A study via density functional theory calculations of transition metal diselenide monolayers

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Abstract. In this paper, the physical properties such as structural, electronic, and magnetic of vanadium diselenide, chromium diselenide, molybdenum diselenide and tungsten diselenide monolayers were studied. The calculations were performed in the hexagonal structure (1H) and using the density functional theory. The computational calculation shows that the exfoliation energies of four monolayers are 18.92 meV/Å², 19.83 meV/Å², 22.42 meV/Å², and 33.85 meV/Å², respectively. While the formation energies values per atom were −2.88 eV, −2.47 eV, −3.31 eV, and −3.98 eV, respectively. The monolayers are thermodynamically stable because the formation energies are negatives. Finally, the band structure study reveals that vanadium diselenide monolayer have a half-metallic ferromagnetic behavior, while the chromium diselenide, molybdenum diselenide and tungsten diselenide monolayers present a direct semiconductor character. Due to these properties the monolayers have potential application in micro, nano electronics, and spintronic devices.

1. Introduction

Successful exfoliation of graphene [1] and the identification of its superior physical and chemical properties drove the search for new bidimensional materials. This quest for new monolayers includes the monolayers of transition metal dichalcogenides (TMDs), where the transition metal is (TM) and the dichalcogen is (D). In fact, many of these monolayers exist nowadays such as vanadium dioxide (VO2) [2], chromium dioxide (CrO₂) [3], molybdenum dioxide (MoO₂) [4], tungsten dioxide (WO₂) [5] and vanadium disulfide (VS₂) [6].

Currently, a new TMDs monolayers. Namely, the diselenides have attracted the interest of researchers due to their promising applications in many technological fields such as rechargeable battery [7], sensors [8], catalysis [9], field effect transistors [10], microelectronics devices [11], spintronics [12] and nanoelectronics [13].

In this work, we study the energetic stability and the structural, electronic, and magnetic properties of transition metal diselenide (TMS₂) monolayers such as vanadium diselenide (VSe₂), chromium diselenide (CrSe₂), molybdenum diselenide (MoSe₂) and tungsten diselenide (WSe₂). These four diselenides have layered structured in volume. Hence, the interactions between two consecutive layers have a Van der Waals (vdW) nature [14]. This weak interaction between layers facilitates the obtention of VSe₂, CrSe₂, MoSe₂ and WSe₂ monolayers through a mechanic exfoliation method. The exfoliation energy of each monolayer is computed in this work.
2. Computational details
All calculations are based on the first principles method with polarized spin within the density functional theory framework using ultra-soft pseudopotentials \cite{15,16}. The effects of exchange-correlation were included in the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) \cite{17}. The computational calculations were accomplished with the Quantum Espresso code \cite{18}. A set of plane waves was used with a cutoff energy of 60 Ry and a $12 \times 12 \times 1$ k-point mesh was chosen for the integration in the first Brillouin zone. The monolayers were built using the periodic slab model in the layered hexagonal structure 1H with space group #187 using $2 \times 2 \times 1$ geometry. Each monolayer has a total of 12 atoms (four transition metals and eight selenides) as seen in Figure 1. In order to avoid interactions between two consecutive monolayers we used a vacuum region of 20 Å. The criteria for energy convergence and atomic forces were $10^{-6}$ Ry and $10^{-3}$ Ry/Bohr.

![Figure 1. Diselenides metal transition monolayer; (a) top view; (b) side view.](image)

The energetic stability of monolayers in diselenide transition metals was studied by calculating the cohesion and formation energies. The cohesion energy is understood as a measure of the binding strength between the atoms that constitute a material \cite{19}. The cohesion energy is given by Equation (1) \cite{20}.

$$E_{\text{Coh/atom}} = \frac{n_{\text{TM}}E_{\text{Tot(TM)}} + n_{\text{Se}}E_{\text{Tot(Se)}} - E_{\text{Tot(TMSe$_2$)}}}{n_{\text{Tot}}}.$$

(1)

where $E_{\text{Tot(TMSe$_2$)}}$ is the total energy of monolayer, $E_{\text{Tot(TM)}}$ is the total energy of the isolated transition metal (TM), $n_{\text{TM}}$ is the total number of atoms in transition metals, $E_{\text{Tot(Se)}}$ is the total energy of a selenium atom, $n_{\text{Se}}$ is the total number of selenium atoms and $n_{\text{Tot}}$ is the total number of atoms in the monolayer. The formation energy is defined as the energy required to form a material from its corresponding elemental atoms. Mathematically speaking, it is defined in Equation (2) \cite{14}.

$$E_{\text{form/atom}} = \frac{E_{\text{coh(TMSe$_2$)}} - [n_{\text{TM}}E_{\text{coh(TM)}} + n_{\text{O}}E_{\text{coh(O)}}]}{n_{\text{Tot}}}.$$

(2)

Furthermore, in order to determine how easily a transition metal diselenide monolayer can be extracted, the exfoliation energy is computed. This corresponds to the energy required to mechanically extract one monolayer from the volume of diselenides and is defined in Equation (3) \cite{21}.
where $E_{\text{tot}}(\text{TMSe}_2)$ is the total energy of the monolayer, $E_{\text{tot/layer}}(\text{bulk})$ is the total energy of the volume per layer and $A_0$ is the area of the volume plane under equilibrium.

3. Results and discussion

In this section, we present and discuss the results regarding the structural and electronic properties of the transition metals diselenides monolayers considered in this work.

