Electronic structure of the thermoelectric materials Bi$_2$Te$_3$ and Sb$_2$Te$_3$ from first-principles calculations

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The electronic structures of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals were calculated using the first-principles full-potential linearized augmented plane-wave method. We studied not only the unrelaxed crystals, which have the experimental lattice parameters and scaled atom coordinates, but also the relaxed crystals, which have the lattice parameters and scaled atom coordinates determined from theoretical structure optimizations. We found that Bi$_2$Te$_3$ has six highest valence-band edges and six lowest conduction-band edges regardless of relaxations. However, by varying structural parameters Sb$_2$Te$_3$ may undergo an electronic topological transition that the number of valence (and conduction) band edges changes between 6 and 12. Moreover, we presented the location of the band edges and the effective mass tenor parameters for electrons and holes associated with those band edges. Furthermore, we discussed the relation of the calculated electronic structures of the two crystals with the electrical properties of Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices.

I. INTRODUCTION

High-performance thermoelectric materials have great impact to our society owing to their applications in cooling and power generation. The performance of thermoelectric materials is described by the figure of merit (ZT),

\[ ZT = S^2 \sigma T / (\kappa_e + \kappa_l) , \]

where \( S \) is the Seebeck coefficient, \( \sigma \) is the electrical conductivity, \( T \) is the temperature of the sample, and \( \kappa_e \) and \( \kappa_l \) are the thermal conductivities due to the electron and lattice, respectively. A higher value of ZT indicates a better thermoelectric performance for the given material. From the definition of ZT [Eq. (1)], it is seen that increasing electrical conductivity and/or decreasing thermal conductivity are constructive in enhancing the thermoelectric performance of materials. Thus, it was suggested that “phonon-glass electron crystal” (PGEC), which has the thermal properties of a glass and the electronic properties of a crystal, would be the best thermoelectric material. This PGEC approach to developing thermoelectric materials has been employed in the thermoelectric research work of clathrates, skutterudites, and disordered and nanostructured materials.

To date, \( p \)-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices have been found to have the highest ZT of about 2.4 at 300 K. The periodic superlattices were grown along their \( c \) axis, in which Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are layered with a weak van der Waals-like bonding. The observed excellent thermoelectric performance is believed to be caused by the phonon-blocking and/or electron-transmitting behavior of the superlattices in their cross-plane direction (\( c \) axis). The phonon-blocking effect in the Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices has been systematically examined. It was found that \( \kappa_l \) of the superlattices could be more than two times lower than that of a solid solution alloy, depending on the period of the superlattice. The reduction of thermal conductivity in superlattices can be explained by assuming that phonon transport at the interface is partially diffuse and partially specular, and that inelastic phonon scattering happens at the interface. For the electron-transmitting effect in the Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices, experimental measurements show that the electron cross-plane mobility increases with the increase of the Sb$_2$Te$_3$ content in the superlattices. In a previous letter, we provided an explanation to that behavior of the Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices based on the first-principles calculation of the effective masses of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals. In this paper, we present the detailed electronic structure calculations for both unrelaxed and relaxed Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals using first-principles methods.

First-principles methods, without any parametrization to experimental results, have been developed and applied to investigating and searching those promising candidates of thermoelectric materials. Particularly, accurate electronic structures of thermoelectric crystals are readily attainable through first-principles calculations. Electronic structure calculations are very important in determining if a material is suitable for thermoelectric applications. This is because the ZT of thermoelectric materials depends on band structures such as the band gap, effective mass and its anisotropy, degeneracy of the band extremes, and carrier mobility. First-principles electronic structure calculations have already been conducted for the Bi$_2$Te$_3$ (Refs. 15 and 18–21) and Sb$_2$Te$_3$ (Refs. 14 and 22) crystals with the experimental lattice parameters. Distinct from those previous works, we compute the electronic structures for Bi$_2$Te$_3$ and Sb$_2$Te$_3$ with fully relaxed crystal structures in this work. Some features in the electronic structures emerge after we relax the crystal structures. For Sb$_2$Te$_3$, we found 12 conduction-band valleys and 12 valence-band valleys for the relaxed crystal, while we found only 6 conduction-band valleys and 6 valence-band valleys for the unrelaxed crystal. The calculated electronic structures in this work are useful to qualitatively estimate the thermoelectric figure of merit of the materials. Moreover, the calculated band structure and effective mass tensor can be used to inform parametrized tight-binding models, which are both atomistic and efficient to perform large scale device simulations.

