Structural stability and electronic properties of bulk, bilayer and monolayer PtX_2 (X = Se and Te)

Hamza A H Mohammed[1,2*], **G M Dongho-Nguimdo**[3] **and Daniel P Joubert**[1]

[1]The National Institute for Theoretical Physics, School of Physics and Mandelstam Institute for Theoretical Physics, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa.
[2]Department of Physics, Shendi University, Shendi, Sudan
[3]College of Science, Engineering and Technology, University of South Africa, P.O. Box 392, UNISA 0003 Pretoria, South Africa

E-mail: `hamzad00@gmail.com`

Abstract. Using first-principles density functional theory, we investigate the structural, stability and electronic properties of the layered bulk, bilayer and monolayer platinum dichalcogenides $PtSe_2$ and $PtTe_2$ compounds in the CdI_2 structure. Our calculations confirm that these compounds are mechanically and dynamically stable. Band structure calculations show that bilayer and monolayer $PtSe_2$ and $PtTe_2$ are indirect band gap semiconductors whereas the bulk structures are semi-metal. The calculated band structure and density of states show that the band gaps decrease when the number of layers increases, which allows band gap engineering for optimal photovoltaic applications.

1. Introduction

Conducting research on clean and renewable energy sources has become necessary nowadays because of concerns about depleting reserves of fossil fuels and environmental pollution. Three-dimensional (3D) and two-dimensional (2D) transition metal dichalcogenides (TMDs) are potential materials for applications in energy conversion devices [1, 2, 3]. Few and multi-layer TMDs are promising as solar energy absorbers since the variation in band gap with the number of layers allows band gap engineering. Monolayer $PtSe_2$ is a semiconductor with a measured band gap of 1.22 eV [4, 5]. Yim C. *et al* [6] demonstrated that multilayer $PtSe_2$ is easy to synthesize and showed that vertically stacked heterostructures of $PtSe_2$ on Si can be used as photodiodes and in photovoltaic cells. The electronic structure of monolayer and bilayer $PtSe_2$ has been calculated using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation approximation with density functional band (DFT) gaps of 1.39 and 0.99 eV for $PtSe_2$ and $PtTe_2$, respectively [7]. Experimental measurements confirm that bulk $PtSe_2$ and $PtTe_2$ are semi-metal [8], while monolayer and bilayer structures are semiconductors with a band gaps of 1.2 eV and 0.21 eV, respectively [4]. Phonon dispersion and electronic properties of bulk, monolayer, and bilayer $PtSe_2$, were also calculated using DFT with the Tkatchenko and Scheffler van der Waal's correction (DFT-TS) [9], that confirmed that the bulk is semi-metallic while monolayer and bilayer configurations are semiconductors with an indirect band gap of $\sim$1.6 eV and $\sim$0.8 eV, respectively. The investigation of electronic and transport properties for monolayer $PtSe_2$ and $PtTe_2$

reported in reference [10] suggest that these compounds have promising properties for thermoelectric applications.
In this study, we investigated the structural, mechanical and dynamical stability and electronic properties of bulk, bilayer, and monolayer $PtTe_2$ and $PtSe_2$. The results showed that the two compounds are stable, and that the band gap increases as the number of layers decreases

2. Computational details

The calculations were performed using Density Functional Theory (DFT), with the projector-augmented wave (PAW) pseudopotential approach as implemented in the VASP package [11, 12]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [13] was used as an exchange-correlation approximation. We performed calculations using converged an energy cutoff of 520 eV for bulk and 350 eV for bilayer and monolayer calculations. We set a vacuum of 15 Å between the periodically repeated layers in the z direction for the monolayer and bilayer system. The self-consistent total energies were converged to 1.0×10^{-8} eV/atom and the residual forces per atom were less than 1m eV/Å. For the integration over the Brillouin zone, a Γ-centred Monkhorst-pack grid [14] of 8×8×6 for bulk and 12×12×1 for the single and double layer were found to be sufficient. A 3×3×3 supercell for bulk and 5×5×1 bilayer and monolayer were used for displacive phonon calculations [15].

