

Density functional theory calculation of monolayer WTe₂ transition metal dichalcogenides doped with H, Li and Be

E. Igumbor^{a,b,*}, R. E. Mapasha^a, W. E. Meyer^a

^a*Department of Physics, University of Pretoria, Pretoria 0002, South Africa.*

^b*Department of Mathematics and Physical Sciences, Samuel Adegboyega University, Km 1 Ogwa-Ehor Rd, Ogwa Edo State Nigeria.*

Abstract

Results based on density functional theory modelling of electronic and structural properties of single layer WTe₂ dichalcogenides doped with X (X= H, Li and Be) were presented. The generalized gradient approximation functional of Perdew, Burke, and Ernzerhof exchange correlation was used for all calculations. Formation energies of X dopant substituted for W (X_W) were obtained to be between 3.59 and 2.61 eV. The Li_W defect with energy of formation of 2.14 eV was energetically the most favourable. For all dopants considered, while the H_W induced no magnetic moment, the Li_W and Be_W induced magnetic moments of 3.44 and 0.05 μ_B , respectively. The band gap of the WTe₂ as a result of the dopants was populated with several orbital ground states, and thus reduced within a few eV. While all X_W were spin polarised and behave as *p*-type dopant, the Li_W defect posses half metallic character.

Keywords: Electronic structure, dopant, formation energy

*Corresponding author

Email address: elgumuk@gmail.com (E. Igumbor)

1. Introduction

Reports have shown that two-dimensional (2D) transition metal dichalcogenides (TMDs) materials are being considered for next generation nanoelectronic device because they are easy to fabricate [?], they have strong light-matter interactions and good optoelectronic response of their field-effect-transistors [?]. Recent reports shown that 2D single, bi and multi layer TMD materials have been successfully synthesized experimentally [? ? ? ?]. Several important properties of 2D TMDs have been predicted either by experimental techniques or theoretical methods [? ? ?]. The electronic and magnetic properties of H, B and C doping of MSe₂, MTe₂ and WS₂ have been reported by Ma *et al* [?]. The single layer MSe₂ and MTe₂ can be efficiently dispersed in common solvent to form a film, so that these materials can be exfoliated into monolayers. In the single layer limit, the indirect band gap of MSe₂ and MTe₂ when doped with non-metals exhibits a direct band gap. Ma *et al* [?] have shown that non-metal vacancies induce spin polarisation in MSe₂. The band gaps of TMDs are known to be affected by impurities, for example, the stable 2H-MoS₂ was predicted to be a semiconductor while the 1T-MoS₂ was predicted to be metallic [? ? ? ?]. In addition to the semi metal nature of WTe₂ [?], it has been previously investigated for the purpose of thermoelectric applications. Notable for its additional structural distortion [?] among the TMDs is WTe₂, which is a binary compound and belongs to a material family that can be tuned by intrinsic or extrinsic doping. According to the report of Augustin *et al* [?], WTe₂ has a highly anisotropic electronic structure, with small pockets of holes and electrons. This unique

property gives WTe_2 an advantage over other TMDs. The structural, electronic, magnetic or optical properties of TMDs such as MSe_2 , WTe_2 , WSe_2 , WS_2 and MTe_2 doped with several materials have been experimentally or theoretically reported [? ? ? ? ? ? ? ?]. However, no prediction of the structural, electronic properties or the energy of formation of the H, Li and Be doping of single layer WTe_2 TMDs have been reported. In this report, density functional theory (DFT) and the generalised gradient approximation (GGA) exchange correlation functional have been used to model and predict the structural, electronic and magnetic properties of X (X= H, Be, Li) doping of single layer WTe_2 TMDs. In addition, the total valence charge transfer and the formation energy of the X_{W} were also predicted. The half metallic and spin non-equilibrium character of dopants in WTe_2 were explored.

