Connecting thermoelectric performance and topological-insulator behavior: Bi$_2$Te$_3$ and Bi$_2$Te$_2$Se from first principles

Hongliang Shi, David Parker, Mao-Hua Du and David J. Singh

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056

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Thermoelectric performance is of interest for numerous applications such as waste heat recovery and solid state energy conversion, and will be seen to be closely connected to topological insulator behavior. In this context we here report first principles transport and defect calculations for Bi$_2$Te$_2$Se in relation to Bi$_2$Te$_3$. The two compounds are found to contain remarkably different electronic structures in spite of being isostructural and isoelectronic. We discuss these results in terms of the topological insulator characteristics of these compounds.

I. INTRODUCTION

Thermoelectric performance is typically quantified in term of a dimensionless figure-of-merit $ZT$, given by the following expression:

$$ZT = \frac{S^2\sigma T}{\kappa}$$

Here $S$ is the Seebeck coefficient or thermopower, $\sigma$ is the electrical conductivity, $T$ the absolute temperature, and $\kappa$ the thermal conductivity. The expression shows that for good performance one desires both high electrical conductivity and Seebeck coefficient, but these are difficult to obtain simultaneously due to opposite dependencies on carrier concentration. Hence thermoelectric performance is a counter-indicated property of materials that does not commonly occur, and determining and optimizing a usable high performance thermoelectric material remains a difficult challenge.

Thermoelectric performance is of considerable engineering and technological importance due to the many potential applications of this technology, which include vehicular exhaust waste heat recovery, energy harvesting, heating and cooling, and solid state energy conversion. In all of these applications higher thermoelectric performance would be extremely beneficial for enhanced device performance. Currently, there are relatively few thermoelectrics with $ZT$ values above unity, the minimum necessary for a thermoelectric to be considered high performance. This has greatly limited the utility of thermoelectrics, leading to substantial efforts aimed at raising $ZT$.

Presently the thermoelectric most employed in applications is Bi$_2$Te$_3$, a narrow gap semiconductor which shows optimized $ZT$ figures of approximately unity at ambient temperature. It is presently used primarily in niche applications.

Of great consequence for potential applications, at temperatures above 300 K, the performance of Bi$_2$Te$_3$ degrades rapidly due to bipolar conduction, or the excitation of carriers of both positive and negative charge. This causes the thermopower to decrease with increasing temperature, the opposite of the usual situation, and in addition causes large increases in the electronic thermal conductivity. Both of these effects are destructive for thermoelectric performance, as suggested by Eq. 1. These effect generally occurs when the semiconductor band gap (about 0.15 eV in Bi$_2$Te$_3$) is not sufficiently large relative to the device operating temperature. In the absence of bipolar conduction, $ZT$ is a strongly increasing function of increasing temperature, with performance ultimately limited only by the decomposition or melting point of the material.

Bi$_2$Te$_3$, therefore, could be an extremely high performance thermoelectric at temperatures of 400 to 500 K, if only its band gap were somewhat larger. This would be of great practical importance given that two major potential applications - exhaust waste heat recovery and solid state thermophotovoltaic conversion - operate at temperatures around 500 K. Part of this work will explore a potential scenario for achieving this.

While Bi$_2$Te$_3$ has been known as a high performance thermoelectric for several decades, it also forms the basis for a family of topological insulators (TI) (Bi,Sb)$_2$(Te,Se)$_3$. Many have observed a connection between these two properties, and various explanations proposed: perhaps the simplest one is the observation that good thermoelectrics are usually heavy atomic mass, small band gap semiconductors, as the heavy atom helps to induce low lattice thermal conductivity, as well as the TI band inversion (via spin-orbit coupling), and the small band gap high carrier mobility. A floor on the degree of band inversion necessary to produce TI is set by the band gap, presumably making large band gap TI’s less common.

However, not every, or even a significant fraction of heavy mass small gap materials, are good thermoelectrics or good TI materials. Furthermore, some materials without heavy mass atoms or small gaps are excellent thermoelectrics, such as...
Mg$_2$(Si,Sn) and Si-Ge. In addition, from an electronic point of view TI behavior is of interest for an undoped material (where the Fermi energy is in the gap) while high thermoelectric performance is usually observed with the Fermi energy doped into the bulk bands.