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PACS number(s): 71.18.+y, 72.15.Jf, 71.20.—b
than $10^{-4}$ hartree and the forces of two subsequent iterations are ensured by checking both the energy and the force: the energy minimum is achieved. The fully relaxed structures of lattice parameters and atomic internal coordinates until cell. For crystal structure relaxation, we alternatively relaxed Bi$_2$Te$_3$ and Sb$_2$Te$_3$,\textsuperscript{15,18–22} has been included in our calculations.

which is essential for calculating the electronic structure of semiconductors.\textsuperscript{20} We set the energy cutoff between the core and valence states at $-1.8$ Ry. In this way, there are 48 valence electrons in a rhombohedral Bi$_2$Te$_3$ (or Sb$_2$Te$_3$) unit cell. For crystal structure relaxation, we alternatively relaxed the lattice parameters and atomic internal coordinates until an energy minimum is achieved. The fully relaxed structures are ensured by checking both the energy and the force: the energies of two subsequent iterations do not differ by more than $10^{-3}$ hartree and the forces of two subsequent iterations do not differ by more than $10^{-5}$ hartree/a.u.

III. RESULTS

A. Crystal structures

Bulk Bi$_2$Te$_3$ (or Sb$_2$Te$_3$) has a rhombohedral crystal structure which is with the space group $D_{3d}^1$ ($R\bar{3}m$) and with five atoms in a unit cell. A rhombohedral structure can be visualized as a layer structure and a hexagonal lattice cell. We plot this hexagonal cell in the left panel of Fig. 1. In the hexagonal cell of Bi$_2$Te$_3$ (or Sb$_2$Te$_3$), there are five individual atomic layers in the sequence of Te-Bi(Sb)-Te-

FIG. 1. Crystal structure of Bi$_2$Te$_3$ and Sb$_2$Te$_3$: (left) hexagonal cell and (right) rhombohedral cell. In the figure, the open cycles represent Bi (or Sb) atoms and the dark cycles represent Te atoms.

II. CALCULATION METHOD

We performed electronic structure calculations using the self-consistent full-potential linearized augmented plane-wave (FPLAPW)\textsuperscript{25} method within density functional theory (DFT) and the generalized gradient approximation (GGA) of Perdew et al. for the exchange and correlation potential,\textsuperscript{26} as implemented in the FLEUR code.\textsuperscript{27} Spin-orbit interaction, which is essential for calculating the electronic structure of Bi$_2$Te$_3$ and Sb$_2$Te$_3$,\textsuperscript{15,18–22} has been included in our calculations. We used 60 $k$ points for the $k$-space integration, which is sufficient for an electronic structure calculation of semiconductors.\textsuperscript{20} We set the energy cutoff between the core and valence states at $-1.8$ Ry. In this way, there are 48 valence electrons in a rhombohedral Bi$_2$Te$_3$ (or Sb$_2$Te$_3$) unit cell. For crystal structure relaxation, we alternatively relaxed the lattice parameters and atomic internal coordinates until an energy minimum is achieved. The fully relaxed structures are ensured by checking both the energy and the force: the energies of two subsequent iterations do not differ by more than $10^{-3}$ hartree and the forces of two subsequent iterations do not differ by more than $10^{-5}$ hartree/a.u.

Bi(Sb)-Te along the trigonal axis. In the right panel of Fig. 1, we plot the rhombohedral unit cell which was adopted in our calculations. The corresponding Brillouin zone for the two crystals is given in Fig. 2.