2. Computational details

Results presented in this report were obtained using DFT as implemented in the Vienna Ab-initio Simulation Package (VASP) [?] within MedeA. The core electrons were separated from the active valence electrons by using the Projector-augmented wave (PAW) method [? ?]. All calculations were performed using the generalized gradient approximation (GGA) functional of Perdew, Burke and Ernzerhof (PBE) [?]. Reports have shown that for 2D TMDs, the GGA is sufficient to accurately predict their electronic, magnetic and optical properties[? ? ? ?]. For this study, the WTe_2 was modelled by a $5 \times 5 \times 1$ unit cell which contains 75 atoms and the energy cut-off was set to 400 eV, which was sufficient for all calculations. In order to avoid any artificial interactions between neighbouring images, the distance between

two adjacent layer was at least 15 Å. The Brillouin zone integrations were sampled by a $2 \times 2 \times 1$ Monkhorst-Pack [?]. Structural relaxation was performed until the Hellmann-Feynman forces on each atom were less than 0.01 eV/Å. The stability of the X_W was predicted by obtaining the energy of formation using Eq. 1.

$$E_{(form)} = E_{(doped)} - E_{(pure)} + n\mu_{(potential)}, \quad (1)$$

where, $E_{(doped)}$ and $E_{(pure)}$ terms are the total energies of the supercell with and without dopant, respectively. The n is the number of atom for when W atom is replaced by the dopant, and $\mu_{(potential)} = \mu_{(host\ atoms)} - \mu_{(dopant)}$ is the difference in chemical potential. The $\mu_{(potential)}$ depends on the material growth and it satisfy the boundary condition. The $\mu_{(potential)}$ is defined within the range of values which corresponds to W-rich and Te-rich conditions. The chemical potential of H, Li, Be, W and Te was calculated using the method of refs. [? ?].

3. Results and Discussion

3.1. Structural properties

Figs. 1a to 1d display the fully relaxed geometric structures of single layer pristine and doped WTe_2 dichalcogenides. The monolayer WTe_2 has a honeycomb structure as shown in Fig. 1. A tungsten atom in WTe_2 is sandwiched between two Te atoms. For the pristine supercell, the bond distances between W–W atoms and W–Te (for the nearest neighbour Te atom) atoms after structural relaxation were 3.51 and 2.73 Å, respectively. These results are consistent with 3.51 Å (W–W nearest neighbour) and 2.72 Å (W–Te

nearest neighbour) theoretical reports [? ?]. The relaxed bond angle 80.27° formed by the W–Te–W atoms is consistent with an earlier report [?]. When the dopants were at the W atomic position (X_W), the bond distances between H, Be, Li and nearest W (Te) after structural relaxation were 3.46 (3.34), 3.66 (2.78), and 3.83 (2.57) Å, respectively. When an atom undergoes stress which raises the internal energy, the whole system experiences strain. This strain is usually caused by the distortion of bond lengths and bond angles from the ideal values. As expected, due to the small size of H atom compare to Te or W atom, the bond length of H–Te after structural relaxation was 22.00% larger than that of the W–Te. While for the case of Be doped WTe_2 , the bond length of Be–Te after relaxation was 5.86% larger than that of the W–Te. However, for the Li doped single layer WTe_2 , the bond length of Li–Te after structural relaxation was 1.83% larger than that of the W–Te. Based on this, we expect the hydrogen doped single layer WTe_2 to induced more strain in the system than Li or Be doped single layer WTe_2 . Considering H, Li, or Be doped monolayer WTe_2 , the atomic bond lengths of H with the host atoms experienced more strain than that of Be or Li with the host atoms. This could play a vital role in predicting the stability (using the formation energy) of the doped system.

3.2. *Electronic properties*

Plots of the band structures of X_W are displayed in Fig.2. The dotted red line represents the Fermi level. Except for the states introduced in the band gap of WTe_2 by the dopants, the H_W and Li_W reduced the band gap by 0.14 and 0.10 eV, respectively. However the Be_W increased the band gap of the WTe_2 by 0.02 eV. Compared to the pristine WTe_2 , dopants introduced im-

purity bands inside the band gap as shown by Fig.2. The introduction of the dopants H, Li and Be splitted the band gap of single layer WTe₂ with several states located at the Fermi level. Impurity bands close to the valence band maximum (VBM) or conduction band minimum (CBM) indicate *p*-type or *n*-type doping, respectively. When H, Li and Be were substituted for W, the impurity bands introduced in the band gap were close to the VBM. We therefore concluded that when dopants were substituted for W the entire system behaves as *p*-type material. This suggests that effective doping of WTe₂ with H, Be or Li could be promising for *p*-type semiconductor band gap engineering.