3. Results and discussions

3.1. Structural parameters

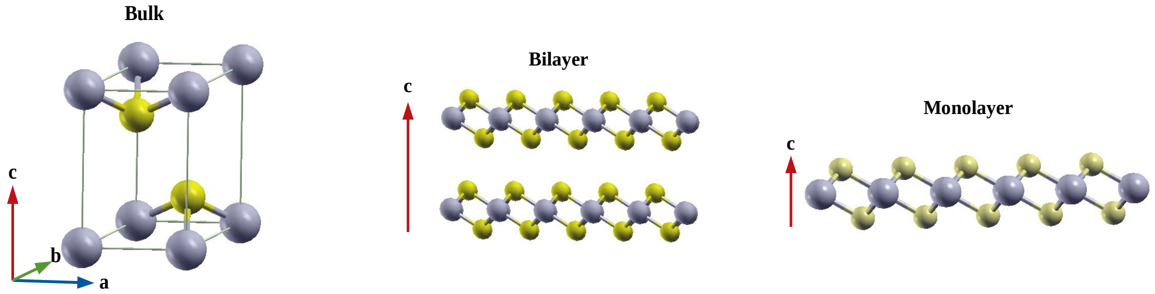


Figure 1. Crystal structure of bulk, bilayer and monolayer $PtTe_2$ and $PtSe_2$. The grey and yellow balls represent the Pt and Se/Te atoms, respectively.

In Figure 1 the bulk, bilayer and monolayer $PtTe_2$ and $PtSe_2$ crystal structures are shown. Our relaxed structural parameters for bulk, bilayer and monolayer, collected in Table 1, is consistent with the available experimental data. Atomic positions in the bilayer and monolayer do not deviate appreciably from the corresponding bulk positions, indicative of strong bonding between the Pt and chalcogen atoms. The calculated cohesive and formation energies of bulk, bilayer and monolayer, also listed in Table 1, are all negative, which suggests that the compounds are stable with respect to decomposition into their constituent atoms or solid components.

3.2. Elastic stability

To obtain the mechanical stability of bulk, bilayer and monolayer $PtTe_2$ and $PtSe_2$, we calculated the elastic constant tensor C_{ij} (i and j are tensor coordinates). $PtTe_2$ and $PtSe_2$ crystallise in

Table 1. Calculated equilibrium lattice parameters, cohesive energy (E_{coh}) and formation energy (E_{form}) per atom, together with the available experimental data.

		$a(\AA)$	$c(\AA)$	$V_o(\AA^3)$	$E_{coh}(eV)$	$E_{form}(eV)$
$PtTe_2$						
	Bulk	4.05	5.11	72.04	-4.43	-0.40
	Exp.[16]	4.01	5.20	72.43	–	–
	Bilayer	4.09	–	–	-3.81	-0.37
	Monolayer	4.05	–	–	-3.80	-0.36
$PtSe_2$						
	Bulk	3.77	4.98	61.11	-4.55	-0.43
	Exp.[17]	3.73	5.08	61.15	–	–
	Bilayer	3.76	–	–	-3.95	-0.39
	Monolayer	3.81	–	–	-3.96	-0.38

a trigonal $P\bar{3}m1$ symmetry, which has six independent elastic constants. The elastic constants listed in Table 2, fulfil the Born stability criteria [18], thus, confirming that bulk, bilayer and monolayer $PtTe_2$ and $PtSe_2$ are mechanically stable. Young's moduli (Y) indicate the resistance of a material to deform when subjected to opposing forces. Bulk moduli (B), describe the ability of a material to resist to volume change. Shear moduli (E), describe the materials respond to shear strain (the deformation of constant volume dimensions) opposing forces are applied. Poisson's ratio (ν), is related to the atomic bonding nature of a material. Our results show that the Young's moduli for bulk are greater than monolayer and bilayer, means Young's moduli is depended on the number of layers. The bulk moduli, shear moduli, Young's moduli and Poisson's ratio for bulk $PtTe_2$ and $PtSe_2$, obtained by the Hill's approach [19]. Young's moduli of the bulk structure depend on the volume, while Young's moduli of bilayer and monolayer depend on the area (called stiffness). Young's moduli increase with the increase of the number of layers, indicative of increased resistance to deformation under the application of opposing forces as the number of layers are increased.