Like thermoelectric performance, topologically insulating behavior is of considerable practical importance due to its potential for technological applications, such as memory applications for computers. Here we show a clearer connection between topologically insulating behavior and thermoelectric performance. Briefly, we will see that complex, non-parabolic band structures are favorable both for TI behavior and high thermoelectric performance. In this work we will see that two materials studied as topological insulators - Bi$_2$Te$_3$ and Bi$_2$Te$_2$Se - appear to have very complex band structures that are in general highly beneficial for thermoelectric performance. These complex band structures are related to TI behavior, as the band inversion necessary for this generally creates complex band structures not typically describable in terms of the usual anisotropic effective mass approximation. Remarkably, the two compounds are very different in the near band edge electronic structures leading to very different transport behavior.

In Figure 1 we depict schematically the effects of spin-orbit coupling in producing the complicated band structures just mentioned. Briefly, the band inversion central to TI behavior is induced by spin-orbit coupling, which then opens a gap at the points where the bands would otherwise cross. As depicted in Figure 1, this generally leads to non-parabolic behavior, often with near-linear Kane band-type dispersions. Thus a single, parabolic, non-degenerate band edge, as shown in the left side of this figure, evolves into a non-parabolic, complex, degenerate band edge, as is often observed in high-performance thermoelectrics. More detailed discussions of these effects can be found in Refs. 3–5.

Bi$_2$Te$_3$ exhibits the band inversion required for topologically insulating behavior, but is inconvenient for studying TI. This is because of its small band gap and small defect formation energies, which mean that low bulk electrical conductivity - a prerequisite for observing the topologically protected surface states - is difficult to attain. This is due both to large bipolar conduction, in the lightly doped intrinsic regime and large band conduction (in the heavily doped extrinsic regime favored by the low vacancy formation energies). This small band gap also presents a substantial hindrance to thermoelectric performance. In this work we will see that two materials studied as topological insulators - Bi$_2$Te$_3$ and Bi$_2$Te$_2$Se - appear to have very complex band structures that are in general highly beneficial for thermoelectric performance. These complex band structures are related to TI behavior, as the band inversion necessary for this generally creates complex band structures not typically describable in terms of the usual anisotropic effective mass approximation. Remarkably, the two compounds are very different in the near band edge electronic structures leading to very different transport behavior.

II. ELECTRONIC STRUCTURE CALCULATIONS

We performed the present calculations using BoltzTraP transport theory with the first principles electronic structure, employing the constant scattering time approximation (see Ref. 14 for a detailed description of this approximation.) The BoltzTraP code$^{15}$ was used for these transport calculations, and the electronic structure obtained using the modified Becke-Johnson potential of Tran and Blaha (TB-mBJ).$^{16}$ This potential gives very much improved band gaps for simple semiconductors and insulators as compared to standard density functionals.$^{16-21}$ These calculations employed the general potential linearized augmented plane wave (LAPW) method,$^{22}$ as implemented in the WIEN2k code.$^{23}$ Experimental lattice parameters, ($a$=4.3792 Å, $c$=30.481 Å for Bi$_2$Te$_3$ and $a$=4.305 Å, $c$=30.00 Å for Bi$_2$Te$_2$Se)$^8$ were used. The free internal atomic coordinates were determined by total energy minimization using the local density approximation (LDA).

The LDA was used because it was found to yield better structural and vibrational properties for Bi$_2$Te$_3$ than generalized gradient approximations when used with fixed lattice parameters for Bi$_2$Te$_3$. The structure relaxation was done treating relativity at the scalar relativistic level, as relaxation including spin-orbit coupling is not supported in WIEN; the
The calculated band gaps are 0.14 eV for Bi$_2$Te$_3$ and 0.22 eV for Bi$_2$Te$_2$Se. Thus the band gap of Bi$_2$Te$_2$Se is significantly larger than that of Bi$_2$Te$_3$, although still smaller than that of the higher temperature thermoelectric PbTe (0.36 eV, by a similar method).

Experiment also shows a similar increase in band gap when Se is added to Bi$_2$Te$_3$, i.e. the optical absorption edge is reported to increase from $\sim 0.15$ eV in Bi$_2$Te$_3$ to $\sim 0.30$ eV at a composition Bi$_2$Te$_2$Se.

