

Calculating Crystal Properties of Bismuth

Telluride Using Wien 2k

By Louise Henderson

Advisor: Janet Tate

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Abstract

Wien2k was used to calculate the band structure and the density of states of bismuth telluride. It was confirmed from previous computational research, that spin-orbit coupling needs to be included in the calculations to give more accurate results. Including spin-orbit coupling resulted in the band structure size to decrease from 0.33 eV to 0.11 eV. Including spin-orbit coupling also caused the band gap to change from being a direct band gap to an indirect band gap. These results will be used as a foundation for more in depth calculations, which will include calculating the band structure and the density of states of bismuth telluride with the addition of dopants, calculating the electrical and thermal conductivity, and calculating the Seebeck coefficient.

1.0 Background

1.1 Bismuth Telluride

Bismuth telluride is a narrow band gap semiconductor with good thermoelectric properties that will be discussed later in this paper. It has a hexagonal lattice type in space group $R\bar{3}m$. All hexagonal crystals have the lattice parameters $a=b\neq c$, $\alpha=\beta=90^\circ$, and $\gamma=120^\circ$. The space group refers to the symmetry operations that when performed on the unit cell form the larger crystal structure. The “R” stands for rhombohedral. The rhombohedral unit cell is shown in Figure 1, three rhombohedral unit cells form the hexagonal unit cell. The “ $\bar{3}$ ” in the space group refers to rotation-inversion. The unit cell is rotated three times before returning to its original position then the rotation is followed by inversion. The “3” also refers to the crystal structure having 3-fold symmetry and $\frac{360^\circ}{3} = 120^\circ$ degrees of rotation. The “m” in the space group represents “mirror” and that there is a plane within the unit cell that reflects the molecule onto itself.

There are three different types of atoms in the structure, one type of bismuth atom, and two types of tellurium atoms. In the figure the purple atoms are tellurium atoms and the blue are bismuth atoms. The molecular formula for bismuth telluride is Bi_2Te_3 but can be rewritten as $Bi_2Te_2Te_1$ to show that there are twice as much of one type of tellurium atom. To differentiate between the two types of tellurium atoms one type will be referred to as “Te1” or “the first tellurium atom” and the other type will be referred to as “Te2” or “the second

tellurium atom.” The difference between the types of tellurium atoms is the distances to their nearest neighbors and what their nearest neighbors are. These differences are important to the crystal properties of the material. The atoms in Bi_2Te_3 are arranged in layers, and so can be classified as a layered semiconductor. The layers are in the order Te2-Bi-Te1-Bi-Te2 and are labeled in Figure 1. Te2 atoms have a layer of more Te2 atoms on one side and a layer of Bi atoms on the other, whereas Te1 atoms are surrounded by only Bi atoms. The bonding between the Te2 and Bi atoms and between the Te1 and Bi atoms are covalent and ionic but between the Te2 atoms they are held together by weaker Van der Waals bonding.

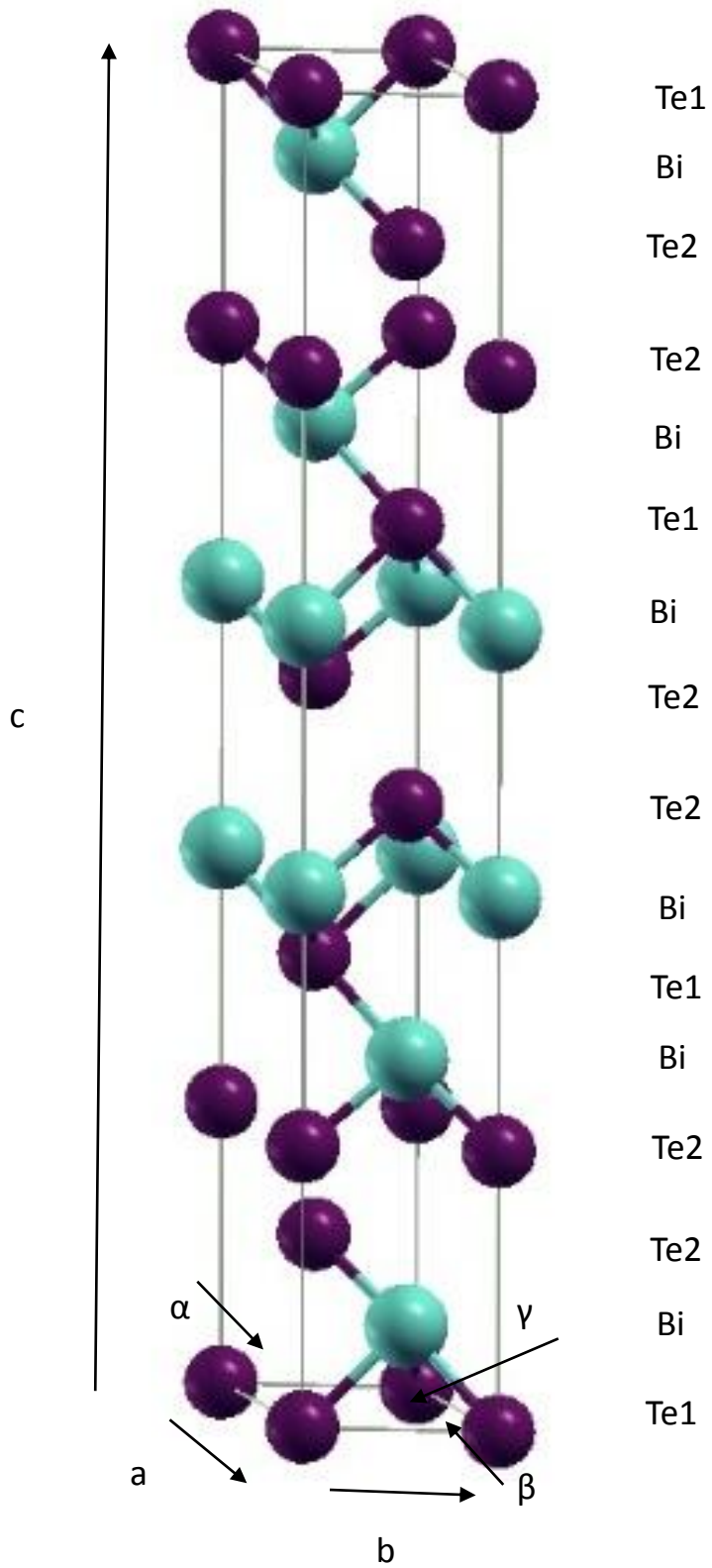


Figure 1 The rhombohedral unit cell of bismuth telluride. The purple atoms are tellurium atoms and the blue atoms are bismuth atoms. The layers are labeled on the right. From XCrySDen.