Table 2. Elastic constants C_{ij} (GPa), elastic bulk moduli B_V (GPa), shear moduli E (GPa), Young's moduli Y (GPa) and Poisson's ratio ν for $PtTe_2$ and $PtSe_2$.

		C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B_V	Y	E	ν
$PtTe_2$											
	Bulk	170.5	53.80	42.07	67.62	45.00	58.31	68.42	105.2	42.26	0.24
	Bilayer	65.32	15.99	–	–	-	–	–	64.11	–	0.24
	Monolayer	64.61	22.89	–	–	–	–	–	56.50	–	0.35
$PtSe_2$											
	Bulk	197.7	67.89	41.32	51.39	40.73	64.91	66.75	102.97	41.42	0.24
	Bilayer	76.52	18.19	–	–	–	–	–	72.19	–	0.24
	Monolayer	65.38	19.37	–	–	–	–	–	59.64	–	0.29

3.3. Dynamical stability

The harmonic phonon dispersion relations were computed along the high symmetry directions. The phonon band structure, total density of states and partial density of states, for bulk, bilayer and monolayer $PtTe_2$ and $PtSe_2$ are presented in Figure 2 and Figure 3, respectively. The phonon partial density of states shows the atomic contribution to the total phonon density. The increase in the range from $PtTe_2$ to $PtSe_2$ can be attributed to the relative atomic weights of Te and Se, with the lighter Se atom contributing to the higher frequencies. All the phonon frequencies are positive, which indicates that the bulk, bilayer and monolayer of $PtTe_2$ and $PtSe_2$ are dynamically stable. Note, the bilayer phonon band structure appear dense compared to the bulk and monolayer. This is due to the increase in the number of atoms per unit cell while the frequency range is almost unchanged for all three configurations.

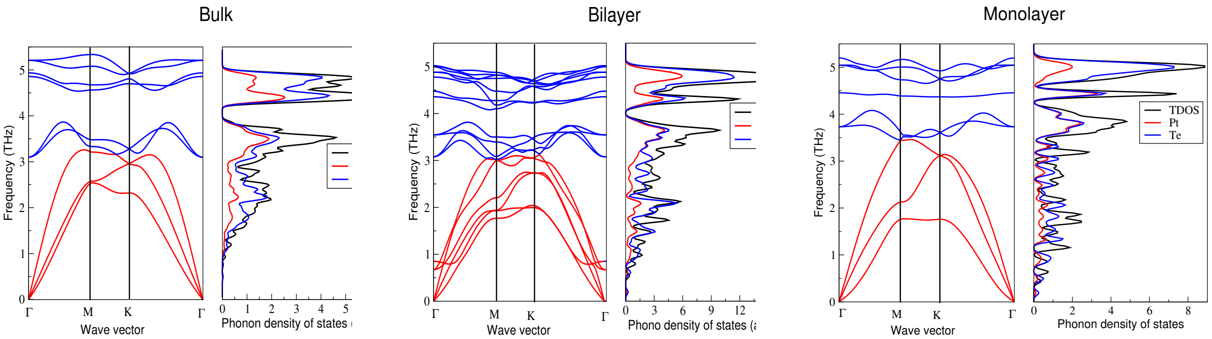


Figure 2. Phonon band structure and density of states of bulk, bilayer and monolayer $PtTe_2$

