# Lattice thermal conductivity of bulk $WSe_2$

**Mahmoud M.A. Mahmoud**[1,2] **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, Sinnar University, Sinnar, Sudan.

E-mail: mahmudalh1@gmail.com

**Abstract.** Research into finding efficient thermoelectric materials has intensified over the past decade. One of the desired features of efficient thermoelectric materials is a low lattice thermal conductivity. In other words, the thermal energy transported by the motion of the atoms in a thermoelectric materials should be small. Recent research suggests that some layered materials may have this property. In this study we used first principles calculations to investigate the structural, electronic, mechanical and vibrational properties of bulk $WSe_2$, a layered material. The lattice thermal conductivity was calculated by using a single-mode relaxation-time approximation in the linearized phonon Boltzmann equation from first-principles an-harmonic lattice dynamics calculations (Phono3py) as well as an iterative self-consistent method to solve the lattice Boltzmann equation(ShengBTE). We find that the lattice thermal conductivity of $WSe_2$ is non-isotropic, with a value of 63.789 and 49.092 $Wm^{-1}K^{-1}$ in the direction of the plane and 2.088 and 1.563 $Wm^{-1}K^{-1}$ perpendicular to the plane for Phono3py and ShengBTE respectively at room temperature. The calculated cross-plane thermal conductivity is close to the experimental value at room temperature, and is in a range which makes this an interesting material as a potential active component in a thermoelectric device.

## 1. Introduction

Transition-metal dichalcogenides (TMDCs) have attracted much attention for a variety of applications [1, 2]. The most intensively studied TMDCs are semiconductors such as tungsten disulfide ($WS_2$), tungsten diselenide ($WSe_2$), and molybdenum disulfide ($MoS_2$)[3]. On the basis of these compounds, a variety of electronic, optoelectronic and thermoelectric devices[4], such as transistors [5] and digital circuits[6] have been explored.

Layered hexagonal $WSe_2$ has $P63/mmc$ symmetry (Space Group #194) and the compound consists of stacked Se-W-Se layers where the hexagonally packed W metal atoms are bonded to six Se atoms in a trigonal prismatic coordination while each Se atom is bonded to three tungsten atoms in a pyramidal geometry. The W-Se bonds within each layer are covalent (strong intralayer interactions), whereas the interlayer interaction has a van der Waals (vdW) type character[7]. Lattice thermal conductivity ($\kappa_l$) plays an indispensable part and crucial role in enhancing the thermoelectric efficiency since the figure of merit that characterizes the thermoelectric properties of a material is inversely proportional to the total thermal conductivity. Considerable theoretical and experimental work has been performed to investigate the thermal properties of $WSe_2$[18, 26]. The lowest $\kappa_l$ ever reported for a dense solid to this date is 0.05 $Wm^{-1}K^{-1}$ for cross-plane lattice thermal conductivity of $WSe_2$ thin films[8].

In this paper, we have investigated the structural, stability, and electronic properties, and the lattice thermal conductivity of $WSe_2$ using first principles. We found that the lattice thermal conductivity of $WSe_2$ is anisotropic and consistent with the experimental value for the cross-plane direction.

The rest of this short paper is structured as follows: In section 2, we include a brief review of the computational details. The results and discussion are presented in section 3, and concluding remarks are summrized in Section 4.

## 2. Computational details

First-principles calculations were performed using Density Functional Theory (DFT) as implemented in the Vienna ab-initio simulation package (VASP)[9, 10]. A Projector-Augmented-Wave approach (PAW) was used to describe the interaction between ions and electrons[11]. The Generalised Gradient Approximation (GGA) exchange-correlation functional used in this study was parametrized by Perdew, Burke and Enzerhof (PBE)[12] while the empirical van der Waals correction scheme with zero damping (DFT-D3) of Grimme was used to take into account van der Waals forces in our calculations[13]. Additionally, the total energy self-consistent convergence criterion and cut-off energy for the plane wave basis were set to be $10^{-8}$ eV/atom and 520eV respectively. Brillouin zone integration for structural properties was performed over a 12x12x2 $\Gamma$ centred grid using a tetrahedron method with Blöchl corrections. Atoms were relaxed till all forces were less than $10^{-3}$ eV/atom. A 9x9x2 $\Gamma$ centred k-point mesh was used for the elastic constant calculations, while for the electronic structure and density of the states a denser k-point grid of 24x24x4 was employed. The electronic structure was calculated with the PBE and modified Becke-Johnson approximation[14] since the latter gives a better approximation for the band gap.

