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Structural, Electronic, and Magnetic Properties of $Zn_{1-x}Au_xO$ Compounds: A First-principles Study

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Abstract First-principles calculations were performed in the framework of Density Functional Theory to investigate the structural, electronic, and magnetic properties of the ZnO, $Zn_{0.75}Au_{0.25}O$, $Zn_{0.50}Au_{0.50}O$, and $Zn_{0.25}Au_{0.75}O$ compounds, in a wurtzite-type structure. The Pseudopotential method was used as implemented in the Quantum Espresso code. The structural properties analysis shows that the compounds' lattice constant increases as increasing the Au concentration in the ZnO structure. The electronic density studies show that the $Zn_{1-x}Au_xO$ compounds (x = 0.25, 0.50, and 0.75) have metallic and ferromagnetic behavior with a magnetic moment of 1.10 μβ/cell, 1.12 μβ/cell, and 1.20 μβ/cell, respectively. The metallic-ferromagnetic behavior is mainly due to hybridization between the Au-5d and O-2p states. These compounds are good candidates for optoelectronic applications.

Keywords: *DFT, structural properties, electronic properties, ZnO*

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1. Introduction

The semiconductor ZnO has been widely studied in experimental and theoretical approaches because of its attractive electronic and optoelectronic properties [1]. The ZnO semiconductor has a direct bandgap localized at the Γ point, which under normal conditions, crystalizes in a hexagonal wurtzite-type structure [2]. ZnO's electronic and optoelectronic properties can be used in wide-ranging applications [3,4], such as photovoltaic diveces [5], in the cosmetic industry by producing sunscreen [6], OLEDs [7,8], perovskite solar cells[9], or photocatalysis [10,11].

The ZnO semiconductor and ZnO doped with different atoms have been widely studied. For example, J. Huang et al. [12] observed enhanced gas sensing properties of ZnO sensors attributed to Au in 2.0 wt% Au-doped ZnO nanorods synthesized via a one-step microwave-assisted hydrothermal method. Fe-doped ZnO experimental approach has also shown room-temperature ferromagnetic properties in the compound [13]. Theoretical studies based on Density Functional Theory (DFT) predict room temperature ferromagnetism in Mo and Co-doped ZnO [14]. Additionally, $Zn_{1-x}Mn_xO$ thin films grown by pulsed Laser technique were found to possess magnetic properties [15].

Recently, Ag-doped ZnO theoretical studies have shown that Ag atoms are energetically more favorable to occupying Zn positions [16]. Further studies have shown that when Ag atoms occupy the Zn positions, Ag performs as an acceptor, but as Ag is localized in the interstitial site acquires a donor's behavior [17,18]. These results have increased the potential ZnO applications in semiconductor materials.

However, in Light-Emitting Devices or sensor process applications, ZnO still has an extensive theoretical range to be studied, e,g. tuning the ZnO physical properties via doping Au atoms. Therefore, novel first-principles calculations based on DFT are explored in the current report, studying the structural, electronic, and magnetic properties of $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds.

2. Computational Methods

The calculations are performed within the DFT [19,20] framework using the pseudopotential method [21] implemented in the Quantum-Espresso package [22,23]. The correlation and exchange effects of the electrons are treated using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [24]. The Kohn-Sham orbitals were expanded into plane waves with a kinetic-energy cutoff of 40 Ry. A kinetic energy cutoff of 400 Ry was used for the charge density. The supercell model was implemented to model ZnO and $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds in a wurtzite

structure. An Au atom occupied the Zn atomic position in a supercell of 8 and 4 for 0.25 and 0.50 Au atomic concentrations, respectively. For 0.75 Au concentration, three Zn atoms were substituted by three Au atoms in a wurtzite supercell of 8 atoms. The integrals over the Brillouin zone were performed using 8x8x6 mesh points selected by the Monkhorst-Pack scheme [25]. The possible magnetic effects of Au on the ZnO structure were computed by considering polarized spin. Finally, the calculations were executed in ve-relax mode, simultaneously optimizing the atomic positions and the supercell's lattice constant. The energy, forces, and pressure convergence criteria were fixed at 1 meV/atom, 1 meV/ Å , and 0.2 kbar, respectively.