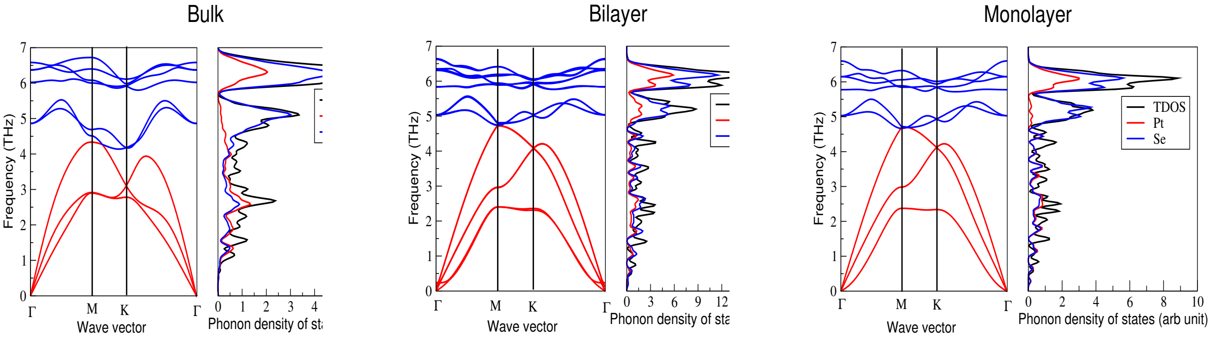
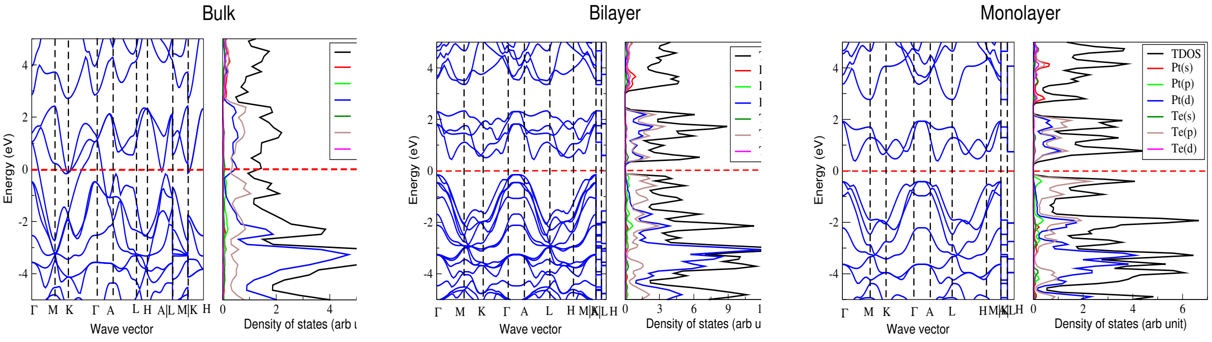


Figure 3. Phonon band structure and density of states of bulk, bilayer and monolayer $PtSe_2$.

3.4. Electronic structure properties

The electronic band structure and density of states (total and partial) of the bulk, bilayer and monolayer $PtTe_2$ and $PtSe_2$ are shown in Figure 4 and Figure 5, respectively. Note that the bilayer band structure appears dense relative to bulk and monolayer due to the doubling of the number of atoms in the unit cell. The electronic structure calculation proved that the bulk phase of both compounds shows overlap between valence and conduction band (semi-metal behaviour), while the bilayer and monolayer are semiconducting with an indirect band gap in both compounds. The conduction band minima (CBM) are located between Γ and M, while the valance band maxima (VBM) are at the Γ point, of the Brillouin zone. In Table 3, we present the band gap values for bulk, bilayer and monolayer for $PtTe_2$ and $PtSe_2$. Our calculated results agreed with some of the previous studies [8, 7, 9]. We find that the band gaps decrease with the increasing number of layers as it was previously reported by the references [3, 20].