1.2 K-space

To find the allowed energy levels that an electron in a solid can have, the Schrödinger equation for the molecular state, Equation 1, has to be solved.

$$H|\Psi\rangle = E|\Psi\rangle \quad (1)$$

The molecular wave function, $|\Psi\rangle$, is a linear combination of atomic wave functions and is a function of the wave vector k .

K -space is the reciprocal space of real space and the first Brillouin zone is the reciprocal lattice in k -space where all eigenstates can be labelled uniquely (Sutton 51).

1.3 Band structure

The band structure, or dispersion relation, of a material is the allowed energies that an electron in the material can have as a function of k . The band structure consists of energy bands that can be classified as either conduction bands, valence bands, or core electron bands. The conduction and valence bands are of the most interest and give information on whether the material is a metal, a semimetal, a semiconductor, or an insulator.

The most important feature of the band structure is the region where electrons cannot have a range of energies for any value of k and is called the band gap. The band gap is

measured from the conduction band minimum to the valence band maximum. Semiconductors and insulators have band-gaps but metals and semi-metals do not and is part of what places a material in one of these categories.

The size of the band gap and whether it is a direct or indirect gap is important to the electronic and optical properties of a solid. A direct band gap occurs when the conduction band minimum, called the conduction band edge, and the valence band maximum, called the valence band edge, are at the same k -point and an indirect band gap occurs when the conduction band edge and the valence band edge are at different k -points. Another important feature is the Fermi Energy, this is the energy where at 0 K all states below it are filled and all states above it are empty.

A related property of a material is the density of states. The density of states is the number of states that an electron can occupy in a material per unit of energy as a function of the energy.

1.4 Spin-orbit Interaction

Spin-orbit interaction describes the interaction between electrons in an atom and the nucleus of the atom. This interaction causes a shift in the allowed energy levels of the electrons. The simplest case of this is in the hydrogen atom where one electron orbits a proton. The electron moves through the electric field of the proton resulting in a motional magnetic field, or from the electron's perspective, as shown below in Figure 2, the proton is orbiting around it and the proton acts like a current loop, which creates a magnetic field at the

center of the loop where the electron is (McIntyre 2012, 388). The energy shifts are caused by the interaction between the intrinsic spin magnetic moment of the electron and the magnetic field resulting from the orbit of the proton (McIntyre 2012, 388).

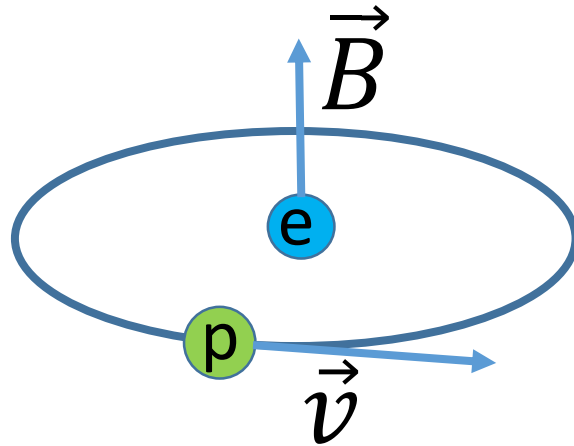


Figure 2 Spin-orbit coupling from the perspective of the electron in a hydrogen atom.

The larger an atom is, the more spin-orbit interaction affects the allowed energy levels by causing energy levels to lose some of their degeneracy. Bismuth with an atomic mass of 208.9804 u and tellurium with an atomic mass of 107.06 u are relatively large atoms so spin-orbit interaction is expected to have a noticeable effect.

1.5 Thermoelectric Materials

Thermoelectric materials are materials that display the Seebeck effect and the Peltier effect. They are typically narrow band gap semiconductors with a band gap of less than 0.25 eV at 300 K (Tritt and Subramanian 2006). A thermoelectric device is made from an array of

thermoelectric couples. A thermoelectric couple consists of a p -type and an n -type semiconductor that are connected through metallic electrical contact pads (Tritt and Subramanian 2006).

A semiconductor can be made p -type or n -type with doping, the addition of impurities in a material. For a semiconductor to be made n -type a donor impurity is added to the crystal (Kittel 209). This donor atom is added to the crystal by replacing an atom, it is not placed in an interstitial location, and contains one more valence electron than the atom that it replaces. When the donor atom is ionized it contributes an electron to the conduction band (Kittel 209). To make a semiconductor p -type it is doped with acceptor impurities that contain one less valence electron than the atom that it replaces. When the acceptor atom is ionized it accepts an electron from the valence band (Kittel 211). Impurities in a semiconductor can also be caused by a missing atom in the crystal, these are called deficit semiconductors (Kittel 209). Bismuth telluride is naturally a p -type semiconductor but it can be doped with excess tellurium atoms to replace bismuth atoms, and iodine or bromine to replace tellurium atoms to become n -type (Tritt and Subramanian 2006).

