Iron doped MSe_2 Monolayers (M=Mo, W): A First-Principles Study of Structural, Electronic, and Magnetic Properties

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Abstract

In this study, we examined the effects of iron doping on the electronic and magnetic properties of transition metal dichalcogenide (TMD) monolayers, specifically $MoSe_2$ and WSe_2, utilizing density functional theory (DFT). Our results demonstrate that strategic doping significantly alters the material properties. Structural analysis reveals that doped systems largely retain the original structure of MSe_2ML (Mo, W), despite exhibiting minor lattice distortions. Total energy calculations indicate that these structures remain stable. The doping of Fe induces significant spin polarization in both $MoSe_2$ML and WSe_2ML. The spin-down and spin-up channels exhibit distinct band gaps: 1.09 eV (D) and 0.24 eV (I) for $MoSe_2$ML, and 1.0 eV (D) and 0.27 eV (D) for WSe_2ML, respectively. Iron doping also induces magnetization in these TMDs. Additionally, the introduction of spin polarization shows that neighbouring atoms around the impurity exhibit slight magnetization due to the localized effects of the dopant. The net magnetic moment for both $MoSe_2$ML and WSe_2ML with iron impurities is approximately 2 μB. The computer simulations enable precise doping which leads to improved and tunable properties of TMDs. Future development in electronics, spintronics and quantum computing are facilitated by the potential expansion of doped TMDs.

Keywords: Doping, Magnetization, Localized effect, Spintronics.
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Introduction

Doping is widely recognized as an effective strategy for enhancing the performance and efficiency of transition metal dichalcogenides (TMDs). A significant body of research has focused on the impact of defects and dopants on the structural, electronic, magnetic, and thermal properties of two-dimensional (2D) materials, demonstrating considerable modifications in these properties [1-5]. TMDs are a varied group of 2D materials, distinguished by their ultra-thin monolayers that feature a transition metal atom positioned between two layers of chalcogen atoms. Transition metal Diselenide have recently attracted considerable interest due to their exceptional properties, which include a direct bandgap, high electron mobility, and excellent chemical stability. Monolayers of MSe_2 specifically display an atomic tri-layer configuration (Se–M–Se, where M = Mo or W) and possess a direct bandgap of around 1-2 eV, rendering them highly suitable for a range of optoelectronic applications. However, there is a dearth of studies on the effect of doping of transition metals like Sc, Ti, V, Cr and Mn in different 2D monolayers. Min Leo studied the electronic and magnetic properties of nickel doped WS2 monolayers [6]. Carmen C. studied the effect of the Li ion donor (Me-Li, *n*-Bu-Li and *t*-Bu-Li) during chemical exfoliation of four different TMDs compounds (MoS_2, $MoSe_2$, WS_2 and WSe_2) in terms of their capacitance is evaluated [7]. Transition Metal Substitution Doping in Synthetic Atomically-Thin Semiconductors was explored by Jian Gao in which they reveal the effect of Nb on WS_2 monolayers [8]. Several theoretical ab initio studies have predicted a rich array of electronic behaviours in transition metal doped systems due to electron occupation of the metal d-orbitals which includes charge doping and magnetic behaviour [8-10]. These monolayers can be synthesized using techniques such as chemical vapor

deposition [11-13]. However, despite their remarkable electronic properties, pristine MSe_2 is intrinsically nonmagnetic. As a result, developing effective methods to induce and manipulate magnetism in MSe_2 monolayers has become a key area of research, particularly for their potential use in spintronic devices, where spin-polarized charge carriers are essential for enhancing functionality [13-16]. The iron doped TMCs can be used potential electrode material for supercapacitor applications and improve energy storage capacity [18]. The emphasis of this paper is to study the electronic and magnetic properties of Iron doped $MoSe_2$ and WSe_2 MLs(monolayers).