Hinsche and co-workers$^{27}$ reported Boltzmann transport calculations for Bi$_2$Te$_3$. They found results similar to ours for the thermopower and conductivity, and in particular found better conductivity for the in-plane directions and higher values of the thermopower for $p$-type doping.

We present the calculated band structure for both materials in Figure 3. Although some of the features, such as the valence bands more than 0.5 eV below the valence band maximum, are similar the fine details of the electronic structure are in fact very different. For example, both band extrema for Bi$_2$Te$_3$ are at off-symmetry locations (the Bi$_2$Te$_3$ valence band maximum V is approximately (2/5,2/5,1/3) in the rhombohedral basis, a non-symmetry point), while both extrema for Bi$_2$Te$_2$Se are at the $\Gamma$ point. This has important implications for thermoelectric performance as the increased band degeneracy of Bi$_2$Te$_3$ is one likely contributor to its high thermoelectric performance. The valence band of Bi$_2$Te$_3$ has two subsidiary maxima located near the Z point, while Bi$_2$Te$_2$Se has two subsidiary valence band local maxima located at different points.

One plausible question to ask, given the argument of the Introduction for the correspondence between the complex band structures favorable for both thermoelectric performance and topological insulators, is the relationship of the above band structures to spin-orbit coupling. In order to address this question we present in Figure 4 the results of calculations in which the effective strength of the spin-orbit coupling is varied from zero to unity (the fully spin-orbit case). As the plots indicate, without spin-orbit both materials are direct gap semiconductors with band edges at the $\Gamma$ point and comparatively
FIG. 5. The calculated isoenergy surfaces of Bi$_2$Te$_3$ and Bi$_2$Te$_2$Se. The energies given represent the isoenergy value, relative to the respective band extrema.

parabolic bands. In both cases, however, as the spin-orbit interaction is turned on the band gap decreases radically until in the strength=0.75 plot the gap is very small - less than a tenth of an eV, and the bands become visibly non-parabolic. Finally, as in the right-hand panel of Figure 1, when the full strength of spin-orbit is applied a new gap opens up - between the Z and $\Gamma$ points for Bi$_2$Te$_3$, but returning to the $\Gamma$ point for Bi$_2$Te$_2$Se, and these band structures do appear to be comparatively non-parabolic. Note also that the motion of the band edges in Bi$_2$Te$_3$ away from the $\Gamma$ point with the advent of spin-orbit automatically implies a more complex Fermi surface structure due to the associated degeneracy, irrespective of the parabolicity of the bands.

By way of comparison, the band structure of Bi$_2$Te$_2$Se is in fact much more similar to that of Bi$_2$Se$_3$, which also has both extrema at the $\Gamma$ point, than that of Bi$_2$Te$_3$, despite being closer to the latter compound compositionally. Further insight can be obtained by plotting the isoenergy surfaces of both materials, as presented in Figure 5. For both materials, for $p$-type doping a highly anisotropic, non-parabolic behavior is evident. Recall that in a parabolic approximation the isoenergy surfaces takes the form of ellipsoids of revolution, even if effective mass anisotropy is considered. Neither of these materials exhibits a $p$-type Fermi surface at all resembling an ellipsoid; for Bi$_2$Te$_3$ at the smallest energies a distinct triangular shape appears, followed at increasing binding energy by a bell-like structure and ultimately augmented with planar “wings”. The shape is very different for Bi$_2$Te$_2$Se, with the initial VBM at $\Gamma$ rapidly evolving into an “X” shaped figure (note that there are in fact 6 subsidiary extrema in this structure), which is then followed by a ring-like feature.

All of these deviations from spherical, or ellipsoidal, shapes can be seen to be beneficial for thermoelectric performance. For a given volume (in this case effectively carrier concentration), a sphere has the minimum surface area (in this case, effectively density-of-states [DOS]), and therefore minimum thermopower, since in the degenerate limit the thermopower is proportional to the DOS mass. Hence all deviations from a spherical isoenergy surface enhance the thermopower, and the greater the deviation the greater the enhancement. An example of this effect can be found in Ref. 28. While a detailed quantitative comparison between the two materials on this basis is not readily available, we may state with some confidence that both materials, when doped $p$-type will benefit from the anisotropy of the electronic structure.