In Table I, we give the lattice parameters and scaled atom coordinates for Bi$_2$Te$_3$ and Sb$_2$Te$_3$ from experimental measurements.\textsuperscript{28} We assumed those values in our calculations of unrelaxed crystals. We also give in Table I the theoretical lattice parameters and scaled atom coordinates obtained from first-principles relaxation calculations. Our theoretical results for Bi$_2$Te$_3$ differ from experimental data by 3.3% for lattice constant $a$, 0.5% for lattice constant $c$, 1.4% for the scaled coordinate of Te atoms, and 0.0% for the scaled coordinate of Bi atoms. Our theoretical results for Sb$_2$Te$_3$ differ from experimental data by 4.5% for lattice constant $a$, 0.4% for lattice constant $c$, 0.9% for the scaled coordinate of Te atoms, and 0.0% for the scaled coordinate of Sb atoms. Thus, our calculated theoretical crystal structures are very close to the experimental ones. In this work, we also

![FIG. 2. Brillouin zone of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals. In the figure, the binary axis (with twofold rotation symmetry) is along $x$, the bisectrix axis (in the reflection plane) is along $y$, and the trigonal axis (with threefold rotation symmetry) is along $z$. The high-symmetry $k$ points are marked in the figure using open circles.](image-url)

TABLE I. Comparison of the theoretically optimized with experimentally measured lattice parameters of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals. In the table, $a$ and $c$ are the lattice parameters in the hexagonal lattice (see the left panel of Fig. 1); $\mu$(Te), $\mu$(Bi), and $\mu$(Sb) are the scaled coordinates of the Te, Bi, and Sb atoms, which are inside the unit cell (see the right panel of Fig. 1), along the trigonal axis ($z$) of the crystals.

<table>
<thead>
<tr>
<th></th>
<th>Bi$_2$Te$_3$</th>
<th>Sb$_2$Te$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theory</td>
<td>Expt.$^a$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>4.53</td>
<td>4.3835</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>30.63</td>
<td>30.487</td>
</tr>
<tr>
<td>$\mu$(Te)</td>
<td>≤0.209</td>
<td>≤0.212</td>
</tr>
<tr>
<td>$\mu$(Bi) or $\mu$(Sb)</td>
<td>≤0.400</td>
<td>≤0.400</td>
</tr>
</tbody>
</table>

$^a$Reference 28.
Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals were evaluated along some high-symmetry $k$-symmetry lines and plotted in Fig. 3. The locations of those Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals using these theoretical values.

performed electronic structure calculations for relaxed Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals using these theoretical values.

### B. Electronic structures

The band structures of both the relaxed and unrelaxed Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals were evaluated along some high-symmetry lines and plotted in Fig. 3. The locations of those high-symmetry $k$ points are marked in the Brillouin zone of Bi$_2$Te$_3$ and Sb$_2$Te$_3$, we found in Fig. 3 two valence-band maxima, along $\Gamma a$ and $ZF$ directions, respectively, and three conduction-band minima, along $\Gamma a$, $ZF$, and $\Gamma Z$ directions, respectively. Shown in Fig. 2, high-symmetry $k$ points $\Gamma$, $a$, $Z$, and $F$ all lie in the plane (denoted as $yz$ plane) containing the bisectric ($y$) axis and the trigonal ($z$) axis. Hence, our results in Fig. 3 indicate that the highest valence-band edge (VBE) and lowest conduction-band edge (CBE) of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ lie in that plane. Here, we found similar results as those from previous first-principles calculations. In addition, Fig. 3 shows that the calculated electronic structures do not differ much between the relaxed and unrelaxed Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals along those high-symmetry lines.

To find the exact locations of VBE and CBE for Bi$_2$Te$_3$ and Sb$_2$Te$_3$, we have sampled the eigenvalues of 525 $k$ points homogeneously distributed in the $yz$ plane within the irreducible Brillouin zone. The VBE and CBE were searched among those extremes of the eigenvalues. Further, we ensured the found VBE and CBE to be the real band edges by evaluating $E$ vs $k$ along various orthogonal directions around those $k$ points. We found that all VBE and CBE of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are within the $yz$ plane but off the high-symmetry lines.

