

Structural and electronic properties of iron doped technetium sulphide

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Abstract. In this paper Density Functional Theory with the inclusion of van der Waals corrections is used to study the effect of Iron doping on the structural and electronic properties of TcS₂ (technetium disulphide) in the $P\bar{1}$ structure. We show that Fe doped TcS₂ is stable against decomposition to its constituent solid components for the configurations examined and that it is possible to modify the bandgap of these indirect bandgap materials by doping. Substitutional Fe doping of TcS₂ decreases the bandgap from the un-doped configuration. The degree of decrease depends on the percentage doping and the doping configuration. We find that at 25 substitutional doping percentage the system is a magnetic semiconductor.

1. Introduction

Transition metal dichalcogenides (TMDCs) are a class of inorganic materials with the formula MX₂ where M is a transition metal (Tc, Mo, W, Nb, Re, Ti and Ta) and X is a member of the chalcogen family (S, Se, Te) [1–3]. TMDCs tend to crystallise in a layered structures that arises from the stacking of planes composed of transition metal atoms sandwiched between two chalcogenide atoms in the form X-M-X as shown in figure 1 for TcS₂ in the $P\bar{1}$ structure. This sandwich layer is internally strongly bonded while the interaction between layers is mainly through van der Waal's forces [4]. The weak inter-layer forces makes it possible to fabricate ultra thin layer by exfoliation or cleavage. TMDCs have a wide range of useful properties, ranging from optical, catalytic, electronic, mechanical, thermal and chemical and this makes them materials of interest for researchers [5–7].

The electronic properties of TMCs range from metallic to semiconducting [8]. To achieve the most practical application of TMDCs in nano-devices, solar energy application and other electronic applications, their electronic and optical properties can be modulated by: the application of external fields, forces, alloying [9, 10], modified layer stacking or doping [11–17]. Recent investigations have shown that application of strain can change the band gap of a TMDC from indirect to direct, while transition from semi-conductor to metal has also been observed in some TMDCs [18, 19]. The band gap of these materials can be tuned by the application of external electric fields [20, 21].

Another method by which the electronic property of a TMDCs can be tuned is doping [16, 17]. It is the purpose of this paper to investigate the structural and electronic properties of pure and Fe doped TcS₂ in the $P\bar{1}$ structure [22], a structure TcS₂ has been synthesized in. To the best

of our knowledge, this is the first time such an investigation is reported. In order to achieve a possible modification of the electronic properties of TcS_2 , we use TcS_2 with the substitution of Fe for Tc. Based on Hick's [23] rule for solubility, the ionic radius of the host and intercalating metal should be close and the doped metal should come from a group adjacent to the host metal in the periodic table. Based on this, we decided investigate substitutional doping of TcS_2 by replacing selected Tc atoms by Fe atom, an element from the adjacent group in the periodic table, having one electron more than Tc in its d-shell. We calculated the DFT electronic band structure of $\text{Tc}_{1-x}\text{SFe}_x$ and $\text{Tc}_{1-x}\text{Fe}_x\text{S}$ ($x = 0.25$ or 0.5), corresponding to 25% and 50% Fe doping respectively by considering modifications of the primitive unit cell only.

The electronic properties of TcS_2 have been studied by some researchers using theoretical and experimental approaches [24–27]. Wilson et. al [27] performed optical measurements which yielded a band gap of 1.3 eV. Fang. et.al [25] using the localized-spherical-wave (LSW) method and Weck et.al. [26] using GGA-DFT reported on the electronic properties of TcS_2 structures. Oviedo-Roa et. al. [24] used a periodic density functional approach to investigate catalytic properties of 4d-transition-metal sulfides. The reported experimental band gap is very close to the optimal band gap of 1.4 eV for solar energy applications. It is the focus of this paper to investigate the possibility of engineering the electronic properties of the TcS_2 for optimal solar energy application through doping. However, due to page restrictions, only modifications of the primitive unit cell of the structure will be considered. An in depth study of an extensive range of configurations will be reported elsewhere.

2. Computational Method

We used Density Functional Theory (DFT) [28, 29] with the inclusion of van der Waals forces as proposed by Grimme (DFT-D2) [30]. Van der Waals corrections are necessary for the accurate description of the structural properties of layered materials. The Projector Augmented Wave (PAW) [31] as implemented in *Vienna ab initio Simulation Package* (VASP) [32, 33] is used to mimic electron-ion interaction and the Perdew, Burke and Ernzerhof (PBE) [34–36] parametrization of the generalised gradient approximation (GGA) [37–39] is used for the exchange correlation potential. The van der Waals correction in DFT-D2 adds a correction to the PBE approximation [30].