With regards to $n$-type, here the situation is substantially different. While Bi$_2$Te$_3$ still affords a substantially anisotropic isoenergy surface, with a discus shape evolving out of a non-$\Gamma$ point extremum, for Bi$_2$Te$_2$Se there is only a single $\Gamma$-centered, relatively cylindrical extremum, and this cylindrical shape is notably “closer” to a spherical shape than that of Bi$_2$Te$_3$. Hence we expect, and will later see, diminished $n$-type performance for Bi$_2$Te$_2$Se relative to Bi$_2$Te$_3$.

We note that all band structures are significantly different from the “pudding-mold” band structure proposed by Kuroki et al$^{29}$ as an explanation for the simultaneous occurrence of high thermopower and electrical conductivity in the cobaltate Na$_x$CoO$_2$. In that band structure a flat upper portion provides the large density-of-states necessary for a high Seebeck coefficient, while a dispersive portion connecting to this provides a light band which favors high conductivity. Here Bi$_2$Te$_3$ in particular, from Figs. 3 and 5, contains near-degenerate band edges resulting from its complex isoenergy surfaces that allow it to attain high conductivity without sacrificing thermopower, a distinct scenario from that of Ref. 29.

Although it is not immediately apparent from the plots, the iso-energy surfaces reflect the rhombohedral symmetry, with the off-symmetry valence band maximum for Bi$_2$Te$_3$ six-fold degenerate and the conduction band minimum located on the trigonal axis two-fold degenerate. For $p$-type Bi$_2$Te$_2$Se, the “X” emanating from the $\Gamma$ point (beginning at -0.05 eV) actually comprises six “arms”, as two of the “arms” are hidden by the projection.

III. BOLTZMANN TRANSPORT CALCULATIONS

Following the electronic structure calculations, we performed Boltzmann transport calculations of the doping and temperature-dependent thermopower and electrical conductivity, within the “constant scattering time approximation”, which shows substantial success in describing thermopower of a large number of materials. Within this theory of diffusive transport the expressions for the thermopower and conductivity are

$$S = \frac{\int dE \sigma(E)(E - E_F) f'(E - E_F)}{\int dE \sigma(E)f''(E - E_F)},$$

and
the inverse scattering rate. The constant scattering time along direction \( N \) becomes 

\[
\text{less anisotropic, and hence less non-parabolic electronic structure. We therefore focus on } p \text{-type behavior in the following.}
\]

The benefits of Bi\(_2\)Te\(_3\)Se relative to Bi\(_2\)Te\(_3\) in the \( p \)-type thermopower should not, however, necessarily be taken as quantitative evidence for likely better, or even equal, thermoelectric performance in Bi\(_2\)Te\(_2\)Se. In order to assess this we plot the average electrical conductivity versus thermopower at 300 K in Figure 7. Figure 7 reveals that in the \( p \)-type (right hand side of plot) region of thermopower around 200 \( \mu \)V/K, the two materials have virtually identical \( \sigma/\tau \), which would indicate comparable thermoelectric transport, if the scattering times are equal. The same behavior is evident at 500 K (not shown). Note that in this comparison we are not referring to the bottom portion of the graphs, near where the thermopower transitions from positive to negative. This region is firmly within the bipolar regime, well below optimal doping, and for which thermoelectric performance is generally poor. Instead we refer to the linear region adjacent to the legend, which is likely near where optimal performance would be found.

The isoenergy surfaces for \( p \)-type Bi\(_2\)Te\(_2\)Se appear to be somewhat less anisotropic than for Bi\(_2\)Te\(_3\), which may explain why the thermopower benefits versus carrier concentration do not remain when compared to \( \sigma/\tau \). With regards to \( \tau \), the scattering times may not be equal, given that in one sample of the line compound Bi\(_2\)Te\(_2\)Se disorder\(^1\) of order 5 percent was observed on the Te/Se sites, which would tend to decrease scattering times and hence electrical conductivity. Optimal electrical conductivity in Bi\(_2\)Te\(_2\)Se therefore may necessitate extremely careful sample preparation in order to minimize this effect.

For a further comparison, in Fig. 8 we depict the calculated power factor \( S^2\sigma/\tau \) (with respect to an average, unknown scattering time) at 300 K for both materials, for \( p \)-type and \( n \)-type, as a function of carrier concentration (carriers per unit cell). The plot depicts comparable behavior for \( p \)-type, consistent with the behavior in Figures 6 and 7, noting that shorter scattering times in Bi\(_2\)Te\(_2\)Se may degrade the performance of this material relative to that of Bi\(_2\)Te\(_3\). For \( n \)-type this figure suggests, consistent with the other figures, that Bi\(_2\)Te\(_2\)Se performance will significantly lag that of Bi\(_2\)Te\(_3\).