Since all calculated extremes in the electronic bands of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ lie in the $yz$ plane, the energy near their VBE and CBE can be expressed as:

$$\frac{2m_e E}{h^2} = \alpha_{xx}k_x^2 + \alpha_{yy}k_y^2 + \alpha_{zz}k_z^2 + 2\alpha_{xy}k_xk_y + 2\alpha_{xz}k_xk_z,$$

where $m_e$ is the free-electron mass, $E$ is the energy relative to the energy of VBE or CBE, and $\alpha_{ij}$ is the component of effective mass tensor. We can calculate the effective tensor $\alpha_{ij}$ by fitting the calculated $E$ vs $k$ to parabolas along various orthogonal directions $(x, y, z, and yz)$. In this work, we varied $k_x$, $k_y$, and $k_z$ between $-0.005$ and $0.005$ Å$^{-1}$ around the VBE and CBE of the Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals.

Below, we present our findings in detail.

#### I. Bi$_2$Te$_3$

Figure 4(a) shows the locations of VBE for the relaxed Bi$_2$Te$_3$ using the contour plot of the highest valence band in the $yz$ plane of the Brillouin zone. We found two band edges, which are marked as VBE and X in the figure. VBE is about 27 meV higher than X and thus is our predicted VBE for the relaxed Bi$_2$Te$_3$. Figure 4(a) also shows that VBE is more isotropic in the $yz$ plane than X. It is noted that band edge X was predicted to be the highest valence-band edge from previous first-principles calculations with local density approximation (LDA) for the exchange and correlation potential. In contrast to their results, our current results of VBE and X are in agreement with those from a previous GGA-DFT calculation. It appears that the difference between LDA and GGA leads to the discrepancy in the predicated location of VBE. In Fig. 4(b), we found one CBE for the relaxed Bi$_2$Te$_3$. Figures 4(c) and 4(d) show the energy contour plots for the unrelaxed Bi$_2$Te$_3$ crystal. In those figures, we located one VBE and one CBE.
We give in Table II the locations of the found band edges of \( \text{Bi}_2\text{Te}_3 \) in the reciprocal lattice. It is found that, for both relaxed and unrelaxed \( \text{Bi}_2\text{Te}_3 \), the VBE and CBE lie inside the \( \text{yz} \) plane of the Brillouin zone. Owing to the high-symmetry of the \( \text{yz} \) plane, there would be a total of 6 degenerate VBEs and CBEs in the Brillouin zone of \( \text{Bi}_2\text{Te}_3 \). Our theoretical results about the location and number of VBEs and CBEs agree well with previous experimental measurements.\(^{29,30}\)

Moreover, the calculated effective mass tensor for the holes at VBE and for the electrons at CBE are given in Table III for both relaxed and unrelaxed \( \text{Bi}_2\text{Te}_3 \). First of all, our results agree satisfactorily with the experimental data\(^{29,30}\) and previous LDA results.\(^{21}\) Compared to those for unrelaxed \( \text{Bi}_2\text{Te}_3 \), the calculated effective mass parameters for relaxed \( \text{Bi}_2\text{Te}_3 \) (especially, for the electrons at CBE) are in better agreement with experiments. However, the improvement is not significant.

