Effect of exchange-correlation functional type and spin-orbit coupling on thermoelectric properties of ZrTe₂

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Abstract

Zirconium ditelluride is a layered two-dimensional transition-metal dichalcogenide and a topological Dirac semimetal. Due to the presence of heavy elements which lead to lower phonon frequencies and thus lower thermal conductivity, and have enhanced spin-orbit coupling, leading to topological properties, we investigate the potential of semi-metallic ZrTe₂ for thermoelectric applications. Furthermore, given its anisotropic structure, the in-plane and cross-plane transport properties are probed in order to understand which direction is favorable for better thermoelectric properties. In this work, we study the effect of different exchange-correlation (XC) functionals on the electronic band structure of ZrTe₂. We show that band structure and specifically the bandgap is extremely sensitive to the choice of the XC functional and the inclusion of the spinorbit interaction in the model. As a result, the electronic and thermoelectric properties are also significantly affected. As expected, the hybrid functional HSE+SOC yields the closest bandgap to the experiment. The Seebeck coefficient of the studied structure is small due to the overlap of the bands. We show that strain can lower the overlap of the bands but cannot open a gap and improve thermoelectric properties.

Keywords: exchange-correlation functional, Seebeck Coefficient *PACS:* 0000, 1111 2000 MSC: 0000, 1111

1. Introduction

Thermoelectric modules are of great interest in various applications such as electricity generation from waste heat [1, 2, 3], solid state refrigeration [4, 5], active cooling [6, 7], and small scale heat scavenging [8, 9, 10]. Thermoelectric modules' power generation efficiency and refrigeration coefficient of performance are assessed by the quality of the materials used as p and n legs. The thermoelectric figure of merit, zT is a dimensionless parameter defined as $zT = \frac{\sigma S^2 T}{\kappa}$, where σ , *S*, *T* and κ are respectively the electrical conductivity, Seebeck coefficient, absolute temperature, and the thermal conductivity. The search for good thermoelectric materials with large figure of merit [11] has been going on for more than half a century now. Original efforts were focused on metals and pure elements, and shifted to heavily doped semiconductors after the historic contributions from Ioffe [3], Goldsmid [2] and others. Today, heavily-doped semiconductors are by far the most studied class of thermoelectric materials. They have electrical

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Figure 1: Power factor multiplied by room temperature (T=300 K) of several semiconductors and semimetals, ranging from hundredth to more than 5 W/m.K. Semimetal/metals are in blue on the right and semiconductors in green on the left. [12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28]

