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1x3-ZnO/MnO multilayer *ab*-initio study

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Abstract

Relaxation structural and spin polarized density band structure calculations using full potential-linearized augmented plane wave (FP-LAPW) method have been performed for study the structural, electronic and magnetic properties of 1x3-ZnO/MnO multilayer. We found that the multilayer have a half-metallic ferromagnetic behavior with a spin polarization of 100% of the conduction carriers and a magnetic moment of 5.0 μ_β/atom-Mn. This half-metallic ferromagnetic character come from the hybridization of the metallic Mn-3d and nonmetallic O-2p orbitals. The multilayer is a good candidate for applications in the diluted magnetic semiconductor field.

Keywords: Density Functional Theory, electronic and magnetic properties, multilayer.

INTRODUCTIÓN

The zinc oxide (ZnO) is a direct bandgap semiconductor that crystalizes in wurtzite structure. Due to its excellent electronic and optoelectronic properties ZnO has been widely studied and has a wide range of technological applications, such as in laser diodes, photocatalysis, transparent conductive electrodes in solar cells, [2], cosmetic products, such as sunscreens [4], optical devices [3], and piezoelectric applications in surface acoustic wave devices [5, 6]. In recent years ferromagnetism at room temperature was recently found by Karmarkar D. et al. [7] in Fe-doped ZnO synthetized by the chemical pyrophoric reaction method. Notably, first-principle calculations based on density functional theory (DFT) [8] predict ferromagnetism at room temperature in Mn-doped ZnO. In addition, Mera J. et al. [9] observed magnetic behavior attributed to Mn in $Zn_{1-x}Mn_xO$ thin films that were epitaxially grown by the pulsed-laser deposition technique. The magnetic properties of ZnO doped with transition metals make it one of the most promising materials for applications in spintronic devices. Devices based on spintronics have several advantages over their conventional electronic counterparts, such as non-volatility, faster data processing speed, low energy consumption and greater integration density [10]. For these reasons, in this paper we investigated the structural, electronic and magnetic properties of the 1x3-ZnO/MnO multilayer due to potential applications in diluted magnetic semiconductors field and other spintronics applications.

COMPUTATIONAL METHOD

The calculations were carry out in the framework density functional theory [10, 11] using the full-potential linearized augmented-plane-wave (FL-LAPW) method, as implemented in the WIEN2k package [12]. The correlation and exchange interaction between electrons are treated 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 multilayer. The equilibrium parameter, such as the lattice constant, the bulk modullus, c/a ratio and, total energy are determinate fitted the calculated data with the Murnaghan equation of state, 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.