Employing a 2x2x2 super cell with a 2x2x2 k-point mesh (72-atoms) of $WSe_2$, the phonon dispersion, density of states (DOS), and specific heat curves were obtained from the finite displacement method as implemented in the PHONOPY package[15]. Using the same supercell and k-point mesh as for the phonon dispersion calculation we determined the lattice thermal conductivity using two methods for comparison. Firstly, a single-mode relaxation-time approximation in the linearized phonon Boltzmann equation from first-principles anharmonic lattice dynamics calculations as implemented in the Phono3py package[16]. Secondly, constructed with 4 nearest neighbor interactions of $WSe_2$, an iterative self-consistent method was used for solving the phonon Boltzmann transport equation (BTE) to calculate the lattice thermal conductivity with the ShengBTE code[17].

## 3. Results and discussion

### *3.1. Structural parameters*

The fully optimized equilibrium lattice constants of $WSe_2$ using PBE+D3 are listed in Table.1 along with previously calculated data[18, 19] and experimental values[21, 20]. Our calculated values are consistent with the experimental values.

### *3.2. Elastic stability*

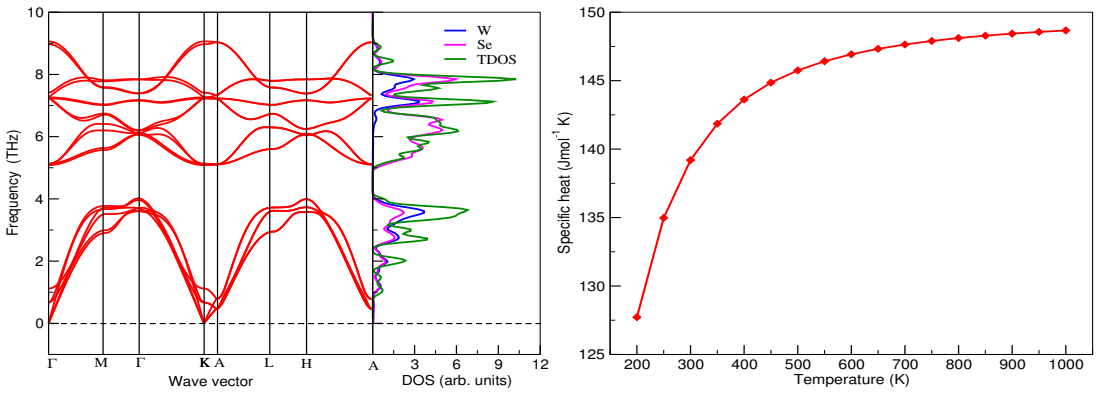
Elastic constants of $WSe_2$ were calculated in order to check the mechanical stability. $WSe_2$ in the hexagonal $P63/mmc$ symmetry has five independent elastic constants, shown in Table.2, together with the previously calculated values. It is clear that the calculated elastic constants of $WSe_2$ are broadly consistent with the previously calculated values[23, 8]. Furthermore, the elastic constants in Table.2 satisfy all the Born stability criteria for a hexagonal structure[22], which indicates that $WSe_2$ is mechanically stable.