conductivity values on the order of $10^5 S m^{-1}$ which is a few orders of magnitude smaller than best metals, but their Seebeck coefficient is more than an order of magnitude larger than metals, making them ideal candidates as thermoelectric materials. For more than half a century bismuth antimony telluride alloy $(Bi_{2-x}Sb_xTe_3)$ had a record zT of around 1. However, using nanostructuring, Poudel et.al. [29] increased the measured zT of bismuth antimony telluride alloys to 1.4, and opened up a pathway to improve the thermoelectric properties of already-known semiconducting thermoelectric materials by further reducing their thermal conductivity. Among semiconductors, recent techniques for zT improvement has been mostly focused on lowering κ by using different strategies such as nanostructuring [30, 31], special geometries [32], half-Heusler alloys [33, 34], and using complex thermoelectrics [35]. Additionally, any growth in σS^2 , known as power factor (PF), could increase zT. Power factor can be improved by engineering either the electronic band structure and/or the scattering rates. Several methods such as resonant doping [36], band convergence [37] and modulation doping [38] have been successfully used to improve the thermoelectric power factor. More novel techniques to increase the thermometric power factor were recently tested including electron-electron correlation in Kondo semiconductors [39], resonant band formation [40, 41, 42], and magnetic semiconductors [43]. In Fig. 1 we show the maximum power factor, which has been optimized as a function of the doping concentration, for several semiconductors and semimetals at 300 K. Semimetals and zero-gap semiconductors have properties in between metals and semiconductors. There has been a recently renewed interest in these materials and they are emerging as promising candidates for thermoelectric applications especially at ambient temperatures and below [44, 45, 46, 47, 48, 49, 50]. In our recent work [44, 51], we showed semimetals are potential candidates for high thermoelectric power factor materials due to concurrent high intrinsic carrier concentration and high mobility. Additionally, asymmetry in the band structure, e.g. heavy holes versus light electrons, yields high Seebeck values which will subsequently enhance the power factor. Furthermore, the presence of heavy elements would lower the lattice thermal conductivity, and as a consequence facilitate the way to achieve greater zT values. Our previous study was focused on bandgap engineering with strain for $TiSe_2$ [52], in which we showed that tensile strain can open up the gap in this semimetal and cause an exponential change in the electron density and therefore electronic properties. Replacements of heavy elements in the structure would lower lattice thermal conductivity and thus raise zT. For this purpose, $ZrTe_2$ seems to be a potential candidate not only due to the same crystal structure as TiSe₂ but also containing heavier elements in the unit cell. Zirconium and Tellurium have been reported to form ZrTe₅, ZrTe₃, and ZrTe₂ phases. ZrTe₅ is known as a Dirac semimetal and has been studied for bipolar conduction [53], quantum spin Hall effect for spintronic applications [54, 55], resistivity anomaly by a temperature-induced Lifshitz transition [56], and anomalous Hall effect [57]. $ZrTe_3$ crystal is described as a set of infinite chains generated by stacking ZrTe₃ prisms along the y-direction [58] in which charge density wave [59] and superconductivity [60] are of interest. $ZrTe_2$ has caught attention in the recent decade as a promising topological transition-metal dichalcogenide compound [61]. To illustrate its topological properties, Wang et al. [62] grew layered ZrTe₂ on SrTiO₃ using pulsed-laser deposition and recorded a magnetoresistance (MR) as large as 3000% at temperature of 2 K under a magnetic field of 9 T. Additionally, electron mobility of the layered ZrTe₂ film was measured to be as high as $1.8 \times 10^4 \ cm^2 V^{-1} s^{-1}$. ZrTe₂ mono-layer was found to be semi-metallic with bands crossing along the Γ to A direction. Near the Fermi level, bands show a linear dispersion featuring massless 3D Dirac fermionic characteristic of topological Dirac semimetals [61]. High-throughput density functional theory (DFT) calculations have recently caught much attention to ease materials exploration and fasten the computations by preparing an amenable data-set of electronic band structures for a variety of compounds in a way to facilitate DFT calculations, however, DFT results are likely to vary depending on the exchange-correlation (XC) functional type, and spin-orbit coupling. As an example due to a low computational expense PBE XC functional is often utilized in high-throughput band structure calculations. In this work, we have used the structure from the materials project[63] as the input and investigated the effect of XC functional type as well as spin-orbit coupling on the structural and electronic properties. More importantly, we depicted how thermoelectric properties may change depending on the DFT input parameters.

2. Computational Methods

First-principles calculations of bulk $ZrTe_2$ were conducted using density functional theory (DFT) with a projector augmented wave method [64] via the Vienna ab initio simulation package (VASP) [65, 66]. Experimental lattice parameters were taken from [61] (a=3.95 Åand c=6.54 Å) and the structure was fully relaxed to find the equilibrium lattice constants with the lowest energy. Various exchange-correlational (XC) functional types including PBE [67], PBEsol [68], and SCAN+rVV10 [69] were tested (see table 1). PBEsol is known to be able to produce the lattice constant relatively accurately. SCAN-rVV10 is, on the other hand, among the latest

Table 1: Relaxed lattice constants of $ZrTe_2$ using different XC functionals with and without spin-orbit coupling. the number in parentheses is the relative deviation from experimental values.

Method	a (Å)	c(Å)
Experiment	3.950	6.540
PBE	3.884 (-1.67 %)	6.582 (0.64 %)
PBE+SOC	3.889 (-1.54%)	6.580 (0.61%)
PBESOL	3.810 (-3.54%)	6.448 (-1.41%)
PBESOL+SOC	3.814 (-3.44%)	6.443 (-1.48%)
SCAN+rVV10	3.911 (-0.99%)	6.436 (-1.59%)
SCAN+rVV10+SOC	3.918 (-0.81%)	6.429 (-1.70%)