3. Results and Discussions

This section presents the calculations' structural and electronic properties results for the binary ZnO compound in the wurtzite structure and the $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds. A detailed analysis of increasing Au concentration effects in the ZnO structure over structural and electronic properties of ZnO is shown.

3.1. Structural Properties

Firstly, ZnO atomic positions were optimized in the wurtzite structure to confirm the calculation method accuracy employed in this research. Upon completing the structural relaxation process, the Lattice constant and bulk modulus (Table 1) results show an excellent correlation with previously theoretical [26,27,28] and experimental [29,30] results reported. The maximum discrepancy is ~ 1.22% for the Lattice constant, which ensures our calculations' reliability. Table 1 shows the structural parameters of the $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds obtained after optimization.

Table 1 shows the main $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds structural parameters obtained after the structural optimization process. The results show that the constant lattice increases as Au concentration atoms increase in the ZnO structure. This occurs because Au's atomic radius (1.44 Å) is larger than the atomic radius of Zn (1.38 A). However, the bulk modulus (related to the material's stiffness) decreases as increasing Au concentration atoms. Further, as the Au concentration atoms increases, the ground state energy decreases, suggesting energetically less stability for $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds in the wurtzite structure. This energetic behavior is due to the Au concentration atoms increase that induces AuO transition for Au, which occurs in the face-centered cubic structure Au2O and Au2O3 arrangements [31]. The $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds' magnetic phase was computed to estimate the ground state energy in the ferromagnetic (FM) and antiferromagnetic (AFM) phases. Several configurations with different spin orientations were calculated for the AFM phase, and the lowest energy configuration was selected. The energy subtraction (ΔE) between FM and AFM phases (ΔE = EFM - EAFM) for the $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds were estimated in -0.45 meV, -0.51 meV, and 0.66 meV, respectively. These results indicate more energy stability for the FM state than the AFM state.

Table 1. Structural parameters. (a) Theoretical GGA [26], (b) Theoretical GGA [27], (c) Theoretical GGA [28], (d) Experimental [29], (e) Experimental [30]

Compound	a_0 (Å)	B_0 (GPa)	E_{0FM} (eV)	E_{0AFM} (eV)
ZnO	3,2857	127,298	-2157,219	-2157,219
	3,260[a]	130,00[a]	-	-
	3,283[b]	146,48[c]	-	-
	3,246[d]	142,60[e]	-	-
$Zn_{0.75}Au_{0.25}O$	3,3080	125,325	-1953,694	-1953,694
$Zn_{0.50}Au_{0.50}O$	3,3136	120,860	-1750,183	-1750,183
$Zn_{0.25}Au_{0.75}O$	3,5674	116,235	-1547,031	-1547,031

3.2. Electronic Properties

The electronic properties of ZnO and $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) were studied by band structure (BS) and density of states (DOS) calculations, and the Fermi level was selected as the zero energy in all cases. The BS and DOS results are shown in Figure 1 and Figure 2, respectively. The ZnO BS indicates semiconductor behavior for ZnO, with a 0.98 eV direct band gap located in the Γ point, as shown in Figure 1(a). The ZnO semiconductor behavior results are consistent with theoretical results previously reported [32,33,34,35]. Additionally, ZnO's states spin-up and spin-down obtained are symmetric, as BS indicates (Figure 1(a)), which is a result of the ZnO not-magnetism condition in the wurtzite structure. The Au-doped ZnO effect is shown in Figure 1(b), 1(c), and 1(d).

Figure 1(b) shows the BS of the $Zn_{0.75}Au_{0.25}O$ compound. The incorporation of Au atoms in the ZnO structure, at $Zn_{0.75}Au_{0.25}O$ percentage, indicated a loss of the semiconductor behavior for the ZnO structure. Hence, incorporating an Au atom induces magnetic effects in the compound, and the ferromagnetic phase is shown as the most energetically favorable.

The compound $Zn_{0.75}Au_{0.25}O$ had a magnetic moment of 1.10 μβ/cell. The $Zn_{0.50}Au_{0.50}O$ composite BS indicates a metallic behavior (Figure 1(c)). The $Zn_{0.50}Au_{0.50}O$ composite acquires a ferromagnetic behavior due to the inclusion of Au, with a magnetic moment of 1.12 μβ/cell. Figure 1(d) shows the BS of the compound $Zn_{0.25}Au_{0.75}O$. The compound has a metallic behavior because spin-up and down states pass across the Fermi level. The compound possesses ferromagnetic behavior, with a magnetic moment of 1.20 μβ/cell.