The plots of the total density of states (TDOS) for X_W are displayed in Fig. 3. The Fermi level of the total density of states is put at zero eV. The dopant H, Li and Be introduced orbital ground states in the band gap of WTe₂. For the H_W as displayed in Fig. 3b, the orbital ground states introduced in the band gap were situated at the Fermi level. The orbital ground states occupy about 0.14 eV of the band gap above the VBM. These states were mainly contributed by the 5*p* and 5*d* orbitals of Te and W, respectively. In addition, orbital hybridization between the 1*s* of H, 5*s* of Te and 6*s* of W were observed. The *d* orbital of the W atom strongly contributed to the orbital ground states in the band gap of WTe₂. For Li_W as displayed in Fig. 3c, the dopant introduced orbital ground states in the band gap of WTe₂ which were located above the VBM. These orbital ground states occupy about 0.44 eV of the band gap up to above the Fermi level from the VBM. The 5*p* and 5*d* orbitals of Te and W atoms, respectively, were the major contributors to the states in the band gap. Another interesting behaviour

observed was the spin dependency of the Li_W system. In a system where the ground states orbital induce orbital states in the band gap, a system is half metallic if one of the spin (the spin-up or majority-spin) is metallic, whereas the Fermi level falls into a gap of the other spin (spin-down or the minority-spin). This is also supported by a situation where a system exhibits properties of metals as well as insulators at the same time depending on the spin direction. For the Li_W system, the spin-up and spin-down were shown to be asymmetric, suggesting half metallic character. Based on this, the Li_W could be a useful material for spintronics application. For the case of Be_W as shown in Fig. 3d, the orbital ground states introduced in the band gap were above the Fermi level from the VBM. These orbital ground states occupied at least about 0.19 eV of the band gap. Orbital hybridization was observed for the Be_W system with contributions from the s , p and d orbitals of Be, Te and W atoms, respectively. In the case of the X_W except for Li (see Fig. 3c), Be and H, did not show any sign of spin polarisation since the spin-up and spin-down were symmetrical.

3.3. Formation energy, magnetic and charge transfer properties

To ascertain the stability of WTe_2 doped with H, Li and Be, the formation energies of the doped systems were calculated. The predicted formation energies of WTe_2 doped with H, Li and Be are listed in Table 1. The formation energy of Li_W is the lowest with energy of 2.14 eV. While the formation energy of the Be_W is lower than that of the H_W , the Li_W under equilibrium conditions is energetically the most favourable. This suggests that the dopant Li is more stable when substituted in WTe_2 than Be and H. The different amount of formation energy for the H_W , Li_W , and Be_W could be attributed

to the amount of the inward strain experienced by the systems along the xy plane. The amount of the induced inward strain experienced by the whole system is attributed to the smaller radii of the dopants compared to that of W. This is also supported by the slightly prolonged X–Te compared to the W–Te bond length.

In order to predict the nature of magnetic properties exhibited by WTe_2 when doped with H, Li and Be, the magnetic moment was calculated. The H_W and Li_W induced magnetic moment of less than $1 \mu_\text{B}$, and the Be_W induced a magnetic moment of $3.45 \mu_\text{B}$ (see Table 1). The total valence charge transfer from the dopants to the single layer WTe_2 was obtained. The total valence charge transferred by H, Li and Be when substituted for W atom were -0.18 , 0.85 and $1.30 e$, respectively. The nature of the valence charge transfer is supported by the fact that the hydrogen atom as a non–metal accepts a charge or form a covalent bond, whereas Li and Be donate a charge through ionic transfer.