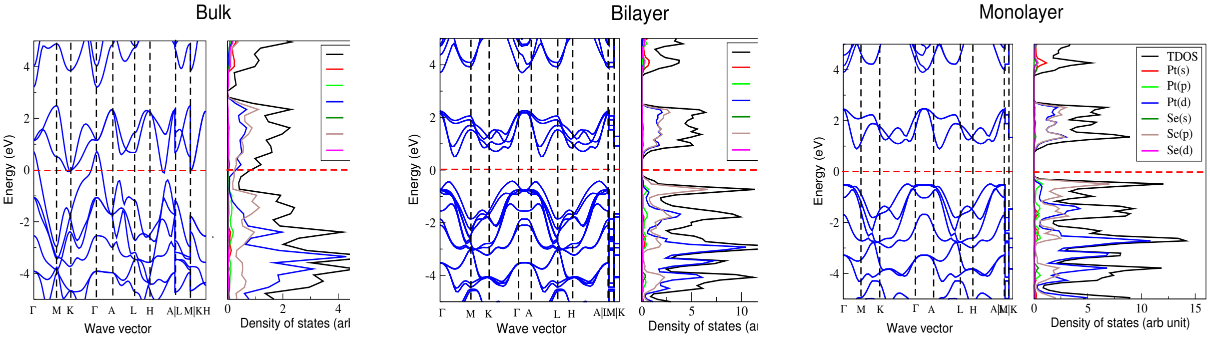


Figure 5. The band structure and density of states of $PtSe_2$ bulk, bilayer and monolayer.

Table 3. Calculated band gap values (in eV) of bulk, bilayer and monolayer $PtTe_2$ and $PtSe_2$.

		bulk	Bilayer	monolayer
$PtTe_2$				
	This study	semi-metal	0.46	0.80
	Other study	semi-metal[8]	—	0.38[10]
$PtSe_2$				
	This study	semi-metal	0.93	1.38
	Other study	semi-metal[8]	0.21[4],0.99[7],∼0.80[9]	1.22[4],1.39[7],∼1.60[9]

4. Conclusion

We studied the structural parameters, mechanical, dynamical and electronic properties of bulk, bilayer and monolayer $PtTe_2$ and $PtSe_2$ using the first-principles Density Functional Theory approach. Our results are in good agreement with available experimental data and previous studies of the structural and electronic properties. Our calculations confirm that the compounds are mechanically and dynamically stable. We found that the bilayer and the monolayer phases of these compounds have an indirect band gap. Our calculations also predicted that the size band gap strongly depends on the number of layers take into consideration in the calculations.

Acknowledgements

We like to acknowledge the all financial support received from University of Shendi, Shendi, Sudan. The authors acknowledge the Centre for High-Performance Computing (CHPC), South Africa, for providing computational resources to this research project.

References

[1] Ferrari A, et al 2015 *Nanoscale* **7** 4598–4810.
[2] Novoselov K S, Fal V, Colombo L, Gellert P R, Schwab M G and Kim K 2012 *Nature* **490** 192.
[3] Xu M, Liang T, Shi M and Chen H 2013 *Chem. Rev.* **113** 3766–3798.
[4] Wang Y *et al* 2015 *Nano Lett.* **15** 4013–4018.
[5] Zulfiqar M, Zhao Y, Li G, Nazir S and Ni J 2016 *J. Phys. Chem. C* **120** 25030–25036.
[6] Yim C, *et al* 2016 *ACS Nano* **10** 9550–9558.
[7] Li P, Li L and Zeng X C 2016 *J. Mater. Chem. C* **4** 3106–3112.
[8] Guo G and Liang W 1986 *J. Phys. C: Solid State Phys.* **19** 995.
[9] O'Brien M, *et al* 2016 *2D Mater.* **3** 021004.
[10] Guo S D and Wang Y 2017 *Semicond. Sci. Technol.* **32** 055004.
[11] Kresse G, and Joubert D 1999 *Phys. Rev. B* **59** 1758.
[12] Kresse G and Furthmüller J. 1996 *Comput. Mater. Sci.* **6** 15-50.
[13] Perdew P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865.
[14] Monkhorst J and Pack D 1976 *Phys. Rev. B* **13** 5188.
[15] Togo A, Chaput L and Tanaka I 2015 *Phys. Rev. B* **91** 094306.
[16] Thomassen L 1929 *J. Phys. Chem.* **2** 349–379.
[17] Furuseth S, Selte K and Kjekshus A 1965 *Acta Chemica Scandinavica* **19** 257.
[18] Mouhat F and Coudert X 2014 *Phys. Rev. B* **90** 224104.
[19] Hill R, 1952 *J. Proc. Phys. Soc.* **65** 349.
[20] Mohammed H A H, Dongho N G M and Joubert D 2019 *Mater. Today Commun.* **21** 100661.