Returning to Figure 6, \( p \)-type Bi\(_2\)Te\(_3\) shows doping levels where the thermopower is above 200 \( \mu \)V/K at temperatures above 300 K, where thermoelectric performance is usually believed to deteriorate. This is most significant at 400 K but is true even at 500 K. This means good thermoelectric performance may obtain at these temperatures. Actual results, particularly at 500 K, will depend sensitively on the exact value of the band gap at these temperatures, as well as on any differences in hole and electron scattering times. Performance would likely be optimized at dopings significantly heavier than those (about \( p = 2 \times 10^{19} \) cm\(^{-3}\)) used for commercial Bi\(_2\)Te\(_3\). This is necessary to minimize bipolar conduction. At 400 K this doping level is approximately \( 4 \times 10^{19} \) cm\(^{-3}\) and at 500 K it is \( 5.8 \times 10^{19} \) cm\(^{-3}\). Due to the close proximity of the bipolar regime performance will rapidly degrade at dopings below these. For \( n \)-type there is no such region of extended higher temperature performance for either

\[
\sigma = \int \left\{ E \sigma(E) f'(E - E_F) \right\} \, dE,
\]

where \( f' \) is the energy derivative of the Fermi function and \( \sigma(E) \) is the energy dependent transport function related to conductivity, \( N(E) < v^2(E)\tau(E) > \). \( N(E) \) the density of states, \( v^2 \) the square of the component of the band velocity on the direction of the interest (i.e. \( v_x \) for conductivity along direction \( x \)), making \( v^2 \) a rank 2 tensor, like the conductivity, \( \tau \) the inverse scattering rate. The constant scattering time approximation is the neglect of the energy (but not doping or temperature) dependence of \( \tau \), so that the transport function becomes \( N(E) < v^2(E) > \tau \), where \( < v^2 > \) is the average Fermi velocity (still a rank 2 tensor).

With these preliminaries completed, we move to the calculated quantities of interest. In Figure 6 we present the thermopower for the two materials, at three temperatures - 300, 400 and 500 K. Note that due to the anisotropy of the electronic structure we have depicted the conductivity weighted thermopower, as would be observed in the polycrystalline sample typically measured in the experiment. For \( p \)-type, one notes that the thermopower is significantly larger for Bi\(_2\)Te\(_2\)Se than for Bi\(_2\)Te\(_3\), as a function of carrier concentration, for all three temperatures. This reflects the differing electronic structure of these two materials, as well as the larger calculated band gap of Bi\(_2\)Te\(_2\)Se. At all three temperatures, \( p \)-type Bi\(_2\)Te\(_2\)Se displays a substantial range of carrier concentration where the thermopower is larger than 200 \( \mu \)V/K. As we have noted elsewhere\(^6\), the Wiedemann-Franz relation essentially necessitates a thermopower magnitude of 200 \( \mu \)V/K or greater for a high performance thermoelectric; it is worth noting that this is the 300 K thermopower of optimally doped Bi\(_2\)Te\(_3\). For \( n \)-type the thermopower of Bi\(_2\)Te\(_2\)Se appears inferior to that of Bi\(_2\)Te\(_3\), even with the larger band gap, presumably due to

\[
\begin{align*}
\text{FIG. 6. Conductivity averaged Seebeck coefficient as a function of carrier concentration for Bi}_2\text{Te}_3 \text{ (solid lines) and Bi}_2\text{Te}_2\text{Se (dashed lines) for } p \text{-type (above zero line) and } n \text{-type doping (below zero line) levels. The horizontal blue lines indicate a thermopower magnitude of 200 } \mu \text{V/K, generally the minimum necessary for a material to be a high performance thermoelectric.}
\end{align*}
\]
Bi$_2$Te$_3$ or Bi$_2$Te$_2$Se.