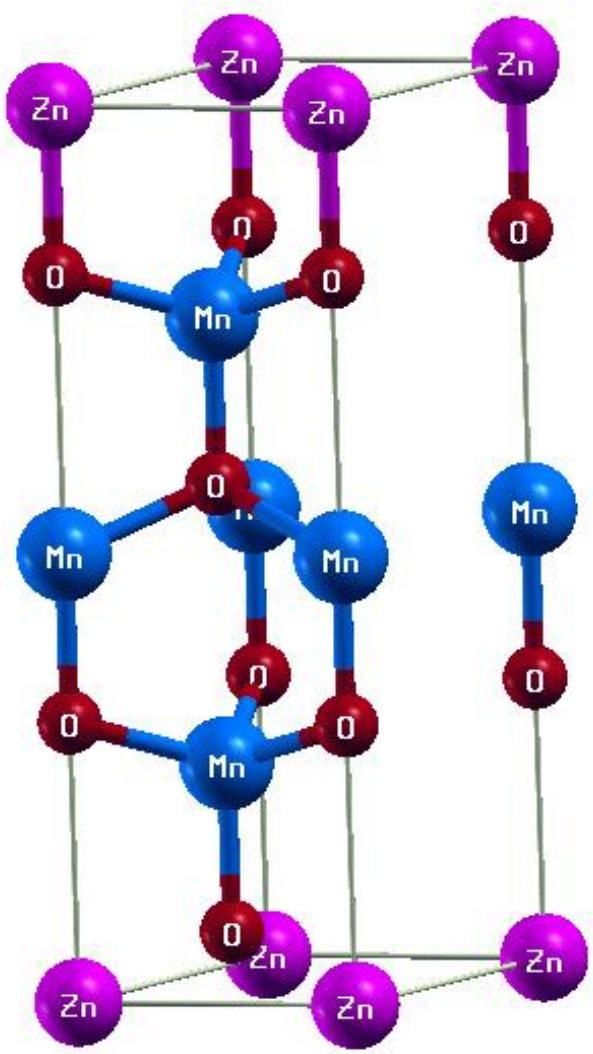

Figure 1. Conventional unit cell for 1x3-ZnO/MnO multilayer in wurtzite structure. Source authors

The 1x3-ZnO/MnO multilayer was modeled in the wurtzite structure intercalating one ZnO layer and three MnO layers in the [0001] direction, as chow in the figure 1. The multilayer was constructed in the wurtzite structure because this is the ground state of the binary ZnO 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

We started presented the results of the structural optimization of the binary ZnO and MnO compounds in wurtzite structure. The main structure parameters were obtained through procedure described in the methodology and using the equation state of Murnaghan, equation 1. For ZnO the calculated values of lattice constant and bulk modullus were 3.267 Å and 142.98 GPa, respectively. These results are very close to those with theoretical reports 3.283 Å [15], 146.48 GPa [16] and are also in good agreement with experimental results 3.246 Å [17] and 142.60 GPa [18]. While the lattice constant and bulk modullus for MnO were 3.29 Å and 112.30 GPa.

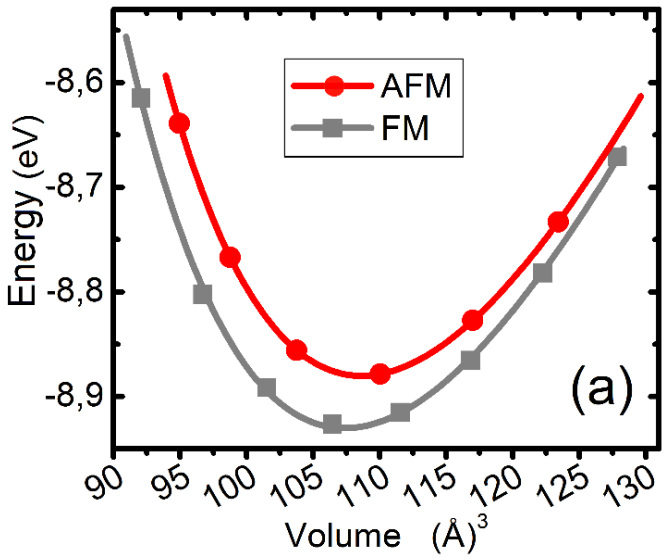

Figure 2. Energy vs volume of the 1x3-ZnO/MnO multilayer in the ferromagnetic phase FM (gray color) and antiferromagnetic phase (red color). Data calculated are points and adjust in the continues curve. Source authors

The calculated values for lattice constant and bulk modullus of 1x3-ZnO/MnO multilayer were 3.393 Å and 121.40 GPa, respectively. Additionally, to determine the most favorable magnetic phase for the multilayer, we calculated the variation of the total energy as a function of the volume in the ferromagnetic (FM) and the antiferromagnetic phase (AFM). The obtained results are show in the figure 2.

We can see in the figure 2, for the multilayer the most favorable 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 -650 meV.

Electronic Properties

The equilibrium lattice constant 3.393 Å was used to calculate the band structure and density states (DOS) along high symmetry points. The figure 3 show the band structure of 1x3-ZnO/MnO multilayer in the wurtzite structure, we take the Fermi Level as zero of energy. The band structure shows the multilayer have a half-metallic ferromagnetic behavior, because near to the Fermi level, the spin up (left) are metallic and spin down (right) are semiconductors. The spin down has an energy gap of 3.70 eV. The multilayer exhibits a spin polarization of 100% of the conduction carriers, which is a requirement of the spin injectors [19-21]. Therefore, the superlattice is a good candidate for potential application in the spintronic field.