The Seebeck effect, or thermopower, is when there is a temperature difference across a material which induces an electrical potential difference across it that is proportional to the temperature difference (Tritt and Subramanian 2006). This effect is used in power-generation devices. The ratio of the voltage difference to the temperature difference is called the Seebeck coefficient and is an intrinsic property of the material. The Seebeck coefficient is α in Equation 2 below. Figure 3 shows this effect in a thermoelectric couple.

$$\Delta V = \alpha \Delta T \quad (2)$$

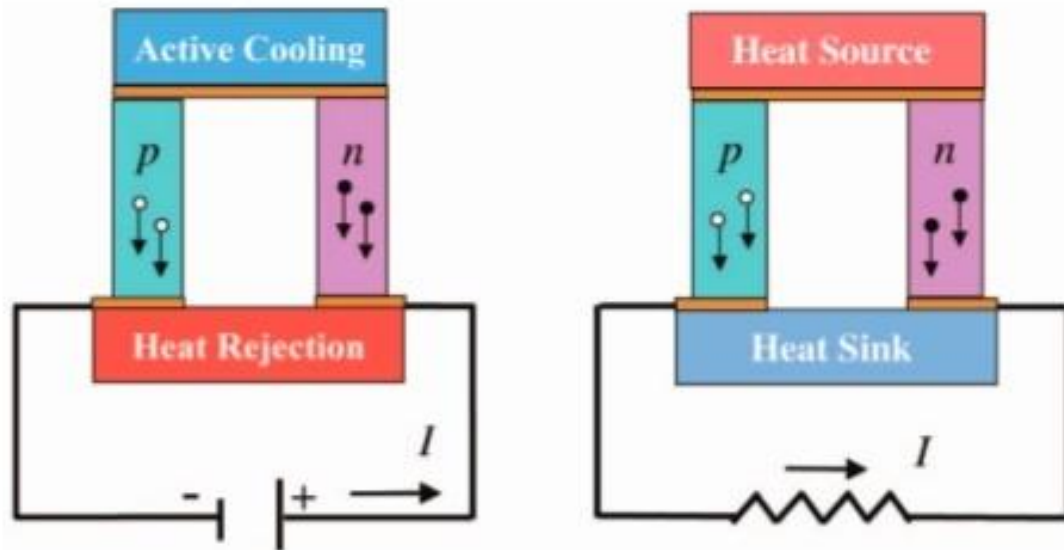


Figure 3 A diagram of thermoelectric couples in the refrigeration mode (left) and the power-generation mode (right). Taken from Tritt and Subramanian (2006).

The Peltier effect is similar to the Seebeck effect. When a current is run through a thermoelectric couple, as shown in Figure 3, heat is rejected on one sides and absorbed on the other causing a temperature gradient. This effect is used for thermoelectric refrigeration devices (Tritt and Subramanian 2006). The Peltier coefficient is related to the Seebeck coefficient in Equation 3 below, where Π is the Peltier coefficient.

$$\Pi = \alpha T \quad (3)$$

There are many factors that contribute to whether a material is a good thermoelectric. A large factor is the materials figure of merit, ZT , which is dependent on the temperature. The larger the ZT is the more efficient the material is. The figure of merit can be represented by

Equation 4 below where α is the Seebeck coefficient, σ is the electrical conductivity, ρ is the electrical resistivity, T is the temperature, and κ is the total thermal conductivity (the lattice and the electronic contributions.)

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{\alpha^2 T}{\rho \kappa} \quad (4)$$

Equation 4 is the figure of merit for a material, the figure of merit for a thermoelectric couple is shown in Equation 5 below.

$$ZT = \frac{(\alpha_p - \alpha_n)^2 T}{\left[(\rho_n \kappa_n)^{1/2} + (\rho_p \kappa_p)^{1/2} \right]^2} \quad (5)$$

For a material to be a good thermoelectric it needs to have a high merit factor, so it must have a high electrical conductivity, a low thermal conductivity, and a large Seebeck coefficient, around 150-250 $\mu V/K$ or larger (Tritt and Subramanian 2006). A high electrical conductivity is considered to be on the order of $10^3 \text{ } 1/\Omega cm$ and a low thermal conductivity is considered to be less than 2 W/mK (Tritt and Subramanian 2006). A good thermoelectric material is generally also a narrow band-gap semiconductor with a band gap of less than 0.25 eV at 300 K (Tritt and Subramanian 2006). Bismuth Telluride has a thermal conductivity of about 1.9 W/mK and a measured Seebeck coefficient of 260 $\mu V/K$ for p -type and 250 $\mu V/K$ for n -type (Mishra et al. 1997).

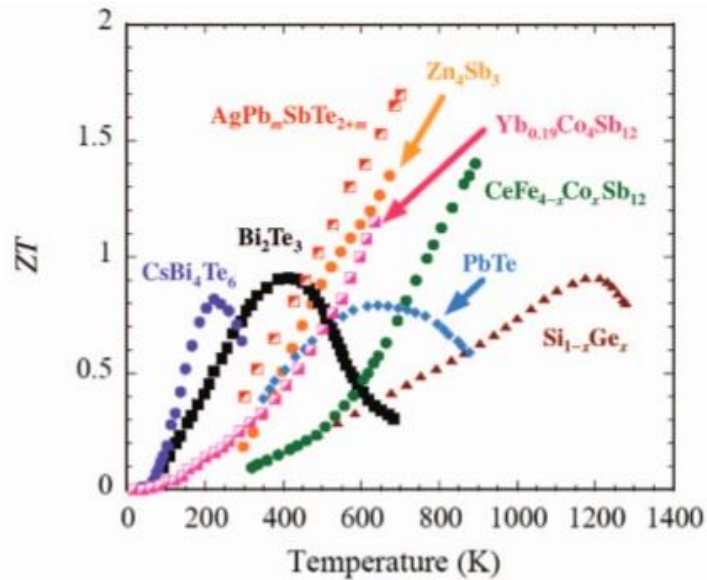


Figure 4 The merit factor for different materials. Taken from Tritt and Subramanian 2006.