Figures 6, 7 and 8 together suggest that the likelihood of Bi$_2$Te$_2$Se performance exceeding that of Bi$_2$Te$_3$ is fairly low, even at the elevated temperatures where its larger band gap would be expected to be of advantage. This has implications for the ongoing search for technologically useful thermoelectrics in the 400 to 500 K range, in particular suggesting that a larger band gap cannot necessarily be considered a panacea for achieving high thermoelectric performance. In this case it is the less favorable electronic structure of Bi$_2$Te$_2$Se relative to Bi$_2$Te$_3$ that is the source of the difficulty, suggesting that even closely related materials are not necessarily equivalent from the standpoint of thermoelectric performance.

We note that, presumably due to the weakly bonded van der Waals layers in both these materials, the lattice parameters determined from a first principles optimization can differ significantly from the experimental lattice parameters used in the foregoing calculations (See Table 1 for the actual values). Given this, it is natural to perform an assessment of the effects of such differences on electronic structure and on the transport quantities depicted in the above plots. We depict such a comparison in Fig. 9 above, for the planar thermopower at 300 K. For $p$-type, the results depict a marginal decrease in Bi$_2$Te$_3$ thermopower, and equally marginal increase in Bi$_2$Te$_2$ thermopower; the main effect of the smaller theoretical lattice parameters is in fact an increase in the calculated band gap of Bi$_2$Te$_2$Se by approximately 0.06 eV. This change, however, only affects the thermopower for Bi$_2$Te$_2$Se at dopings around $10^{18}$ cm$^{-3}$, far below optimal doping, so for the purposes of assessing thermoelectric performance the effects on $p$-type of the theoretical lattice parameters are essentially nil. With regards to $n$-type, the effects of the experimental lattice parameters are somewhat larger, but are of similar magnitude (and the same sign) for both materials, so that on a comparative basis here too the effects are rather small. Finally, we note use of the experimental lattice parameters generally gives better agreement with experiment in these van der Waals materials and so retain their usage for the electronic structure calculations presented here.

IV. LATTICE DYNAMICS CALCULATIONS

Lattice dynamics, or phonon band structure and transport, ultimately determines the lattice thermal conductivity, a key quantity affecting thermoelectric performance. To this end we have performed lattice dynamics calculations for Bi$_2$Te$_2$Se, using density functional theory in Blochl’s projector augmented-wave (PAW) method within the LDA as implemented in VASP. A $3 \times 3 \times 3$ k-point grid in a $3 \times 3 \times 3$ supercell was used, along with an energy cutoff of 300 eV. Cell parameters and internal coordinates were both relaxed until internal forces were less than 2 meV/Å. The optimized lattice constants for Bi$_2$Te$_2$Se are $a=4.265$ Å and $c=29.328$ Å.

In Figures 10 and 11 we present the phonon band structure and site-projected density of states for Bi$_2$Te$_2$Se. Note that in Figures 10 and 11 we also include a band structure and density-of-states for Bi$_2$Te$_3$ calculated from one of our previ-
ous works, using the same methods. We immediately note a great similarity in the phonon bandstructures, with the main difference being slightly larger frequencies in Bi$_2$Te$_2$Se and a somewhat larger gap in the 2 - 2.5 Thz region in Bi$_2$Te$_2$Se. It is noteworthy that the phonon band structures are so similar while the electronic band structures are so different. Part of this is that phononic transport tends to be less variable than electronic, but a more fundamental reason is that for thermoelectrics and topologically insulators, only the region near the band extrema is of relevance and these can clearly vary more widely than the entire electronic structure. The sound speeds for Bi$_2$Te$_2$Se are somewhat higher than for Bi$_2$Te$_3$ - in the nearly planar Γ-L direction the Bi$_2$Te$_2$Se sound speeds (transverse modes first) are 1524, 1763 and 2500 m/sec while the corresponding values for Bi$_2$Te$_3$ are 1395, 1728, and 2394 m/sec. For the c axis Γ-Z direction the values for Bi$_2$Te$_2$Se are 1781 (degenerate transverse mode) and 1994 m/sec, and the corresponding values for Bi$_2$Te$_3$ are 1774 and 1811 m/sec. The significantly lighter mass of Se relative to Te is likely responsible for the higher phonon frequencies and sound speeds of Bi$_2$Te$_2$Se.

Given the higher sound speeds, the lattice thermal conductivity of Bi$_2$Te$_2$Se may be somewhat higher than that of Bi$_2$Te$_3$. Note, however, that the sound speeds for Bi$_2$Te$_2$Se are still comparatively low, so that fairly low lattice thermal conductivity can be expected in the Bi$_2$Te$_2$Se material. The lower longitudinal c-axis sound speed would suggest somewhat lower thermal conductivity in this direction than in plane.

