrons remaining in the Mn atom, two occupy the doubly degenerate state e_g, and three electrons occupy the triply degenerate state $t_{2g.}$ Therefore, in the $Zn_{0.75}Mn_{0.25}O$ compound, both the majority spin state as well as the minority spin state of the Mn-3d are completely occupied because the doubly degenerate state, e_g, and triply degenerate state, t_{2g}, are completely full. Consequently, 5 valence electrons produce a total magnetic moment of 5 μ_β/atom-Mn. Therefore, the allowed compounds have a half-metallic ferromagnetic behavior.

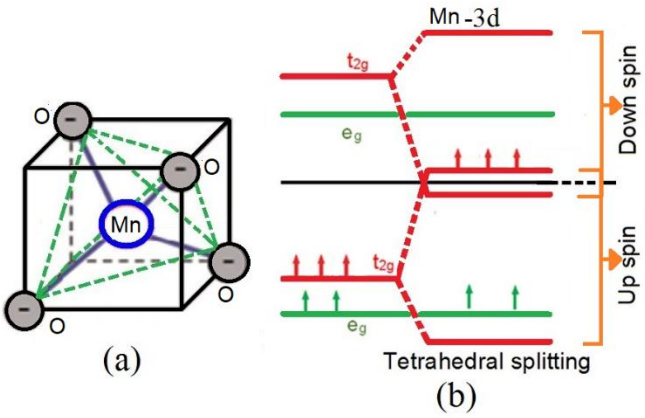

Figure 5. a) Mn atom located in tetrahedral symmetry created by four O atoms, and (b) split between e_g and t_{2g} due to tetrahedral symmetry for both up-spin and down-spin. There is no contribution from the down-spin. Source: Authors

CONCLUSIONS

In summary, in the framework of density functional theory, we performed theoretical studies of the structural, electronic and magnetic properties of the $Zn_{0.75}Mn_{0.25}O$ compound used the pseudopotential method. In the structure wurtzite lattice constant and bulk modullus of the compound are 3.322 Å and 141.40 GPa, respectively. The band structure and density of state study show that compound has a half-metallic ferromagnetic behavior, due to close the Fermi Level spin up are metallic and spin down are semiconductor. The presence of magnetic effects in the compound occur because there are strong polarization and hybridization between Mn-3d and O-2p states.

The magnetic moment of compound is 5.0 μ_β/Mn-atom. due to last property $Zn_{0.75}Mn_{0.25}O$ compound is good candidate for application in the diluted magnetic semiconductor, injector spin and other applications in the spintronics.

ACKNOWLEDGEMENTS

The authors are very grateful to the Investigations center of the Universidad de Córdoba for its financial support.

REFERENCES

[1] S. Limpijumnong, S. Jungthawan, Phys. Rev. B 70 (2004) 054104.

[2] H. Wang, C. Xie, W. Zhang, S. Cai, Z. Yang, Y. Gui, J. Hazard, Mater, 141 (2007) 645.

[3] S. Hong, T. Joo, W. Park, Y. Jun, G.C. Yi, Appl. Phys. Lett. 83 (2003) 4157.

[4] J. Schulz, H. Hohenberg, F. Pflucker, E. Gartnera, T. Willa, S. Pfeiffera, R. Wepf, V. Wendel, H. Gers-Barlag, K.P. Wittern, Adv. Drug Deliv. Rev. 54 Suppl.1 (2002) S157.

[5] J.Q. Xu, Y.P. Chen, Y.D. Li, J.N. Shen, J. Mater. Sci. 40 (2005) 2919.

[6] J. Zhou, N.S. Xu, Z.L. Wang, Adv. Mater. 18 (2006) 2432.

[7] D. Karmakar, S.K. Mandal, R.M. Kadam, P.L. Paulose, A.K. Rajarajan, T.K. Nath, A.K. Das, I. Dasgupta, G.P. Das, Phys. Rev. B 75 (2007) 144404.

[8] H. F.M. Sluiter, Y. Kawazoe, P. Sharma, A. Inoue, A.R. Raju, C. Rout, U.V. Waghmare. First-Principles-Based Design and Experimental Evidence for a ZnO-Based Ferromagnet at Room Temperature. Phys. Rev. Lett. 94 (2005) 187204.

[9] J. Mera, C. Córdoba, J. Doria, A. Gómez, C. Paucar, D. Fuchs, O. Morán, Thin Solid Films 525 (2012) 13.

[10] Hohenberg, P., Kohn, W.: Phys. Rev. B 136, 864 (1964)

[11] Kohn, W., Sham, L.J.: Phys. Rev. A 140, 1133 (1965)

[12] K. Schwarz, P. Blaha, S.B. Trickey, Molecular Physics 108 (2010) 3147.

[13] J. Perdew, K. Burke, M. Ernzerhof, Physical Review Letter 77 (1996) 3865.

[14] H. Monkhorst, J. Pack, Special points for Brillouin-zone integrations, Phys Rev B, 13 (1976) 5188

[15] F.D. Murnaghan, The Compressibility of media under pressure, Proc. Natl. Acad. Sci. U.S.A. 30 (1944) 244–247

[16] X. G. Xu, H.L. Yang, W. Yong, Z. De-Lin, J. Yong, Chin. Phys. B 21 (2012) 047504.

[17] W. López, J. A. Rodríguez, Revista Colombiana de Física 43 (2011) 162.

[18] S.K. Neogi, R. Karmakar, A.K. Misra, A. Banerjee, D. Das, S. Bandyopadhyay, Journal of Magnetism and Magnetic Materials 346 (2013) 130.

[19] S. Desgreniers, Phys. Rev. B 58 (1998) 14102.

[20] H. Heddar, A. Zaoui, M. Ferhat, Superlattices and Microstructures 53 (2013) 16.

[21] C. Vargas-Hernandez, M. Espitia-Rico M, R. Báez, Half-metallic ferromagnetism of $Zn_xMn_{1-x}O$ compounds: A first-principles study, Computational Condensed Matter, 4 (2015)1-5.

[22] Miguel J. Espitia-Rico y John H. Díaz-Forero, Cálculo computacional de las propiedades magnéticas de la superred 1x1-MnO/ZnO. Tecno Lógicas Vol. 19, No. 36, enero-junio de 2016, pp. 41-48

[23] X.Y. Cui, B. Delley, A.J. Freeman, C. Stampfl, Phys. Rev. Lett. 97 (2006) 016402.

[24] B. Hu, B.Y. Man, C. Yang, M. Liu, C.S. Chen, X.G. Gao, S.C. Xu, C.C. Wang, Z.C. Sun, Applied Surface Science 258 (2011) 525.

[25] S. Picozzi, M. Lezaic, New Journal or Physics 10 (2008) 055017.