A $5 \times 5 \times 4$ Γ -centred Monkhorst-Pack mesh was used for sampling the Brillouin zones and the energy cut-off used in the calculations is 520 eV. These parameters were found to be adequate to energy convergence of less than 0.1 meV.

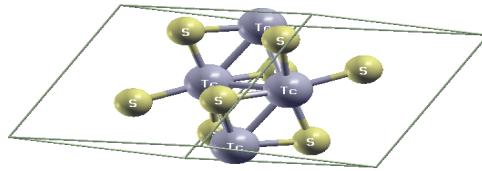
3. Results and discussions

3.1. Structural Properties

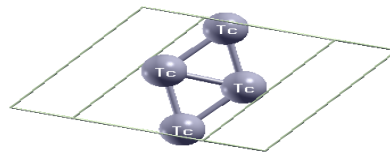
In order to determine the equilibrium properties of each of the studied structures, we calculated the cohesive energy per atom (E_{coh}) as a function of volume per atom V (eV) and fitted a third order Birch-Murnaghan equation of state (EOS) [40] to the calculated values. The volume which corresponds to the lowest cohesive energy is taken as the equilibrium volume of the structure and all subsequent calculations of the structure are carried out at this volume.

In the $P\bar{1}$ structure, the chemical unit per unit cell is Tc_4S_8 (figure 1a). In the $P\bar{1}$ equilibrium structure the Tc layer is sandwiched between two layers of S atoms. The four Tc atoms do not lie on a plane, but are slightly buckled. There are two Tc atomic positions that have different environments, labelled Tc1, Tc4 and Tc2, Tc3, respectively, in figure 1b.

For the 25% substitutional doping case there are 2 symmetrically distinct possibilities for replacing the Tc atom by Fe while for 50% doping there are 3 symmetrically distinct possibilities as shown in table 1.



(a) TcS_2



(b) Positions of Tc atoms.

Figure 1: Primitive unit cell for Technetium Sulphide in the $P\bar{1}$ structure and the positions of the four Technetium atoms.

Table 1: Configurations for substitutional doping of Tc by Fe of TcS_2 in the $P\bar{1}$ structure. Numbers in the top row refer to the labelling of atomic sites in figure 1b

	1	2	3	4
un-doped	Tc	Tc	Tc	Tc
d1.0.25	Fe	Tc	Tc	Tc
d2.0.25	Tc	Fe	Tc	Tc
d1.0.50	Fe	Fe	Tc	Tc
d2.0.50	Fe	Tc	Tc	Fe
d3.0.50	Tc	Fe	Fe	Tc

In table 2 the equilibrium parameters for the Technetium Sulphide and Iron doped structures are listed.

Table 2: Technetium Dichalcogenides equilibrium lattice parameters, bulk modulus, Cohesive energy E_{coh} per atom, volume, Formation energy (E_f) per atom and magnetic moment per unit cell in Bohr magnetons.

Material	a(Å)	c/a(Å)	B_0 (GPa)	B'_0	E_{coh} (eV)	V_0 (Å ³)	E_f (eV)	Magnetic moment
TcS ₂ (un-doped)	6.37 (6.37[a])	1.06 (1.04 [a])	28.80	12.78	-5.22	217.08 (213.39[a])	-0.62	0.00
50 percent doping								
d1_0.50	6.32	1.20	29.09	9.98	-4.75	204.72	-0.51	0.00
d2_0.50	6.28	1.20	30.29	8.12	-4.72	205.92	-0.48	0.00
d3_0.50	6.28	1.20	32.34	11.15	-4.69	204.24	-0.45	0.00
25 percent doping								
d1_0.25	6.40	1.31	29.63	10.12	-4.94	211.80	-0.52	1.00
d2_0.25	6.41	1.31	30.32	12.70	-4.95	211.92	-0.53	1.00

a = Experimental values, reference [22]

From the table 2 it is clear that the obtained TcS₂ values for the lattice constants and volume of the unit cell that our results agree well with the available literature. Since the cohesive energy and formation energy (the quantities that are used to determine the stability of the studied structures) follow the same trend, we will therefore resort to the use of formation energy which is the energy liberated when the system is decomposed into its constituent solid components, as measure of stability of the structures.