Moving to the calculated phonon density-of-states (Fig. 11), we note immediately the prominent Se peak around 3.5 Thz, near the top end of the spectrum. This is reasonable considering the lower mass of Se relative to Te and Bi. The lower frequency modes below 2.5 Thz are most predominantly Bi, which again comports with the extremely heavy mass of Bi. One final point of interest is that there is a nearly complete gap opened around 2.5 Thz. This gap is more prominent than in Bi$_2$Te$_3$ and this is again likely a result of the lighter Se atom increasing the frequency of the highest modes found between 2.5 and 4 Thz. This also can be seen in Figure 10, where for Bi$_2$Te$_2$Se there is a gap of approximately 0.3 Thz at the Γ point but essentially no gap at this point in Bi$_2$Te$_3$.

It is of interest to compare the behavior of the Se atom partial DOS in Bi$_2$Te$_2$Se in Fig. 11 (top) with that of Te1 in Bi$_2$Te$_3$ in Fig. 11 (bottom), since these two atoms occupy
the same between-layer site (see Fig. 2). As the Figure indicates, the Te1 DOS is almost entirely (excepting the acoustic regime) comprised of a single peak around 2.7 GHz, while the Se DOS is comprised of three separate peaks at 3, 3.5 and 3.8 GHz. All these Se peaks energies are higher than the Te1 peak in Bi2Te3, as expected given the lighter mass of Se, but the split in these Se peaks is of interest. We suspect its origin is the effectively more complex physical structure of Bi2Te2Se in containing three distinct atomic masses rather than two, which splits what would otherwise be a more singular peak.

V. DEFECT ENERGY CALCULATIONS AND PHASE STABILITY

It is well known that Bi2Te3 tends to form off stoichiometry due to low anti site defect formation energies. Within this context it is of interest to consider the defect formation energies in Bi2Te2Se as these will provide important information about the nature and magnitudes of defect formation, and associated scattering, in this material. We limit ourselves to Se/Te antisite defects as due to the equivalent charge count this context it is of interest to consider the defect formation in the framework of Blöchl’s projector augmented-wave (PAW) method within the local density approximation (LDA) as implemented in VASP. We use a 4×4×1 conventional hexagonal unit cell containing 240 atoms, and the 2×2×1 Monkhorst-Pack k-point grid together with an energy cutoff of 500 eV. The force convergence criterion acting on atoms is less than 0.01 eV/Å. The experimental lattice constants are used for Bi2Te2Se, Bi2Te3, Bi2Se3, Bi, Se, and Te as listed in Table I.

For the defect calculations, the formation energies ΔH for defect in the charge state q are given by

\[ \Delta H_{D,q}(E_F, \mu) = (E_{D,q} - E_H) + \sum_\alpha n_\alpha (\Delta \mu_\alpha + \mu_\alpha^{\text{solid}}) + q(E_v + E_F). \]  

Since we only concern ourselves with the SeTe and TeSe antisite defects with the same valence states, q equals 0. In the first term, \( E_{D,q} \) and \( E_H \) are the total energies of a solid with

![Table I. The lattice constants we use in this work.](image)

![FIG. 12. Calculated ranges of chemical potentials of the elements involved in Bi2Te2Se and related competing phases. The range of thermodynamical stability of Bi2Te2Se is defined by the trapezoid ABCD.](image)

and without defect D, respectively. The second term represents the energy of the atom of species α added (\( n_\alpha = 1 \)) or removed (\( n_\alpha = 1 \)) from a reservoir of that species with chemical potential \( \mu_\alpha = \Delta \mu_\alpha + \mu_\alpha^{\text{solid}} \).