Figure 2 shows the total density of states (DOS) and the orbitals that contribute most to the electronic behavior of ZnO and $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds. Figure 2(a)'s left panel shows the DOS of ZnO, and Figure 2(a)'s right shows a DOS zoom near the Fermi level. The DOS confirms the semiconducting behavior of ZnO. In the valence band, there are two regions. The Zn-3d states dominate the low-energy region between -6 eV and -4 eV, and the O-2p states mainly govern the high-energy region between -2 eV and the Fermi level. At the same time, in the conduction band, the main contribution comes from the Zn-4s orbitals. These results agree with the research based on ZnO properties using the Heyd-Scuseria-Ernzerhof screened hybrid density functional reported by Wróbel et al. [36].

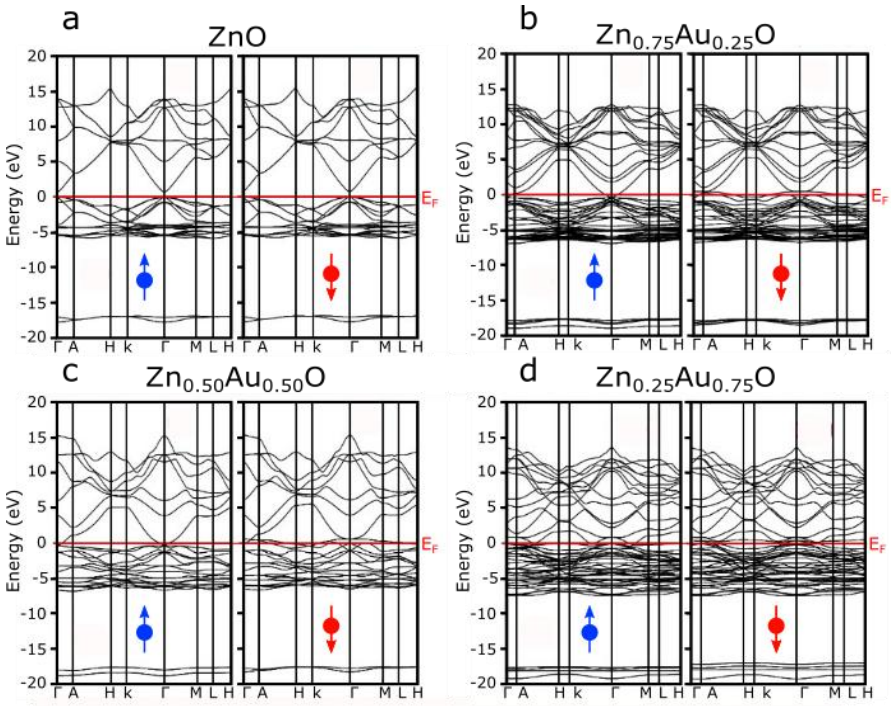

Figure 1. Band structure: (a) ZnO, (b) $Zn_{0.75}Au_{0.25}O$, (c) $Zn_{0.05}Au_{0.50}O$, and (d) $Zn_{0.25}Au_{0.75}O$