4. Summary

Results of DFT modelling of structural, electronic, magnetic and charge transfer process of X (X=H, Li, Be) doping of single layer WTe_2 2D TMDs have been presented. Amongst the dopant, the Li doping of WTe_2 is energetically the most favourable with a formation energy of 2.14 eV . The band gap of the WTe_2 was populated by s , p and d –orbital ground states as contributed by both the host and dopant atoms. The dopants H, Li and Be splitted the band gap of the single layer WTe_2 with several states located at the Fermi level. The substitution of H, Li and Be in WTe_2 behaves as

p-type dopant. The Be_W induced a higher magnetic moment of 3.45 μ_B that is higher than that of the Li_W. While the Li_W exhibits half metallic character, it also shows a tendency for a promising materials for spintronics application.

5. Acknowledgement

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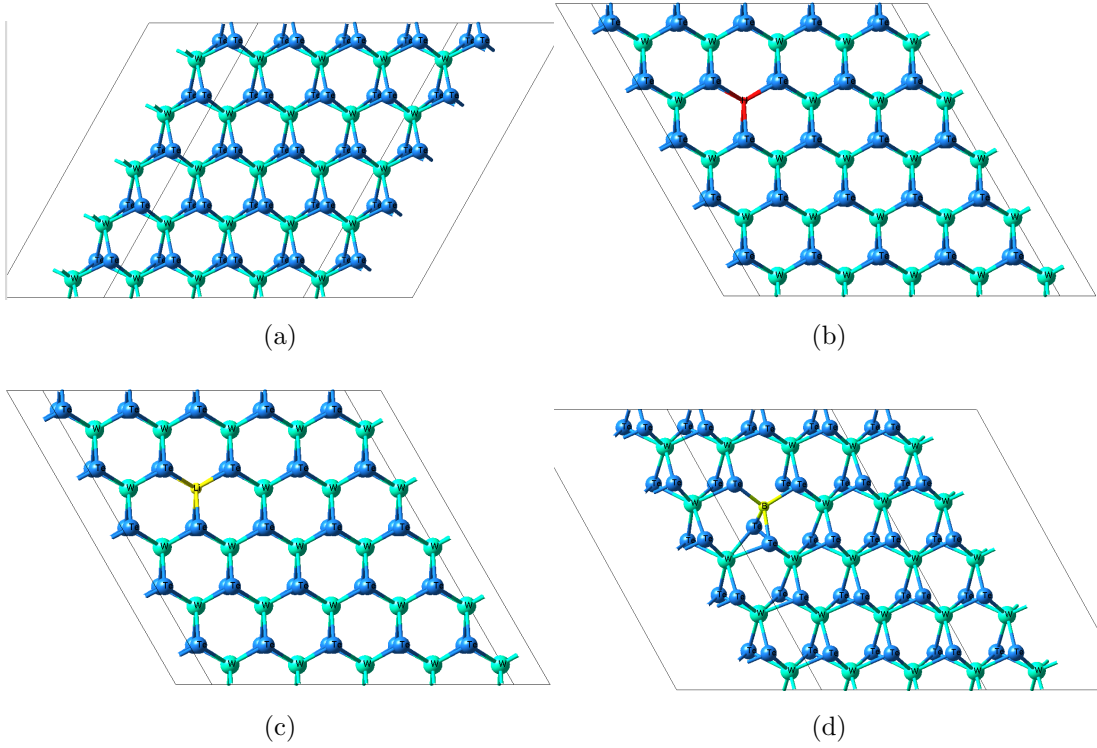


Figure 1: Fully relaxed geometric structures of single layer pristine and doped WTe_2 dichalcogenides: (a) pristine; (b) with H impurity at the W site; (c) with Li impurity at the W site and (d) with Be impurity at the W site.

Figure 2: Plots of band structures for the pristine WTe_2 , H doped WTe_2 , Li doped WTe_2 and Be doped WTe_2 . The dotted red line represents the Fermi level which at 0 eV and the blue lines in the band gap represent the states induced as a result of the dopant.

Table 1: The energy of formation $E_{(form)}$ (eV) and magnetic moment μ_B of the WTe_2 doped with H, Be and Li.