3.1. Structural properties

Figure 1 shows the top and side views of the TMSe$_2$ (TM = V, Cr, Mo and W), monolayers along with the main parameters that characterize structural relaxation: lattice constant $a$, distance between transition metal and selenium atoms $d_{\text{TM-Se}}$, distance between selenide atoms $d_{\text{Se-Se}}$ and the angle $\theta$ between the Se – TM – Se atoms. The resulting parameters along with the cohesion, formation and exfoliation energies are shown in Table 1. As seen in Table 1, the values obtained for the main structural parameters are consistent with the values reported by [14,21]. This ensures the reliability of our calculations.

Furthermore, the cohesion energies of the monolayers are positive which indicates that the atoms are strongly bonded between each other and that it is more energetically favorable for the atoms to be bonded in the monolayer compared to its free atoms. Additionally, the values of the formation energies are negative meaning that the monolayers are energetically stable, with WSe$_2$ being the most stable monolayer since its energy is more negative. We note that the formation energy for the MoSe$_2$ monolayer is slightly higher than the value stated in [14]. This discrepancy can be explained by the fact that this work uses GGA, and the referenced article uses the local density approximation (LDA).

The exfoliation energies for monolayers VSe$_2$, CrSe$_2$, MoSe$_2$ were obtained resulting in 18.92 meV/Å$^2$, 19.83 meV/Å$^2$ and 22.42 meV/Å$^2$, respectively. These values are close to the exfoliation energy of graphene (21.00 meV/Å$^2$) [22]. In contrast, the exfoliation energy obtained for the WSe$_2$ monolayer is 33.85 meV/Å$^2$. According to Björkman et al. [23], monolayers are easily exfoliable when their energies remain within 15 meV/Å$^2$ and 21 meV/Å$^2$, while they are potentially exfoliable for energies ranging between 22 meV/Å$^2$ and 130 meV/Å$^2$.

### Table 1. Mainly structural parameters, cohesion, formation, and exfoliation energies.

| Monolayer | Method | $a$ (Å) | $d_{\text{Se-Se}}$ (Å) | $d_{\text{TM-Se}}$ (Å) | $\theta$ (°) | $E_{\text{coh/atom}}$ (eV) | $E_{\text{form/atom}}$ (eV) | $E_{\text{Ext}}$ (meV/Å$^2$) |
|-----------|--------|--------|-----------------|-----------------|--------|----------------|----------------|----------------|
| VSe$_2$   | GGA    | 3.31   | 3.31            | 2.49            | 81.92  | 15.40          | -2.88          | 18.92          |
|           | LDA$^a$| 3.24   | 3.17$^a$        | 2.45$^a$        | 80.49$^a$| 15.47$^a$     | -2.17$^a$     | -              |
| CrSe$_2$  | GGA    | 3.20   | 3.32            | 2.42            | 80.96  | 16.46          | -2.47          | 19.83          |
|           | LDA$^a$| 3.13$^a$| 3.11$^a$       | 2.38$^a$        | 81.54$^a$| -              | -              | -              |
| MoSe$_2$  | GGA    | 3.32   | 3.32            | 2.44            | 79.78  | 16.23          | -3.31          | 22.42          |
|           | GGA$^b$| 3.33$^b$| 3.35$^b$       | 2.55$^b$        | -      | -              | -2.25$^b$      | -              |
|           | LDA$^a$| 3.24$^a$| 3.32$^a$       | 2.50$^a$        | 83.05$^a$| 17.47$^a$     | -2.96$^a$      | -              |
| WSe$_2$   | GGA    | 3.35   | 3.34            | 2.55            | 81.23  | 18.45          | -3.98          | 33.85          |
|           | GGA$^b$| 3.34$^b$| 3.34$^b$       | 2.55$^b$        | -      | -              | -              | -              |
|           | LDA$^a$| 3.25$^a$| 3.34$^a$       | 2.51$^a$        | 83.24$^a$| 19.07$^a$     | -              | -              |

$^a$Ataca et al [14], $^b$Ersan et al [21]

3.2. Electronic properties

Figure 2 shows the band structure of the monolayers considered in this research. The VSe$_2$ monolayer in Figure 2(a) exhibits a metallic and ferromagnetic behavior. Furthermore, the monolayer has a total magnetization different from zero, given that the spin-up electronic states (red lines) are not symmetrical to the spin-down electronic states (blue lines). The monolayer has a magnetic momentum of
1.975 $\mu\beta/V$ – atom. In contrast, the CrSe$_2$, MoSe$_2$, and WSe$_2$ monolayers have a semiconductor behavior with a direct gap located in the point K of the Brillouin zone and respective values of 0.77 eV, 1.50 eV and 1.61 eV. The gap obtained for WSe$_2$ is in agreement with previous theoretical (1.62 eV [24]) and experimental (1.50 eV [25]) results.

4. Conclusions

In summary, the structural and electronic properties of transition metal diselenide monolayers (vanadium diselenide, chromium diselenide, molybdenum diselenide, and tungsten diselenide) were studied using first-principles calculations. We concluded that monolayers vanadium diselenide, chromium diselenide, and molybdenum diselenide are energetically stable and easily exfoliable. Meanwhile, the tungsten diselenide monolayer is potentially exfoliable. The vanadium diselenide exhibiting a metallic behavior with a magnetic momentum of 1.975 $\mu\beta/V$ – atom. Monolayers chromium diselenide, molybdenum diselenide, and tungsten diselenide have a semiconductor behavior with direct band-gaps located in the K point and respective values of 0.77 eV, 1.50 eV and 1.61 eV.

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