Figure 4 shows the merit factors of eight materials. Thermoelectric materials tend to peak at around $ZT = 1$ but there are no theoretical or thermodynamic reasons for this limit (Tritt and Subramanian 2006). The merit factor for bismuth telluride peaks at about 400 K which is shown in Figure 3, so at that temperature it is most efficient. Bismuth telluride may not be the best thermoelectric material but it is the most studied, and has been studied for over thirty years and this is one of the reasons it was chosen for this project.

1.5 Wien2k

Wien2k is a program package that uses density functional theory (DFT) and the full-potential (linearized) augmented plane wave + local orbitals ((L)APW+lo) method to calculate electronic properties of solids (www.wien2k.at).

DFT uses the Born-Oppenheimer approximation which assumes that the electrons in a solid are in their ground state and it uses the independent electron approximation. The independent electron approximation assumes that all the electrons in a solid are moving independently from one other but experience an effective potential from the other electrons (Sutton 206). DFT states that when assuming these approximations it is only necessary to know the electronic charge density to find the ground state properties of the solid (Sutton 206). The local density approximation (LDA) is also used in DFT calculations. This approximation takes the charge density in a volume element in the solid then uses the exchange-correlation potential to find the exchange correlation energy of the volume element while ignoring that the charge density varies throughout the solid (Sutton 209). Part of the effective potential felt by an electron in the solid is the exchange-correlation potential.

2.0 Methods

Wien2k and XCrySDen was used for the band structure and density of states calculations. XCrySDen is a program used for Crystalline and molecular structure visualization (www.xcrysden.org). For each calculation done a new session should be made, and each session should have a different name to avoid possible errors. To create a structure for the material the user opens "StructGen" in Wien2k and then inserts "3" in the box labeled "Number of atoms," this is the number of inequivalent atoms in the crystal. After clicking "Generate Template," the space group, lattice parameters and lattice type can be entered. The structure also needs a title, and as with the session name this title should be different from other crystal

structure names in other sessions to avoid possible errors. The user chooses "166_R-3m" for the space group and the lattice parameters are entered, which are $a = b = 4.38029$, $c = 30.54569$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. These values are from the article by Aliabad and Kheirabadi (2014).

As previously mentioned bismuth telluride has one type of bismuth atom and two types of tellurium atoms, the positions of one of each type of atom needs to be specified. The positions used were also from the article by Aliabad and Kheirabadi (2014). This is done in the boxes labeled "Pos 1" by the labels "Atom 1," "Atom 2" and "Atom 3." The first box by each of these labels is what atom it is by the symbol, bismuth is "Bi" and tellurium is "Te." The second box by each label is the name chosen for each atom. The first set of boxes labeled "Atom 1" is bismuth and was named "Bi." The position used was (0.4001,0.4001,0.4001). "Atom 2" is the first tellurium atom and was named "Te1." The position used was (0,0,0). "Atom 3" the second tellurium was named "Te2." The position used was (0.2095,0.2095,0.2095). In these boxes the atomic number Z can also be specified however putting this in manually often causes an error and it is better to leave them as zero and let the program put in the atomic number from the type of atom it is. Once this is done the structure is saved by clicking "Save Structure" at the bottom of the page. There are four options given "Set RMT automatically and continue edited" is done once and the user can choose to reduce the RMTs (radial muffin tin) by a percentage, 0% is chosen and the structure is saved again. This time out of the options given "save file and clean up" is chosen and the structure file is complete.

Next the calculation is initialized. In the initialize calculation page every button needs to be clicked through in order that it is highlighted. If there is a file with the option of being saved

it should be saved. Most of the options given can be left as default. Under the “x lstart” button the exchange correlation potential can be chosen but it is left as the default “PBE_GGA” or the Generalized Gradient Approximation. This exchange correlation potential was used in the article that the results were compared to. When the “x kgen” button is reached the number of k -points was chosen to be 200 for the density of states calculation and 100 for the band structure calculation. Because the k -points are only quasi-continuous it is not always best to have a larger number. Once all the options have been gone through the SCF cycle is ran and spin-orbit coupling can be added to the calculations at this point. It takes ten cycles for the program to calculate the correct charge density?? Under “Utils.” there is a “show dayfile” option that displays when the program goes through a cycle and when the calculation is completed.

At this point the band structure and density of states can be calculated. To calculate the density of states the user choses the option “DOS” under “Tasks.” Most of the options are left as default but for the program to calculate the partial density of states the “(session name).int” file needs to be edited. Figure 5 is the default file and the file is changed to contain information for the s and p orbitals of all three atoms and the interstitial states as in Figure 6.

```

Title
-0.50 0.002 1.500 0.003 # EMIN, DE, EMAX, Gauss-broadening(>de)
  1  N  0.000           # NUMBER OF DOS-CASES specified below, G/L/B broadening (Ry)
  0  1  total           # atom, case=column in qtl-header, label
  1  1  Atom1 tot
  1  2  Atom1 s
  1  3  Atom1 p
  2  1  Atom2 tot

```

Figure 5 The default (session name).int file

```

Title
-0.50 0.002 1.500 0.003 # EMIN, DE, EMAX, Gauss-broadening(>de)
 11  N  0.000           # NUMBER OF DOS-CASES specified below, G/L/B broadening (Ry)
  0  1  total           # atom, case=column in qtl-header, label
  1  1  Bi tot
  1  2  Bi s
  1  3  Bi p
  2  1  Te1 tot
  2  2  Te1 s
  2  3  Te1 p
  3  1  Te2 tot
  3  2  Te2 s
  3  3  Te2 p
  4  1  Interstitial

```

Figure 6 The (session name).int used to plot the partial density of states.

The numbers in the first column in Figure 6 correspond to which atom it is, “0” is for all atoms, “1” is bismuth, “2” is the first tellurium atom, “3” is the second tellurium atom, and “4” is for the interstitial states. The “11” is the total number of partial density of states specified in the file. The numbers in the second column correspond to the orbitals, “1” is the total, “2” is for *s*-orbitals, and “3” is for *p*-orbitals. Wien2k can calculate the partial density of states for other orbitals but the *s*-orbitals and *p*-orbitals are relevant for Bismuth Telluride. After this file

is edited the remaining options are gone through and the "(session name).outputt file is saved and the density of states can be plotted.