Figure 2: Band structure of bulk $ZrTe_2$ calculated without spin-orbit coupling (left) and with SOC (right). Results from *PBE* are shown using solid black lines, HSE-06 results are shown with blue and *mBJ* results are shown with red lines. All calculations are done at the PBE+SOC-optimized lattice constants

family of functionals which is capable of handling van der Waals interactions, and is relevant in the case of layered 2d transition metal dichalcogenides. The kinetic energy cutoff was chosen to be 500 eV, and a $18 \times 18 \times 12$ Monkhorst–Pack k-point mesh in the first Brillouin zone was selected to cover electronic states. While PBEsol and SCAN- rVV10 are used to perform lattice parameter optimization, in order to lessen the underestimated bandgap, HSE06 [70]($\alpha = 25$ Fock exchange $\mu = 0.2\text{Å}^{-1}$), and the modified Becke-Johnson (mBJ) [71, 72](*CMBJ* = 1.3) exchange correlation functionals were used with and without spin-orbit coupling (SOC) effect, using the PBE+SOC-optimized lattice constants. The latter functional turned out to produce the closest lattice parameters to the experimental ones.

Hybrid functionals such as HSE are found to be more accurate in electronic properties calculations of systems with a gap in their spectrum. For large systems, however, the exact Hartree-Fock exchange calculation is computationally considerably heavier. Heyd et.al. [70] developed an approach (called HSE) based on a screened Coulomb potential to remedy the bandgap problem. Later, Becke et.al. introduced an effective potential approximation[71, 72] (called MBJ) which recovers the Talman-Shadwick potential in atoms which does not require heavy computation of two-electron integrals. Details of each exchange-correlation functional is explained in the corresponding references. This approximation is not as accurate as HSE but is faster to compute and is an improvement over the standard PBE functional approach. Transport properties were assessed via the semi-classical Boltzmann transport equation and the constant relaxation time approximation (CRTA) as implemented in the BoltzTraP code [73]. The interpolating k-point grid converged after taking a grid 45 times denser than the initial DFT grid. All calculations were conducted with T=300 K. Herein, an ad-hoc constant relaxation time of 10 fs was assumed in order to develop an order-of-magnitude value for electrical and thermal conductivites in standard units. Apart from the Seebeck values, there is no claim on the accuracy of the value of the relaxation time and the resulting conductivities. One may optionally state conductivity results as conductivity per relaxation time.

3. Results

Table 1 summarizes the optimized lattice constants obtained for different functionals, among all XC functional types, PBE+SOC yields the closest lattice constant to the experimentally measured ones. Zr-Te bond length in the relaxed structure of PBE+SOC was found to be 2.875 Å very close to 2.89 Å which is the bond length experimentally measured through Extended X-ray Absorption Fine Structure (EXAFS) [74]. Adopting the PBE+SOC lattice constants, we proceeded with the band structure calculations using various XC functional types PBE, mBJ, and HSE06. To ease the comparison between SOC and no SOC, we put the two band structures side by side in Fig.2. For PBE, it is observed that SOC has pushed down the conduction band at *L* point (0.22 eV), in addition to band splitting at the Γ point.HSE bands seem to only slightly modify the PBE bands, whereas mBJ conduction bands show a large upward shift of 0.57 eV. Moreover, effective mass values significantly rely on the XC functional type: as an example the effective mass at the Γ point for mBJ and HSE functionals are respectively 29 % and 8% smaller compared to PBE.

Muhammad et.al. [74] synthesized $ZrTe_2$ and experimentally measured the band gap to be -0.27 eV. This value is fairly close to HSE+SOC bandgap of -0.30 eV. Bandgap predictions of other XC functionals are depicted in Fig. 3. It is noteworthy to add Muhammad et.al. [74] claimed to open a gap by alloying and upon partial substitution of tellurium with selenium.



Figure 3: Band gap values range from -0.88 eV (mBJ+SOC) to -0.09 eV (mBJ). Negative bandgap values signify that there is overlap between conduction and valence bands, and the former have states of lower energy than the latter.



Figure 4: Projected band structure of PBE+SOC, of p-orbitals of Te (a) and d orbital of Zr (b) within 2 eV of the Fermi level. Color bars show the contribution of each orbital from 0 (blue) to the highest contribution 0.7 (red). Right: Projected density of states of PBE+SOC, of orbitals of each species, Zr and Te. Dominant states are d orbitals of Zr in the conduction and p orbitals of Te in the valence bands.