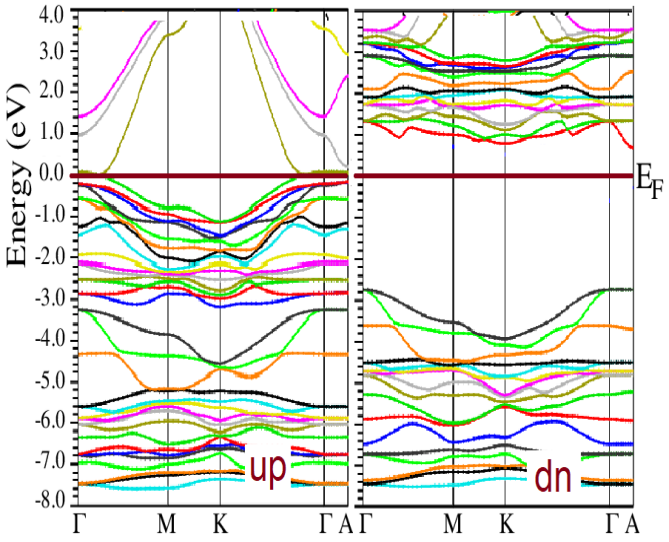

Figure 3. Band structure of 1x3-ZnO/MnO multilayer in the wurtzite structure. Source: Authors.

The figure 4 show the DOS of the multilayer. The DOS prove that multlayer have a half-metallic behavor. Because the majority spin are metallic and minority spin are semicontor. We can see that close the Fermi Level the DOS is mainly dominated by the Mn-3d states and, to a lesser extent, by the O-2p states, which cross the Fermi level.

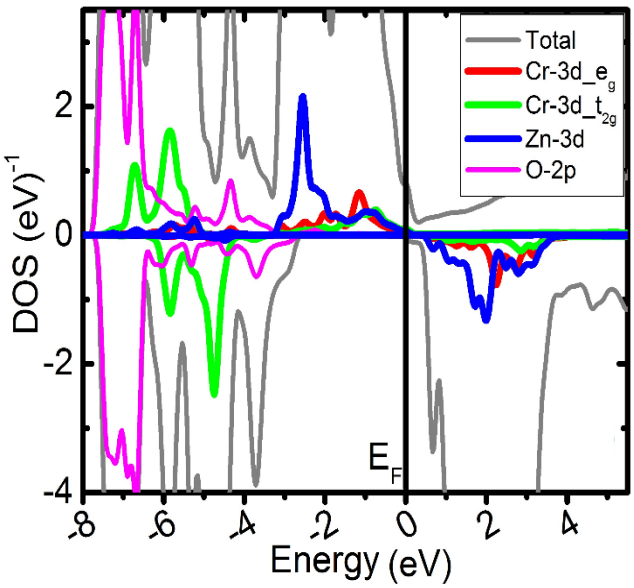

Figure 2. Band structure of 1x3-ZnO/MnO multilayer in the wurtzite structure. Source: Authors

The 1x3-ZnO/MnO multilayer acquire magnetic properties, due to polarization and hybridization of the Mn-3d and O-2p orbitals. With a magnetic moment of 15.0 μ_β/cell. the value of the magnetic moment is integer, this result confirm again that multilayer have half-metallic ferromagnetic behavior.

CONCLUSIONS

In this work, we reported theoretical studies of the structural, electronic and magnetic properties of the 1x3-ZnO/MnO multilayer. We used the density functional theory calculation in the framework of pseudopotential method. In the ground state the lattice constant and bulk modullus of the multilayer are 3.393 Å and 121.40 GPa, respectively. The band structure and density of state analyze reveal that multilayer has a half-metallic ferromagnetic behavior, due to near the Fermi Level spin up are metallic and spin down are semiconductor. The presence of magnetic effects in the multilayer occur because there are strong polarization and hybridization between Mn-3d and O-2p states. The magnetic moment of multilayer is 15.0 μ_β/cell. Due to last property the 1x3-ZnO/MnO multilayer is excellent candidate for application in the diluted magnetic semiconductor, injector spin and other applications in the spintronics.

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