To obtain a value for the band gap the user selects "show all files" under "files." There are two files "(session name).dos1ev" and "(session name).dos2ev." The ".dos1ev" file contains information about the total density of states, the bismuth atom contributions to the density of states, and the first tellurium atom contributions to the density of states. The ".dos2ev" file contains information about second tellurium atom and the interstitial states. Because the band gap is where the total density of states is zero for the ".dos1ev" file is selected. The energy ranges where the total density of states is zero ($<10^{-4}$) is the band gap.

To calculate the band structure XCrysdn is used to choose a k -path in the first Brillouin zone. After the k -path is saved under "Tasks" there is the option titled "bandstructure" that is chosen. "from xcrysdn" is chosen from the pull-down menu then the button "create (session name).klist_band" is clicked on. All the options are gone through, the option "edit (session name).insp" needs to be edited. At the top of the file there is a value for the Fermi Energy that needs to replace the "0.xxxx" in the file then the file is saved. The remaining option is selected and the band structure can be plotted.

3.0 Results/Discussion

3.1 Density of States

The results for the band structure and the density of states were compared to the results in the article by Aliabad and Kheirabadi (2014) and were found to match. These results were also obtained using Wien2k and were done with and without spin-orbit coupling. However in this article the band structure was only shown for the energy ranges 1.0 eV to -1.0 eV.

The density of states without including spin-orbit coupling are shown in Figures 7-10 and are very similar to the density of states including spin-orbit coupling shown in figures 11-14. When not including spin-orbit coupling, the band gap was found to be 0.19049 eV when considering the total density of states to be exactly zero. When considering values less than 10^{-4} to be zero the band gap is 0.32654 eV. The band gap found when including spin-orbit coupling and considering the density of states to be exactly zero was found to be 0.02721 eV and when considering values less than 10^{-4} the band gap is 0.10885 eV. The band gap found in the article also decreased when including spin-orbit coupling, from 0.28 eV to 0.12 eV. The measured value for the band gap have been found to be 0.11 eV and 0.16 eV (Aliabad and Kheirabadi). The results for the density of states from the article are shown in Figure 15.

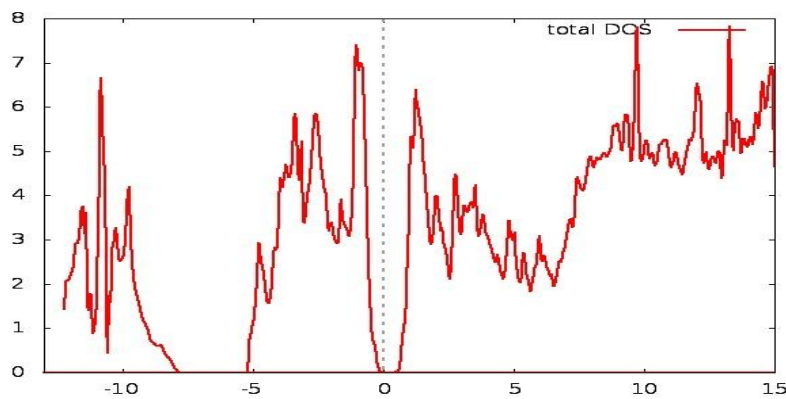


Figure 7 Total density of states not including spin-orbit coupling.

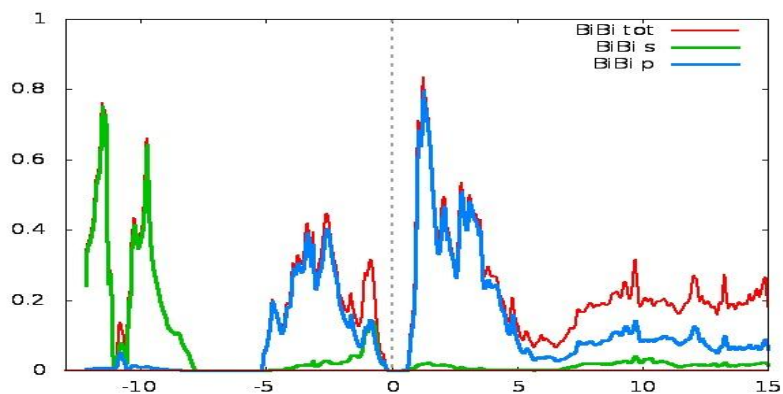


Figure 8 Bismuth atom contributions to the density of states not including spin-orbit coupling.

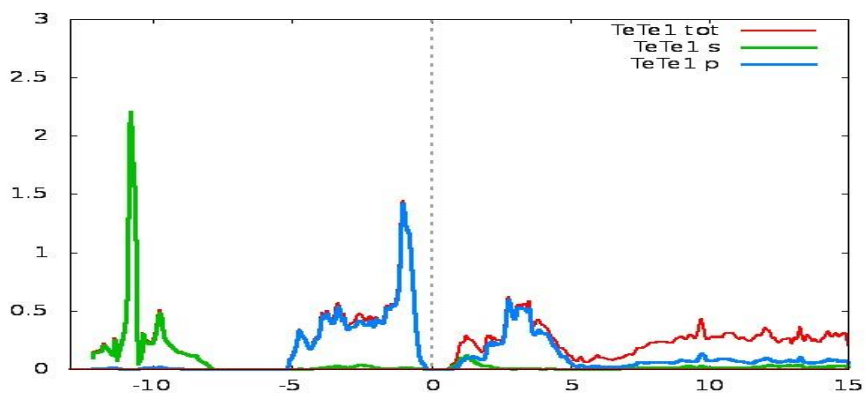


Figure 9 The first tellurium atom contributions to the density of states not including spin orbit coupling.