Figure 4 depicts the orbital-projected band structure of ZrTe₂under PBE XC functional including SOC effect. The SOC effect is of great importance not only because of a significant alteration in the overlap between L and the Γ point but it is also reported to cause a band inversion at the Γ point [75] as ZrTe₂ was reported to be a topological transition-metal dichalcogenide [61]. The band structure computed in this work is in agreement with previous calculations [75]. Projected density of states in Fig. 4 reveals the Zr-Te bond is a chemical bond between d-orbitals of zirconium (blue DOS) and p-orbital of tellurium (green DOS). In order to evaluate the atomprojected band structure, eigenfunctions were projected on each atomic orbital show the contribution of orbitals around the intrinsic Fermi level. Calculated projected wave functions show that the valence band close to the Fermi level is mainly of the p orbital of Tellurium, whereas the conduction band around Fermi level is mainly made of d orbitals of Zirconium. This is also in agreement with projected density of states shown in Fig. 4 (right). In contrast to ZrTe5 which is magnetic [76, 77], ZrTe2 is non-magnetic. There are four electrons in the s and d orbitals of Zr which fill the 2 electrons missing in p-orbitals of each Te, such that d orbitals of Zr are empty. Additionally, the total magnetization as well as the orbital magnetization were confirmed to be zero in our calculations.

Next, we studied the thermoelectric properties using semi-classical Boltzmann transport equation within the constant relaxation time approximation (CRTA). The electrical conductivity (σ), the Seebeck coefficient (S), and the electronic part of thermal conductivity (κ_{el}) tensors at a given temperature, T, can be obtained from:

$$\frac{\sigma_{ij}}{e^2} = \int \left(-\frac{\partial f(E,\mu,T)}{\partial E}\right) \Xi_{ij}(E) dE \tag{1}$$

$$\frac{(\sigma \cdot S)_{ij}T}{e} = \int (-\frac{\partial f(E,\mu,T)}{\partial E})(E-\mu)\Xi_{ij}(E)dE$$
(2)

$$K_{ij}T = \int (-\frac{\partial f(E,\mu,T)}{\partial E})(E-\mu)^2 \Xi_{ij}(E)dE$$
(3)

in which f is the Fermi-Dirac distribution function and e is the electron charge, μ is the chemical potential, and $\Xi(E)$ is the transport distribution function (differential conductivity), and is defined as:

$$\Xi_{ij}(E) = \frac{1}{\Omega N_k} \sum_{n,k} \nu_i(n,k) \nu_j(n,k) \tau_{n,k} \delta(E - E_{n,k})$$
(4)

where Ω is the unit cell volume and $v_i(n, k)$ is the ith Cartesian component of the velocity of the nth band at wave vector k with N_k k-points. The electronic part of the thermal conductivity is given by $\kappa_{el} = K - \sigma S^2 T$

Finally, τ is electron relaxation time which we take arbitrarily to be 10 fs just so that physical quantities have the correct units. Although this might be a reasonable assumption for the evaluation of the Seebeck coefficient, for an accurate evaluation of the intrinsic electrical and electronic thermal conductivity, one needs to quantitatively calculate electron-phonon scattering rates as a function of energy. There is no claim of accuracy on the reported results on conductivities in this paper, which are really conductivities "per relaxation time".

As $ZrTe_2$ crystallizes in the space group of (\overline{p} 3m1), thermoelectric properties are anisotropic along a and c-axis. Figure 5 shows the in-plane (XX) on the right, and the cross-plane (ZZ) on the left, plots of the Seebeck coefficient using different functionals. The Seebeck coefficient values of all three XC functionals are relatively close to each other. Since SOC effect turned out



Figure 5: Theoretical Seebeck coefficients of bulk $ZrTe_2$ for various XC functional types with SOC versus chemical potential in the cross-plane (a) and in-plane (b) directions.

to play a significant role in band structure, herein, SOC was included in all thermoelectric properties calculation, although *mBJ* functional without SOC, shown in the supplementary materials, resulted in the highest Seebeck values due to the semi-metallic electronic structure in addition to the asymmetry of bands (Fig.5 in the supplementary materials). Such a drastic variation (from 170 to 20 μ v/K) highlights the importance of XC functional type as well as the SOC effect on thermoelectric properties. On the contrary, electrical conductivity of the semi-metallic band structure (*mBJ* without SOC) is significantly lower(see the supplementary materials), about 2 orders of magnitude, compared to metallic structures (Fig. 6). Similarly, the semi-metallic structure exhibits the lowest electronic thermal conductivity due to lower carrier concentration. It is noteworthy to add ZrTe₂ shows a higher electronic thermal conductivity compared to similar compounds e.g. TiSe2₂ [52] because of larger overlap between valence and conduction bands.