Computational Details

The calculations were performed using the SIESTA simulation package, which utilizes density functional theory (DFT) to solve the electronic structure of materials. The exchange-correlation interactions are taken care using the Generalized Gradient Approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. For basis sets, the double zeta plus polarization (DZP) method is employed with a confinement energy of 20 eV and a mesh cutoff of 300 Ry. Structural optimization is conducted using the Conjugate Gradient (CG) method with a convergence criterion of 0.01 eV/Å. The Brillouin zone is sampled using a 3×3×1 k-point mesh, based on the Monkhorst-Pack scheme.

Results and Discussion

The $MoSe_2$ and WSe_2 monolayers are designed as 6×6 supercells containing 108 atoms (36 metal atoms and 72 chalcogen atoms). In each case, one metal atom (Mo or W) is replaced by an iron atom, and optimized these structures which show that doping with Fe results slight lattice distortions near the impurity site.

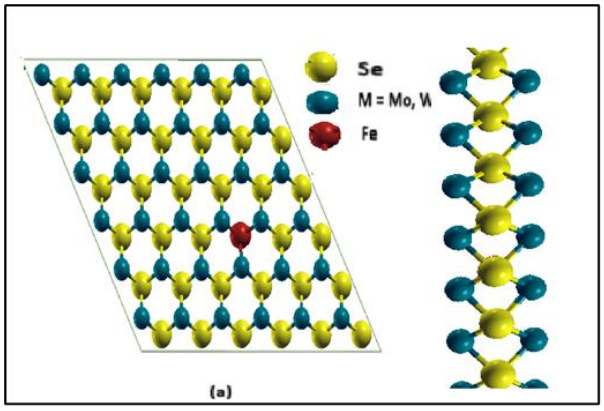

Figure 1: Optimized geometric structures of (a) MSe_2 ML (front view) and (b) side view.

The overall geometry of the monolayers is maintained, with the lattice constants for pristine $MoSe_2$ and WSe_2 optimized to 3.289 Å and 3.345 Å respectively. These values are

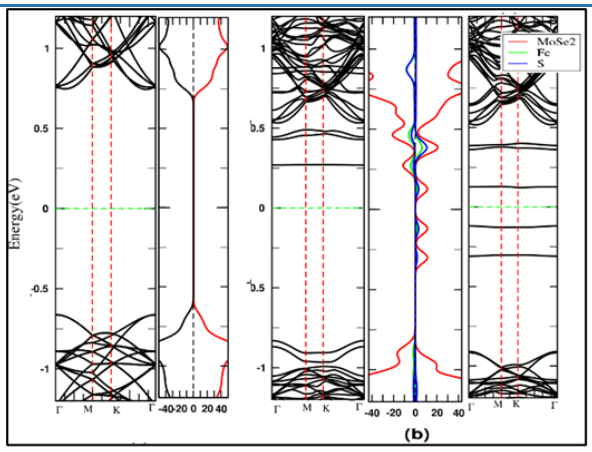

Figure 2: (a) Electronic band structure and DOS of $MoSe_2$ and (b) $Mo_{0.097}Fe_{0.028}$ Se_2. Red lines represent TDOS and blue lines represents DOS of Se) in the neighbouring atoms of impurity. Vertical Red dotted lines are symmetric M, K -points, Dark green lines for bandgap line. The Fermi level is at 0eV represented with dotted light green colour.

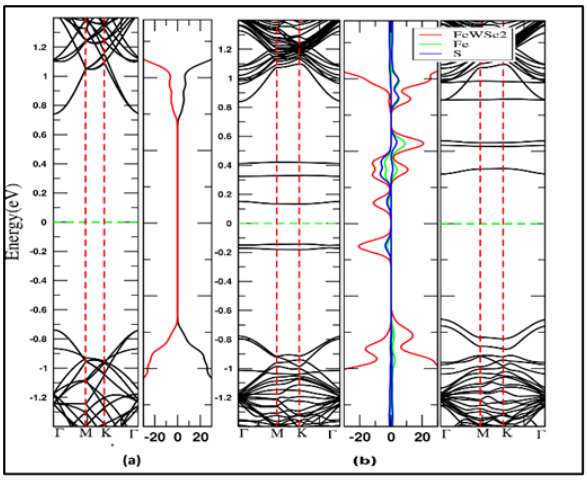

Figure 3: (a) Electronic band structure and Density of states (DOS) of WSe_2 and (b) $W_{0.972}Fe_{0.028}$ Se_2