The formation energy is given by

$$E_f(S_m Tc_n Fe_o^{solid}) = E_{coh}(S_m Tc_n Fe_o^{solid}) - \frac{mE_{coh}(S^{solid}) + nE_{coh}(Tc^{solid}) + oE_{coh}(Fe^{solid})}{m + n + o} \quad (1)$$

where m, n and o are integers representing the number of sulphur, technetium and iron involved in the formation the system in question.

A positive value of formation energy at a given temperature and pressure signifies instability in the structure and tendency of the structure to decompose to its constituent solid components. On the other hand, the more negative the value of the formation energy, the more stable the structure is. Our results suggest that the doped structures are stable with respect to decomposition to their component solids and the energetically most favourable doped structures are in the order of d1_0.50, d2_0.25, d1_0.25, d1_0.50, d2_0.50 and d3_0.50.

We note that there is induced magnetisation for 25% doping. Roughly half to the total magnetisation is from the Fe atom and one Tc atom in a ferro magnetic arrangement, in both cases. In the case of d1_0.25, there is induced magnetization on Tc_2 due to the presence of Fe_1. For d2_0.25, the induced magnetization is on Tc_3 due Fe_2. Magnetic moments associated with other atoms are negligible. For the 50% doping, there is no net magnetization and no magnetic moments associated with any atom in the structures. The magnetic semiconductors are materials of interest in the field of spintronics.

3.2. Electronic Properties

TcS₂ and its Fe doped derivatives studied in this report are indirect band gap materials. In table 3 the band gaps for the different configurations are listed. We can see that from the table that the dominant contributing orbital character remains Sulphur p-type, S(p), in all cases, apart from the d2_0.50 configuration, despite the relatively high doping levels considered. The Fe orbitals have little contribution at the band edges. However, as a result of hybridisation with the Fe s-orbitals in all cases apart from the d1_0.50 configuration where the dominant hybridisation is with Fe(d), the band gap of the doped system is narrowed in all cases.

Table 3: Band gaps DFT-D2 and MBJ (in brackets) for un-doped and Fe doped TcS₂ systems with their dominant contributing orbitals at the band edges

Configuration	Bandgap (eV)	others	Dominant orbitals at the band edge	
			VBM	CBM
un-doped	0.94 (1.20)	0.9[b]	S(p)	S(p)
d1_0.25	0.22 (0.60)		S(p)	S(p)
d2_0.25	0.31 (0.54)		S(p)	S(p)
d1_0.50	0.36 (0.48)		S(p)	S(p)
d2_0.50	0.20 (0.41)		S(p)	S(s)
d3_0.50	0.18 (0.42)		S(p)	S(p)

b = reference [26]

The formation energies of the different doping configurations (see table 2) are relatively close and it is likely that all configurations will be found in a real system. Local bandgaps of doped systems will probably differ from region to region. From table 3 we note that substitutional doping of TcS₂ with Fe can significantly change the bandgap. In all cases studied here the bandgap is decreased from that of the un-doped configuration.

4. Conclusions

In this preliminary report we numerically investigated the feasibility of substitutionally doping TcS₂ with Fe. We only explored a sub-set of possible doping configurations for a 25% and 50% substitutional doping. Other configurations are possible if larger unit cells are considered and this is part of ongoing work.

We found that by including van der Waals corrections to the PBE approximation, accurate structural properties for TcS₂ in the $P\bar{1}$ structure, a layered structure, can be determined from numerical simulations. This encourages us to believe that accurate predictions of the structural properties for the Fe doped TcS₂ configurations can be determined using the same approach. The sub-set of doped configurations we considered are all predicted to be stable against decomposition to their component solids. We are testing for stability against structural deformations.

The indirect DFT-D2 bandgaps are sensitive to doping with the bandgaps of all the doped configurations smaller than the bandgaps of the un-doped systems.

DFT bandgaps are not accurate predictors of the fundamental or optical bandgaps, though the MBJ values tend to be reasonably accurate. Challenging numerical techniques such as GW [41] and BSE [42] approaches must be used for accurate predictions of band gaps and electronic structure. The general trend found here, that doping decreases the band gap, is expected to prevail when more accurate GW and BSE techniques are used.

We found that the 25% substitutionally Fe doped TcS₂ structures are magnetic semiconductors. These systems merit further investigation as materials of interest to spintronics.

In summary, we have shown numerically that Fe doped TcS₂ can be stable and that it is possible to engineer the band gap by doping.

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