Pristine	Doped system	$E_{(form)}$	μ_B
WTe_2	H_W	3.59	0.00
	Li_W	2.14	3.44
	Be_W	2.61	0.05

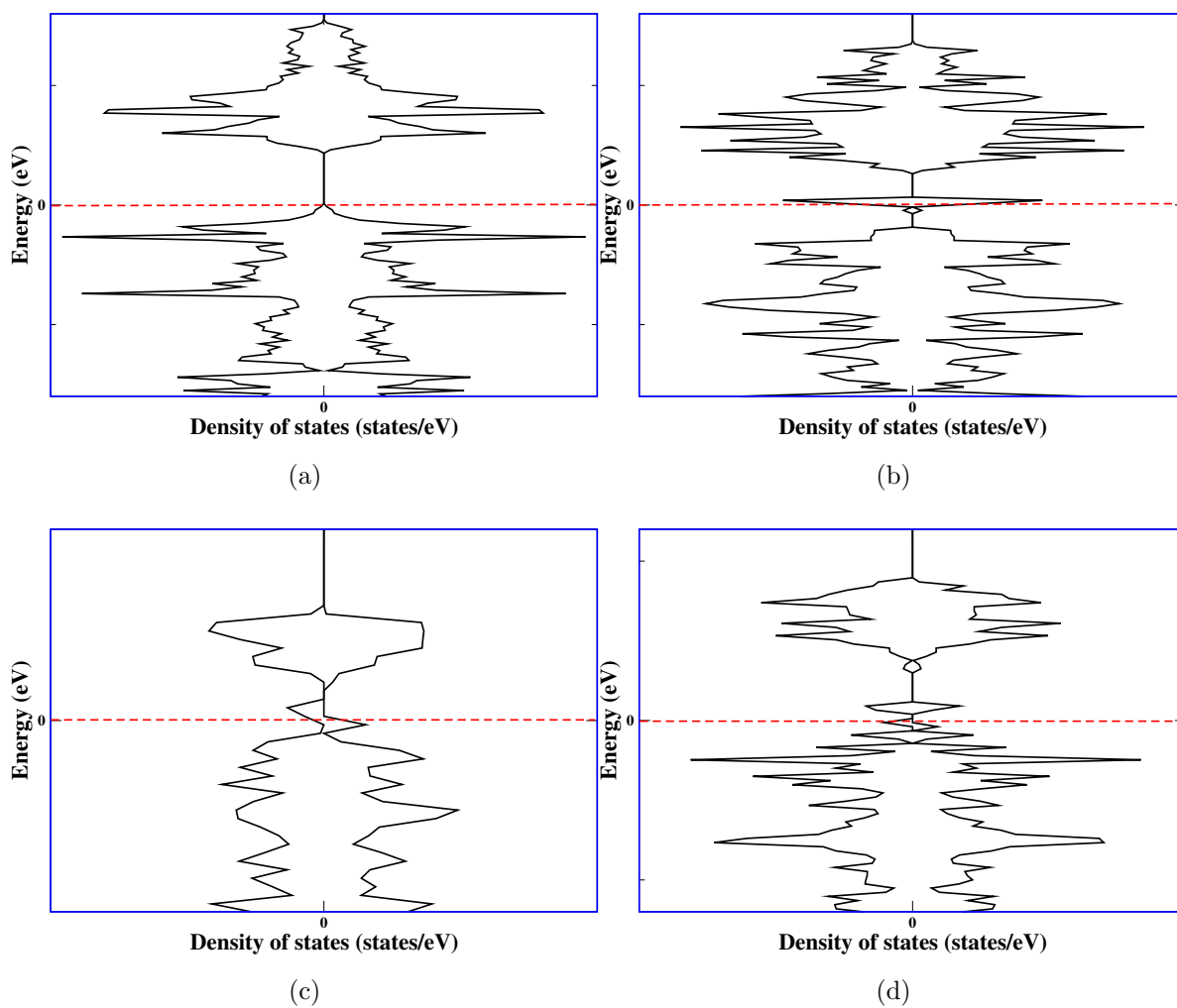


Figure 3: Total density of states for (a) pristine WTe₂ (b) H_W, (c) Li_W (d) Be_W. The red dash line is the Fermi level which is at 0 eV.