**Table 1.** Calculated equilibrium lattice constants of $WSe_2$, together with the previously calculated and experimental values.

| | $a(\AA)$ | $c(\AA)$ |
|---|---|---|
| This work (PBE+D3) | 3.290 | 12.990 |
| Previous calc[18]. | 3.312 | 12.872 |
| Previous calc[19]. | 3.285 | 12.748 |
| Expt[21]. | 3.282 | 12.960 |
| Expt[20]. | 3.278 | 12.963 |

**Table 2.** Calculated five independent elastic constants of $WSe_2$, along with the previously calculated values in (GPa)

| | $c_{11}$ | $c_{12}$ | $c_{13}$ | $c_{33}$ | $c_{44}$ |
|---|---|---|---|---|---|
| This work | 190.16 | 33.401 | 8.4932 | 45.342 | 13.401 |
| Previous calc[23]. | 190.76 | 41.71 | 21.18 | 59.62 | 39.26 |




(a) (b)

**Figure 1.** (a) Phonon dispersion and DOS for bulk $WSe_2$. (b) Temperature dependence of specific heat capacity in $Jmol^{-1}$ K.

*3.3. Dynamical stability*

The calculated phonon band structure and density of states of $WSe_2$ are represented in Fig. 1(a). The phonon frequencies are in the range of $0 - 9$ THz. All the phonon frequencies are positive, which indicates that the structure of $WSe_2$ is dynamically stable. Since the primitive cell of $WSe_2$ contains six atoms, eighteen independent vibration modes can be found, in which six are acoustic modes and the remaining modes correspond to optical ones.

According to the results of the phonon dispersion, the specific heat capacity of bulk $WSe_2$ is calculated and shown in Fig. 1(b). It can be seen the specific heat increases monotonically with the increase of temperature until it attains the saturation value 147.326 $Jmol^{-1}$ K which is known as Dulong-Petit classical limit[25].

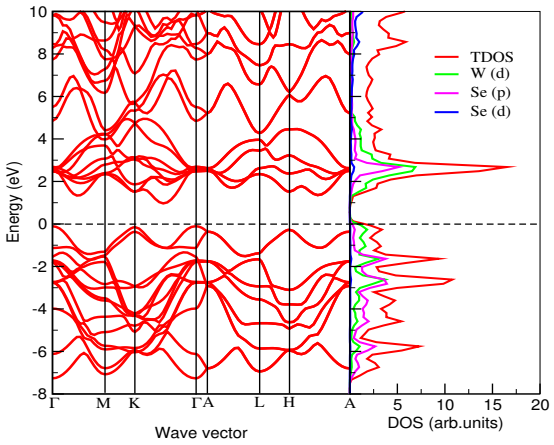



**Figure 2.** Band structure, TDOS, and PDOS of $WSe_2$ using MBJ.

*3.4. Electronic properties*

The band gap was estimated using PBE+D3 and the modified BeckeJohnson (MBJ) functional, which is known for its ability to improve the accuracy and precision of standard semilocal functionals like PBE. The band structure of $WSe_2$ along high symmetry points in the first Brillouin zone is shown in Fig. 2, with total (TDOS) and partial (PDOS) density of states.

The predicted band gaps using PBE+D3 and MBJ are 0.95 eV and 1.07 eV respectively. It is an indirect band gap with the valence band maximum at Γ and the conduction band minimum located about halfway between Γ and $K$. The MBJ result is in better agreement with the experimental value of 1.2 eV[24] than the PBE+D3 value. Density of states around Fermi level (set to zero) are dominated by W(d) and Se(p) states, and there is hybridization between the W and Se atoms in the region of valence bands.

*3.5. Lattice thermal conductivity*

The lattice thermal conductivity of $WSe_2$ at 300 K calculated with the two methods is listed in Table 3 together with previously calculated and experimental values. For both the single-mode relaxation-time approximation in the linearized phonon Boltzmann equation (Phono3py) and the self-consistent phonon Boltzmann transport equation (ShengBTE) approaches, the lattice thermal conductivity is anisotropic. The thermal conductivity in-plane is much higher than in the cross-plane direction for both approximations. All the calculated in-plane values for the thermal conductivity are considerably higher than the experimental value, while the cross-plane values are smaller than previously calculated values [18, 28] using ShengBTE, and bigger than the calculated value [28] using the Klemens model. The experimental values from Ref. [26] listed in Table 3, were determined for compacted single-crystal horizontal $WSe_2$ platelets and a direct comparison may not be justified. Our calculated cross-plane thermal conductivity is close to the experimental value. The ratio of our calculated in-plane and cross-plane thermal conductivities is close to 30 for both calculations. This is consistent with the ratio for thin film, cross-plane disordered structures, as reported in Ref.[26].