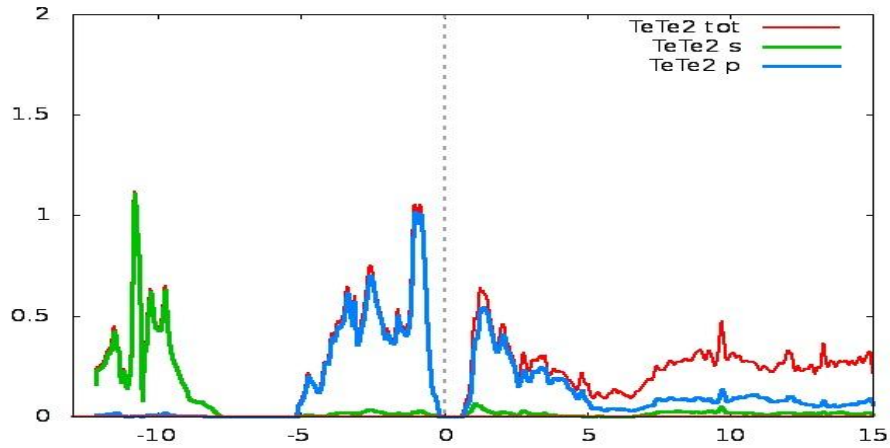


Figure 10 The second tellurium atom contributions to the density of states not including spin-orbit coupling.

The partial density of states shows that the s -orbitals of both types of tellurium atoms contribute the most states to the core bands and that the p -orbitals of both types of tellurium atoms contribute the most states to the valance bands. The p -orbitals of the bismuth atoms contribute the most to the conduction bands and most of the bismuth atoms s -orbital contribute to the core bands but not as much as the tellurium atoms.

Figures 11-14 are the density of states and partial density of states including spin-orbit coupling. The results for which atoms contribute the most to either the core, valance, and conduction bands are the same.

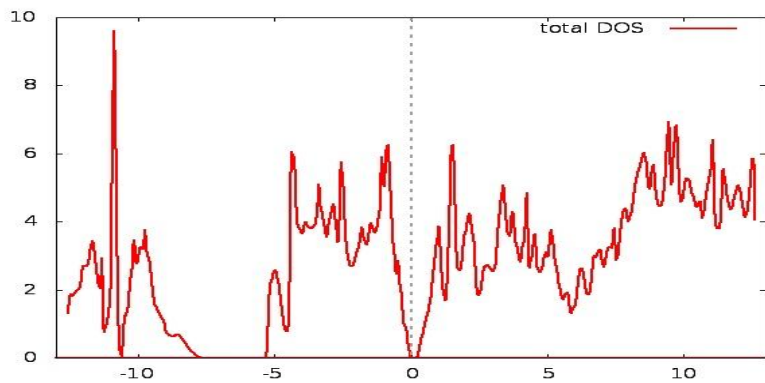


Figure 11 The total density of states including spin-orbit coupling.

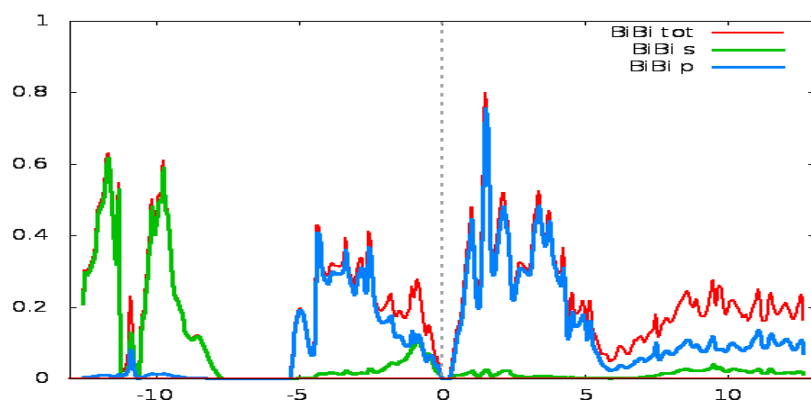


Figure 12 The bismuth atom contributions to the density of states including spin-orbit coupling.

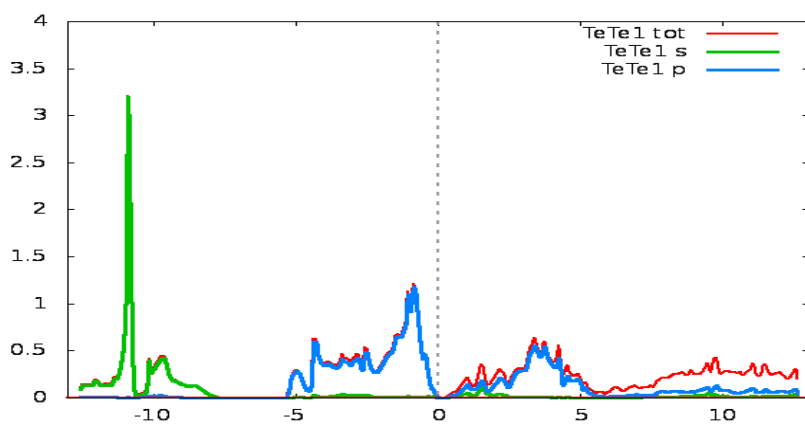


Figure 13 The first tellurium contributions to the density of states including spin-orbit coupling.

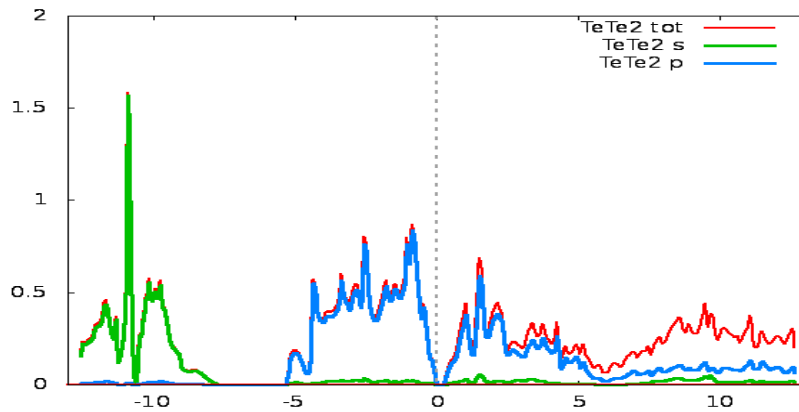


Figure 14 The second tellurium atom contributions to the density of states including spin-orbit coupling.