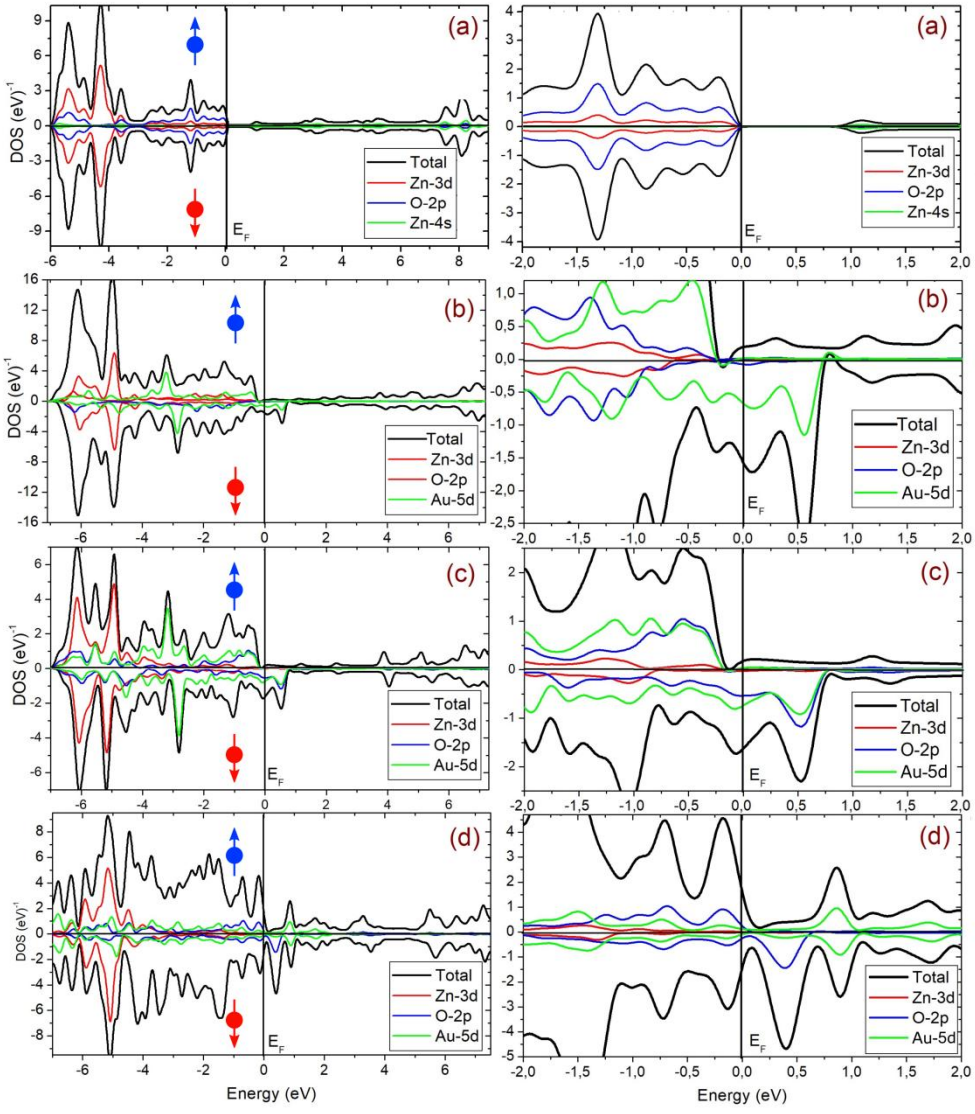

Figure 2. DOS (a) ZnO, (b) $Zn_{0.75}Au_{0.25}O$, (c) $Zn_{0.50}Au_{0.50}O$ and (d) $Zn_{0.25}Au_{0.75}O$

Figure 2 (b, c, and d) on the left panel show the DOS of the $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) components, respectively. Figures 2(b,c, and d) on the right panel shows a DOS zoom near the Fermi level. The DOS results confirm the metallic character of the $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) compounds. The metallic character is associated with the Zn-3d, O-2p, and Au-5d states which cross the Fermi level (Figures 2(b,c, and d)). The magnetic properties of the compounds are generated primarily due to the hybridization between the Au-5d and O2p states. A similar result was obtained in theoretical work on Ag-doped ZnO, where the main contribution to the electronic and magnetic properties comes from the hybridization between the Ag-4d and O-2p states [37].

4. Conclusions

In summary, in the results, first-principles calculations were performed to study the effects of incorporating Au into the ZnO structure over the structural, electronic, and magnetic properties of the allowed compounds $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75). The results demonstrated that as the concentration of Au atoms increases, the lattice constant of the compounds increases, and in contrast, the ground state energy of the compounds decreases as the Au concentration increases. Additionally, the results demonstrated that due to the incorporation of Au into the ZnO structure, the $Zn_{1-x}Au_xO$ (x = 0.25, 0.50, and 0.75) composites possess metallic and ferromagnetic behavior, with magnetic moments of 1.10 μβ/cell, 1.12 μβ/cell and 1.20 μβ/cell, respectively, which mainly are generated by the hybridization between the Au-5d and O-2p states.

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