consistent with experimental and computational results found in the literature [17]. The introduction of iron leads to a minor reduction in the M-Se bond length near the impurity atom(table1), due to the smaller atomic radius of Fe relative to Mo or W. Despite these changes, the systems remain stable, and the binding energy calculations confirm that $Mo_{0.972}Fe_{0.028}Se_2$ and $W_{0.972}Fe_{0.028}Se_2$ are energetically favourable. The binding energies of pristine $MoSe_2$ (4.401 eV) and WSe_2 (4.950 eV) are slightly higher compared with $Mo_{0.972}Fe_{0.028}Se_2$ (4.2 eV) and $W_{0.972}Fe_{0.028}Se_2$ (4.87 eV) showing reduced values. This reduction suggests that doping may destabilize the monolayer to some extent but could also increase the material's reactivity, which is beneficial for applications requiring high catalytic activity or sensor sensitivity. The binding energy is calculated by using the formula

$$E_b = \frac{E_{total} - \{nE + mE_M + lE_{Fe}\}}{n + m + l}$$

Table 1: Table 1: The calculated structural parameters such as optimized lattice constant (a), average bond distance between adjacent atoms $d_{(M\text{-}Se)}$ (M=Mo, W) and Fe- Se, binding energy (E_b) and Bandgap (E_g) values, $\mu_{atom(n)}$ and μ_{tot} represents the magnetic moment.

System	a (Å)	E_{tot} (eV)	$d_{M\text{-}Se}$ (Å)	E_b (eV)	Eg (eV)	$\mu_{atom\ (n)}$ (μ_B)	μ_{tot} (μ_B)
$MoSe_2$	3.340	37215.987	$2.560_{Mo\text{-}Se}$	-4.401	1.46 (D)		0.0
$Mo_{0.972}Fe_{0.028}Se_2$	3.340	37520.918	$2.531_{Mo\text{-}Se}$, $2.432_{Fe\text{-}Se}$	-4.231	1.09(D↓), 0.24(I↑)	$1.651_{Fe(1)}$, $0.085_{Mo(6)}$, $0.015_{Se(6)}$	2.0
WSe_2	3.345	41268.1950	$2.571_{W\text{-}Se}$	-4.950	1.49 (D)		0.0
$W_{0.972}Fe_{0.028}Se_2$	3.345	41670.3294	$2.587_{W\text{-}Se}$, $2.461_{Fe\text{-}Se}$	-4.863	1.0(D↓), 0.27(D↑)	$1.544_{Fe(1)}$, $0.219_{W(6)}$, $0.014_{Se(6)}$	2.0