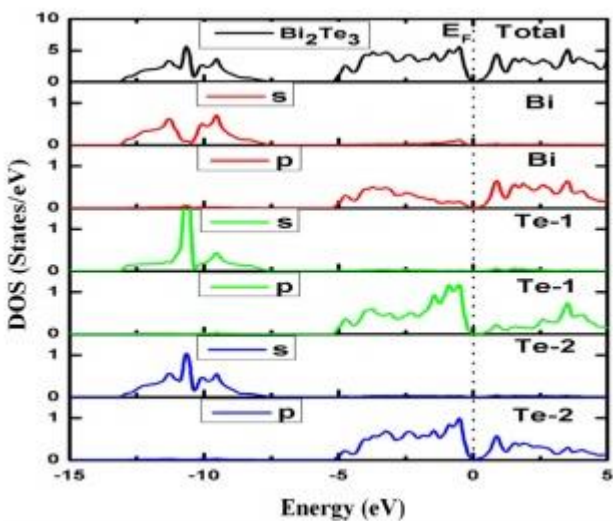


Figure 15 The density of states results from Aliabad and Kheirabadi (2014).

3.2 Band structure

XCrySDen shows the reciprocal lattice of the crystal and with this the path in k -space for the band structure to be calculated can be chosen. Figure 16 shows the reciprocal lattice and the path that was chosen is shown in blue and goes from Γ to Z to F and then back to Γ . These

points were chosen so the results could be compared to the results in the article by Aliabad and Kheirabadi (2014) which used the same k -path. The results from the article are shown in Figure 18.

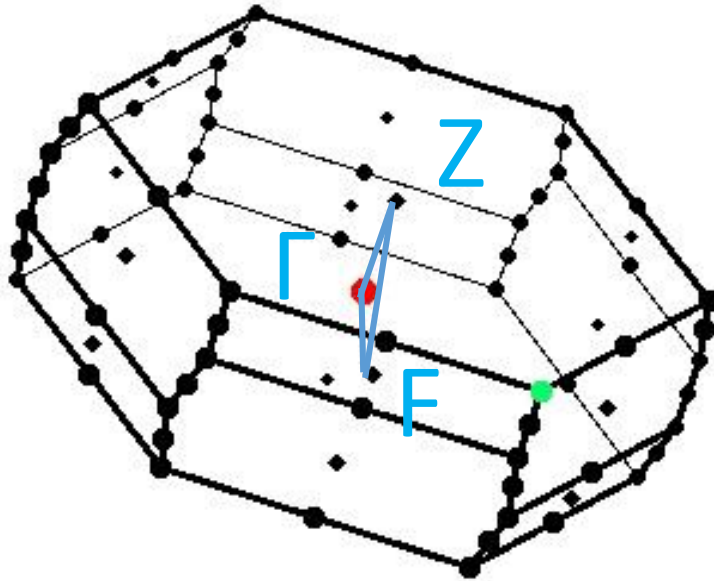


Figure 16 The first Brillouin zone of bismuth telluride. From XCrySDen.

The band structure without spin orbit coupling was done first and is shown in Figure 17. The conduction band minimum and the valence band maximum are both at the Γ point making it a direct band gap, with a size of 0.33 eV. This area is magnified on the right.

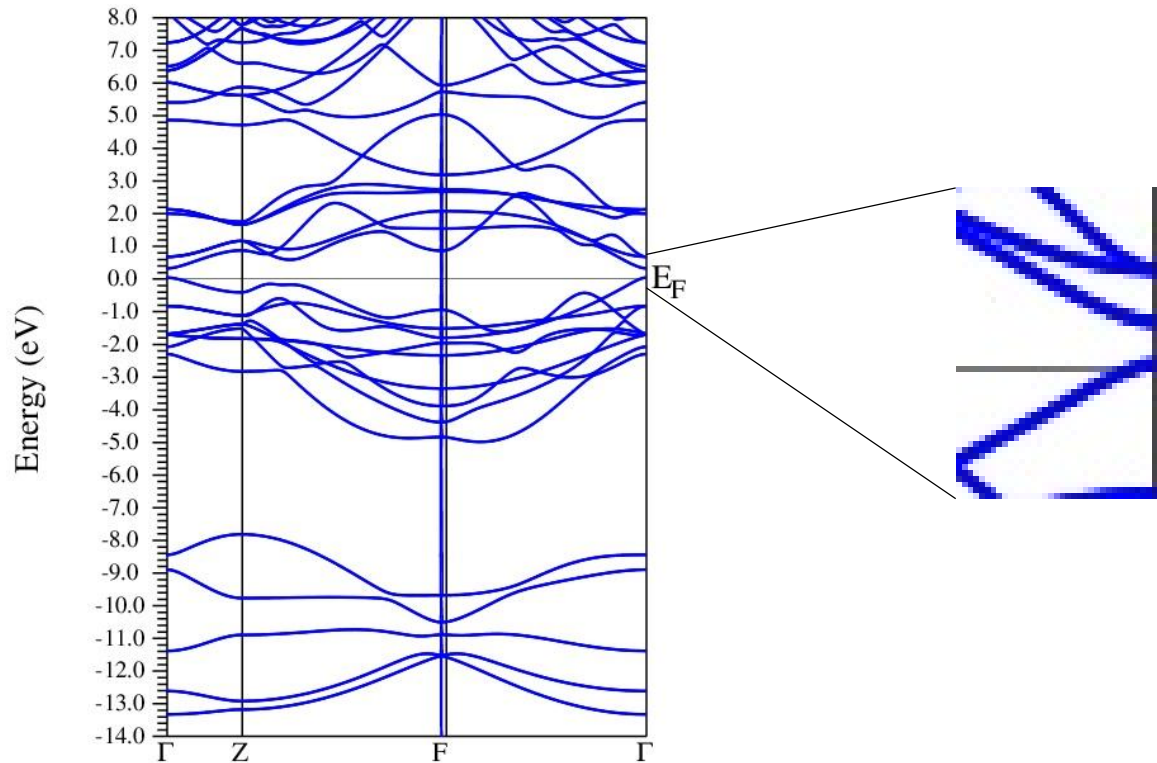


Figure 17 The band structure of bismuth telluride without including spin-orbit coupling.