Under equilibrium conditions for the crystal growth, the chemical potentials \( \mu_\alpha \) must satisfy certain conditions in order to form a stable host compound. Other competing phases (including elemental solids) must be avoided. In order to maintain the stability of Bi2Te2Se during growth and avoid competing phases (e.g., Bi, Te, Se, Bi2Te3 and Bi2Se3), the relative chemical potential \( \Delta \mu_\alpha \) must satisfy the following limits.

\[ 2\Delta \mu_{\text{Bi}} + 2\Delta \mu_{\text{Te}} + \Delta \mu_{\text{Se}} = \Delta H(\text{Bi2Te2Se}) = -1.478\text{eV} \]  

\[ \Delta \mu_{\text{Bi}} \leq 0, \Delta \mu_{\text{Te}} \leq 0, \Delta \mu_{\text{Se}} \leq 0, \]  

\[ 2\Delta \mu_{\text{Bi}} + 3\Delta \mu_{\text{Te}} \leq \Delta H(\text{Bi2Te3}) = -1.123\text{eV}, \]  

\[ 2\Delta \mu_{\text{Bi}} + 3\Delta \mu_{\text{Se}} \leq \Delta H(\text{Bi2Se3}) = -1.964\text{eV}. \]

All calculated heats of formation of ternary and binary compounds in this work are given for per formula unit.

Eqs. 5-8 are projected to the two dimensional panel with two independent variables, \( \Delta \mu_{\text{Te}} \) and \( \Delta \mu_{\text{Se}} \) as shown in Figure 12. The thermodynamically stable ranges of chemical potentials of the elements in Bi2Te2Se (trapezium, ABCD) are obtained by excluding the regions of chemical potentials in which competing phases are thermodynamically stable as shown in Figure 12.

Our calculated formation energies of antisite SeTe and TeSe are are collected in Table 2, with relative chemical potentials at the corresponding A, B, C, and D points in Figure 12.

Figure 12 asserts that Bi2Te2Se is only thermodynamically stable within a narrow Te-Se compositional range, above which Bi2Se3 would be formed and below which Bi2Te3 would be performed. From Table II, we see that certain defect structures, such as TeSe, have defect energies as low as 0.041
TABLE II. The calculated defect formation energies for antisite defects Se_{Te} and Te_{Se} with chemical potentials at A, B, C, D points.

|        | A         | B         | C         | D         |
|--------|-----------|-----------|-----------|-----------|
| Δμ_{Te} | (0.41, 0.65) | (0, -0.24) | (0, -0.37, -0.73) | (0, -0.36) |
| Se_{Te} | 0.115     | 0.115     | 0.228     | 0.228     |
| Te_{Se} | 0.154     | 0.154     | 0.041     | 0.041     |

eV. When one considers putative synthesis conditions of 1000 K, this would in equilibrium yield a Te_{Se} defect concentration of order 50 percent, an absurdly large number. Hence it will be important to synthesize under conditions towards the Se-rich side. Even here, though, the defect formation energies are low - 0.115 eV for Se_{Te} defects and 0.154 eV for Te_{Se} defects, both less than twice the thermal energy at 100 K, so that substantial numbers of defects are likely to be formed at typical synthesis conditions.

There are two main points to be gleaned from these results. Firstly, since the defect formation energies are small and asymmetric, substantial numbers of defects will form and the number of Te_{Se} and Se_{Te} defects will not be equal, so the material will likely form off stoichiometry. Secondly, and more importantly, since the electronic structures of the two compounds Bi_{2}Te_{3} and Bi_{2}Te_{2}Se are so different, these large numbers of defects are likely to induce substantial alloy scattering, which is likely to significantly impair mobility. It may also reduce the lattice thermal conductivity, but given that this is already likely to be fairly low, the mobility reduction is likely to be the larger effect.

VI. CONCLUSION

Topological insulators, such as Bi_{2}Te_{3} and Bi_{2}Te_{2}Se considered in this work, of necessity have complex band structures due to the band inversion central to the topologically insulating behavior. These complex band structures, in particular highly non-parabolic isoenergy surfaces, are also those favored by high performance thermoelectrics, and these two studied materials appear to contain such anisotropic features, though rather different in the specifics. The relationship between thermoelectric performance and TI behavior is thus through the band structure as it relates to transport. TI materials necessarily have highly non-parabolic shapes that generally lead to corrugated isoenergy surfaces at the doping levels of interest for thermoelectrics. These corrugated surfaces are favorable for obtaining the combination of high conductivity and high thermopower required in a high performance thermoelectric.

The favorability of complex non-parabolic band structures for both TI behavior and high thermoelectric performance suggests that future searches for such technologically promising materials may benefit from a consideration of the degree of complexity and anisotropy of the electronic structure of materials studied. It will be of interest to pursue these potentially useful behaviors from this perspective.

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