Validity of electrical conductivity and electronic thermal conductivity calculations could be evaluated by Wiedemann–Franz law [78] which relates electrical conductivity to thermal conductivity of a metal by $L_0 = \frac{\kappa}{\sigma T} = 2.44 \times 10^{-8} W\Omega K^2$ where L_0 is the Lorenz number. Regardless of XC functional type, the computed Lorenz number deviates by less than 5% from the theoretical value of Lorenz number. It is worth noting that the Lorenz number is independent of the relaxation times assuming the same relaxation times for both thermal and electrical currents of electrons. The power factor states the trade-off relationship between carrier concentration and



Figure 6: Theoretical electrical conductivity of bulk $ZrTe_2$ for various XC functional types with SOC versus chemical potential along cross-plane (a) and in-plane (b) directions for an arbitrarily chosen τ of 10 fs.



Figure 7: Electronic thermal conductivity of bulk $ZrTe_2$ for various XC functional types with SOC versus chemical potential along cross-plane (a) and in-plane (b) directions for an arbitrary relaxation time scale of $\tau = 10$ fs.



Figure 8: Theoretical power factor multiplied by room temperature for bulk $ZrTe_2$ HSE06+SOC for an arbitrary relaxation time scale of $\tau = 10$ fs



Figure 9: Band gap of $ZrTe_2$ applying PBE (green circles) HSE06 (pink triangles) XC-functional and Zr-Te bond length (orange squares) changes versus an in-plane strain. Changes in the bandgap are not large as Zr-Te bond length increases and then decreases with a tensile strain.



Figure 10: Average Seebeck coefficient changes versus in-plane strain for bulk $ZrTe_2$ HSE06+SOC under 0 and 2% tensile strain.

Seebeck coefficient and gives an estimation of the current-activated heat flow, although report of zT requires the total thermal conductivity. Having calculated the Seebeck coefficient and electrical conductivity, we proceeded with the computation of the power factor of ZrTe₂ within the constant relaxation time approximation. In order to convert the unit to the same unit as thermal conductivity, one may multiply the power factor by the absolute temperature (PF×T). Figure 8 exhibits the PF×T at room temperature. Due to the metallic electronic structure of ZrTe₂ PF×T is not large, but as one can see from the figure.9, it can strongly vary with the chemical potential, i.e. by doping.

Band structure engineering of materials through strain has been utilized to modify the electronic dispersion and subsequently electronic properties. Gui et.al. [79] studied electronic structure of graphene under applying a planar strain by first-principles calculations and reported a symmetrical strain distribution keeps band-gap zero while the pseudogap linearly diminishes versus the strain strength. In contrast, an asymmetrical strain distribution was found to open a gap at the Fermi level. Herein, a symmetric in-plane strain was applied to $ZrTe_2$ bulk structure varying from -2% to 2%. Moving from a 2% compressive strain to a 2% tensile strain overlap between valence and conduction band decreases about 100 and 130 meV for PBE and HSE06 XC functional types, respectively. These are relatively small compared to previously studied materials such as $TiSe_2$ [52], $PdSe_2$ [80], MoS_2 [81, 82], and Ge [83]. Such a small change in band gap of $ZrTe_2$ could be understood from small deviations in Zr-Te bond length shown in Fig. 9. The band width is inversely proportional to bond length. Therefore, the band width does not largely change, thus, only small changes emerge in overlaps between conduction and valence bands. As a consequence, the Seebeck coefficient changes slightly by applying a planar strain to the structure (see Fig.10).

4. Conclusion

We studied the impact of XC functional type as well as SOC on $ZrTe_2$ electronic structure which may switch from metallic to a semi-metallic state (mBJ without SOC). Depending on the XC functional type and SOC, the band gap varied from -0.09 eV to -0.78 eV, but closest agreement with experimental data of -0.27 eV was found with HSE+SOC (-0.30 eV). Likewise PBE+SOC and SCAN+rVV10 provided the closest agreements with the experimental lattice constants. Subsequently, thermoelectric properties including Seebeck coefficient and electrical conductivity and the electronic thermal conductivity strongly changed with the XC functional choice. This behavior is justified by a larger overlap between valence band at Γ point and conduction band at L points which gives rise to a larger free charge carrier concentration. Lastly, applying an in-plane strain caused a small shift in bands due to small changes in Zr-Te bond length and subsequently band width. The Seebeck coefficient did not however dramatically change due to a non monotonic change of the Zr-Te bond length with strain.

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