The band structure including spin orbit coupling is shown in figure 18. At the Γ point there is no longer a conduction band minimum or a valence band maximum. The conduction band minimum is now between the Γ and the Z points and the valence band maximum is now between the Z and F points, because they are not at the same k point the band structure now has an indirect band gap, with a size of 0.11 eV. Including spin-orbit coupling in the calculations brings the band gap closer to the experimental values of 0.11 eV and 0.16 eV (Aliabad and Kheirabadi 2014).

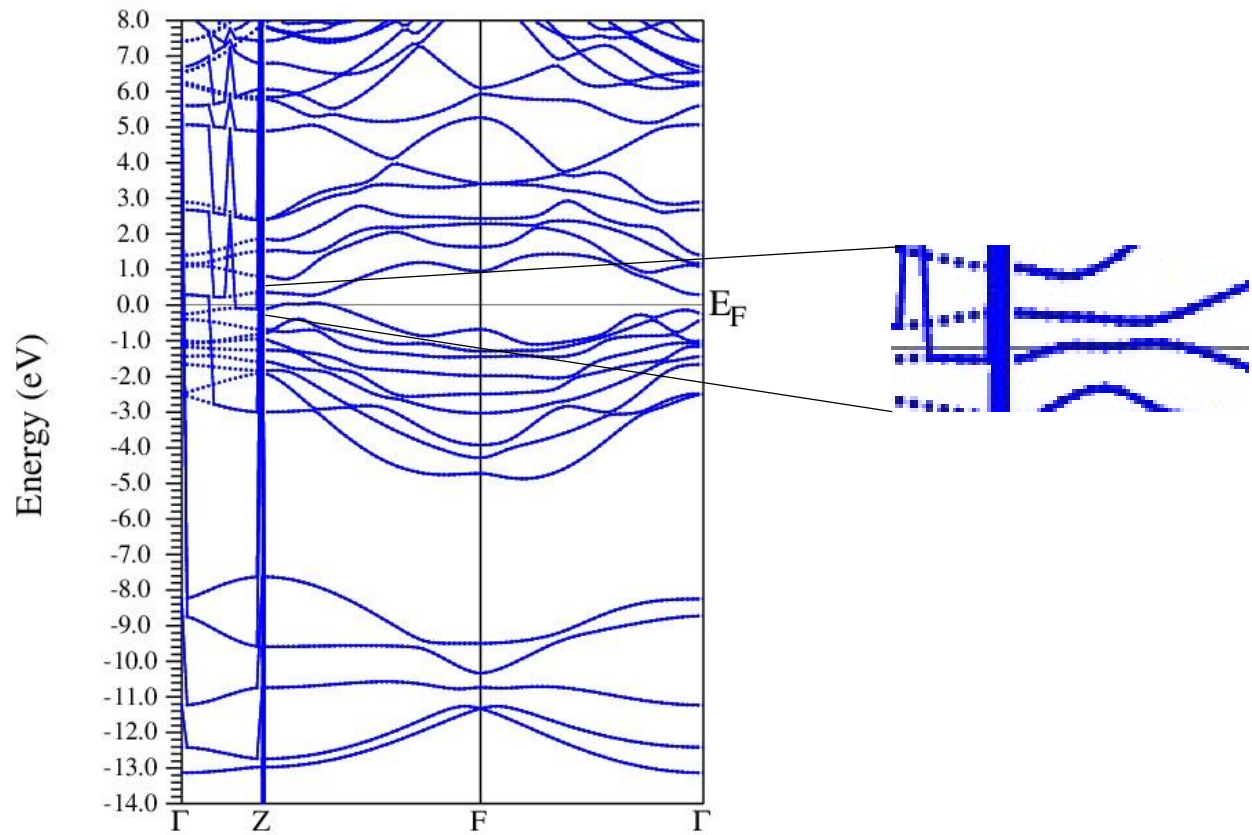


Figure 18 The band structure of bismuth telluride including spin-orbit coupling.

The sharp vertical lines that deviate from the dotted lines in Figure 18 are errors, however the dotted lines match the calculated band structure in the literature that it was compared to.

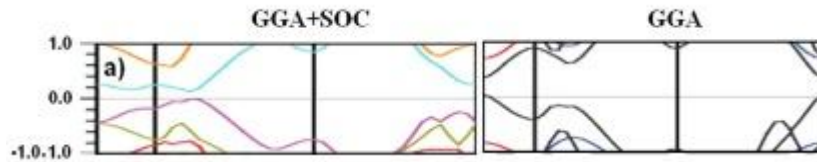


Figure 19 The band structure results from Aliabad and Kheirabadi 2014. Including spin-orbit coupling is on the left and not including spin-orbit coupling is on the right.

4.0 Conclusion/ Future Work

Using Wien2k the density of states and the band structure of bismuth telluride and be calculated. The calculated band gap was found to decrease from 0.33 eV to 0.11 eV when including spin orbit coupling and it was found to change from a direct band gap to and indirect band gap.

Future work would include further exploration of the thermoelectric properties of bismuth telluride. This would include calculating crystal properties including dopants such as excess tellurium, iodine, and bromine. The electrical conductivity, thermal conductivity, and the Seebeck coefficient could also be calculated.

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