In order to compare the temperature dependent thermal conductivities of $WSe_2$ , we present the calculated lattice thermal conductivities of $WSe_2$ in the range 200 to 1000 K based on Phono3py and ShengBTE in Fig. 3(a). The thermal conductivity with derivative density of states as function of frequency at 300K are shown in Fig. 3(b). We can see that the thermal conductivity of $WSe_2$ by ShengBTE is much lower than that obtained using phono3py in the whole calculated temperature range. It is also shown that both lattice thermal conductivities

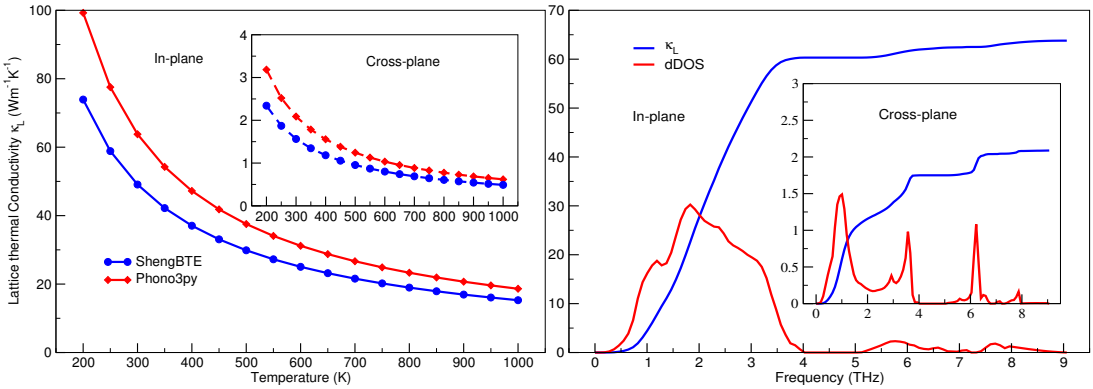



**Figure 3.** (a) Lattice thermal conductivity $Wm^{-1}K^{-1}$as a function of temperature. (b) Cumalative lattice thermal conductivity and derivative density at 300 K as a function of frequency.

decrease with increasing temperature.

Using Mattheissens rule [27] the average lattice thermal conductivity of $WSe_2$ is 5.88. 4.41, and 4.38 $Wm^{-1}K^{-1}$ for Phono3py, ShengBTE, and experimental respectively.

**Table 3.** Lattice thermal conductivities of $WSe_2$ in $Wm^{-1}K^{-1}$ at 300 K.

| | Phono3py | ShengBTE | Sheng[18] | Sheng[28] | Klemens[28] | Expt[26] |
|---|---|---|---|---|---|---|
| In-plane | 63.789 | 49.092 | 50 | 69.58 | 14.795 | 9.7 |
| Cross-plane | 2.088 | 1.563 | 6 | 7.02 | 0.90 | 2.09 |

## 4. Conclusion

We have investigated the structural, electronic, mechanical and dynamical properties as well as the lattice thermal conductivity of bulk $WSe_2$ from a first principles Density Functional Theory approach. We confirmed that van der Waals forces play an important role in the inter-layer interaction of $WSe_2$ and that the compound is mechanically and dynamically stable. Furthermore, we showed that the thermal conductivity of bulk $WSe_2$ is highly anisotropic with the in-plane thermal conductivity much higher than the cross-plane thermal conductivity. Our calculated cross-plane conductivities are numerically close to the known experimental value, but the in-plane values are considerably larger than the experimental value. The reason for this is not clear. The low cross-plane thermal conductivity is encouraging and suggests that an in-depth study of transport properties of $WSe_2$ to investigate its thermoelectric properties is justified.


## Acknowledgements

One of the authors (Mahmoud M.A. Mahmoud) would like to acknowledge the financial support received from Sinnar University, Sinnar, Sudan. We also wish to acknowledge the Centre for High Performance Computing (CHPC), Cape Town, South Africa, for providing us with computing facilities.

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