where E_{total} is the total energy of the studied system, E_M, E_{Se} and E_{Fe} are energy of the isolated atoms constituting the system and n, m and l are number of M (Mo, W), Se and Fe atoms in the respective studied system. The electronic band structures and density of states (DOS) of pristine and Fe-doped MLs are examined. For pristine monolayers, both $MoSe_2$ and WSe_2 exhibit direct bandgaps of approximately 1.46 eV and 1.49 eV respectively listed in table1. These findings are in good agreement with previous reports. When Fe is introduced into the monolayers, spin polarization occurs. For $Mo_{0.972}Fe_{0.028}Se_2$, the spin-down channel exhibits a direct bandgap of 1.09 eV, while the spin-up channel has an indirect bandgap of 0.24 eV. Similarly, for $W_{0.972}Fe_{0.028}Se_2$, the spin-down channel shows a direct bandgap of 1.0 eV, and the spin-up channel has a direct bandgap of 0.27 eV. This reduction in bandgap could be useful for spintronic devices that exploit spin-polarized carriers. In the case of Fe-doped $MoSe_2$ and WSe_2, iron acts as p-type dopants which tends to create holes in the valence band, and can enhance the photocurrent and overall photosensitivity of the material. This p-doping improves the efficiency of light absorption and charge separation, which are key factors in photodetector performance [19]. In contrast, when it acts as n-dopant, which adds electrons to the conduction band, is clearly observed through electronic band structures. While it may increase the electron density, it might also reduce the material's ability to capture electrons. This process may also lead to a diminished ability of the material to effectively capture other charge carriers, potentially impacting its overall performance in electronic applications. However, the ideal doping method and concentration might vary depending on the specific application and the properties of the TMDs, so it is still an area of active research [18-20]. The pristine MSe_2MLs are nonmagnetic but $M_{0.972}Fe_{0.028}Se_2$MLs are observed to be magnetic in nature. Their magnetic behaviour is clear from their spin resolved electronic band structure and DOS (figure 2(b) and 3(3b)). We have plotted PDOS corresponding to impurity atom (Fe) and Se atom in the neighbourhood of impurity. We observed the value of spin magnetic moment acquired by each neighbouring atom of impurity shown in table 1. The magnetic properties of $Mo_{0.097}Fe_{0.028}Se_2$ and $W_{0.097}Fe_{0.028}Se_2$ MLs are analysed through calculations of spin vector. Both systems exhibit Ferromagnetic behaviour, with a net magnetic moment of approximately 2μB per monolayer. The magnetic moment primarily arises from the Fe dopant, which acquires a moment of approximately $1.6\mu_B$. Additionally, neighbouring atoms, such as Mo/W and Se, show slight magnetization due to the localized effects of the Fe impurity (Fig.4). In $Mo_{0.972}Fe_{0.028}$ Se_2, the surrounding six Mo atoms acquire magnetic moments of 0.085μB, while the Se atoms have a negligible moment. In $W_{0.972}Fe_{0.028}Se_2$, the neighbouring six W atoms acquire magnetic moments of 0.219 μB, and the Se atoms show a similarly small contribution. This localized magnetization is consistent with the expected influence of the Fe impurity on the surrounding atoms.

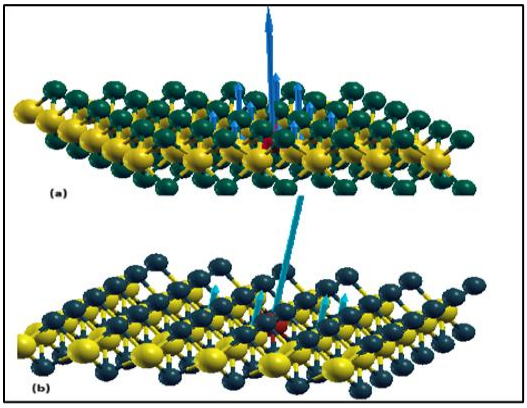

Figure 4: Spin vector in (a) $Mo_{0.097}Fe_{0.028}$ Se_2 and (b) $Mo_{0.097}Fe_{0.028}$ Se_2

Conclusion And Future Prospective

Our first-principles study reveals that Fe doping

significantly alters the electronic and magnetic properties of $MoSe_2$ and WSe_2 monolayers. The doping induces spin polarization, leading to distinct band gaps. These findings suggest that $Mo_{0.972}Fe_{0.028}Se_2$ and $W_{0.972}Fe_{0.028}Se_2$MLs hold great potential for spintronic applications, where the tunable spin-polarized electronic states could be harnessed for advanced device technologies. Our study provides a comprehensive understanding of the impact of Fe doping on the properties of TMD monolayers, offering a pathway for the development of new materials for energy storage devices, superconductors, photocatalysis and magnetic semiconductors.

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