2. \( \text{Sb}_2\text{Te}_3 \)

For relaxed \( \text{Sb}_2\text{Te}_3 \), we found in Figs. 5(a) and 5(b) two valence-band edges (VBE1 and VBE2) and two conduction-band edges (CBE1 and CBE2) in the \( \text{yz} \) plane of the Brillouin zone. VBE1 and VBE2 differ in energy by 4.9 meV; CBE1 and CBE2 differ in energy by 1.6 meV. Since the energy difference is very small, we count both of them as Fermi surface pockets. Interestingly, we found in Figs. 5(c)

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**FIG. 4.** Contour plots of the eigenvalues of (a) the highest valence band of relaxed \( \text{Bi}_2\text{Te}_3 \), (b) the lowest conduction band of relaxed \( \text{Bi}_2\text{Te}_3 \), (c) the highest valence band of unrelaxed \( \text{Bi}_2\text{Te}_3 \), and (d) the lowest conduction band of unrelaxed \( \text{Bi}_2\text{Te}_3 \) in the \( \text{yz} \) plane, where \( Z=[0.5,0.5,0.5] \) and \( a=[0.64,0.43,0.43] \) in the basis vectors of the reciprocal lattice. In the figures, the locations of VBE and CBE are marked. In (a), symbol X marks the location of VBE found in previous LDA calculations (Refs. 20 and 21). In the plots, the energy difference is 10 meV between two neighboring lines.

We give in Table II the locations of the found band edges of \( \text{Bi}_2\text{Te}_3 \) in the reciprocal lattice. It is found that, for both relaxed and unrelaxed \( \text{Bi}_2\text{Te}_3 \), the VBE and CBE lie inside the \( \text{yz} \) plane of the Brillouin zone. Owing to the high-symmetry of the \( \text{yz} \) plane, there would be a total of 6 degenerate VBEs and CBEs in the Brillouin zone of \( \text{Bi}_2\text{Te}_3 \). Our theoretical results about the location and number of VBEs and CBEs agree well with previous experimental measurements.\(^{29,30}\)

Moreover, the calculated effective mass tensor for the holes at VBE and for the electrons at CBE are given in Table III for both relaxed and unrelaxed \( \text{Bi}_2\text{Te}_3 \). First of all, our results agree satisfactorily with the experimental data\(^{29,30}\) and previous LDA results.\(^{21}\) Compared to those for unrelaxed \( \text{Bi}_2\text{Te}_3 \), the calculated effective mass parameters for relaxed \( \text{Bi}_2\text{Te}_3 \) (especially, for the electrons at CBE) are in better agreement with experiments. However, the improvement is not significant.

**TABLE II.** Location of the valence-band edge (VBE) and conduction-band edge (CBE) of \( \text{Bi}_2\text{Te}_3 \) (shown in Fig. 4) given by the basis vectors of the reciprocal lattice.

<table>
<thead>
<tr>
<th>Band edges</th>
<th>Locations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Relaxed ( \text{Bi}_2\text{Te}_3 )</strong></td>
<td></td>
</tr>
<tr>
<td>VBE</td>
<td>[0.662,0.584,0.584]</td>
</tr>
<tr>
<td>( X^a )</td>
<td>[0.531,0.348,0.348]</td>
</tr>
<tr>
<td>CBE</td>
<td>[0.673,0.579,0.579]</td>
</tr>
<tr>
<td><strong>Unrelaxed ( \text{Bi}_2\text{Te}_3 )</strong></td>
<td></td>
</tr>
<tr>
<td>VBE</td>
<td>[0.650,0.584,0.584]</td>
</tr>
<tr>
<td>CBE</td>
<td>[0.652,0.585,0.585]</td>
</tr>
</tbody>
</table>

\(^a\)Band edge \( X \) is 26.7 meV lower than VBE in the highest valence band.
and 5(d) for unrelaxed Sb$_2$Te$_3$ only one VBE and one CBE in the yz plane of the Brillouin zone. VBE of the unrelaxed Sb$_2$Te$_3$ corresponds to VBE1 of the relaxed Sb$_2$Te$_3$, while CBE of the unrelaxed Sb$_2$Te$_3$ corresponds to CBE2 of the relaxed Sb$_2$Te$_3$. Our calculations show that VBE2 and CBE1 are not stable band edges anymore for the unrelaxed Sb$_2$Te$_3$. Therefore, we predicted a 12-band model (12 valence valleys and 12 conduction valleys) for the relaxed Sb$_2$Te$_3$ but a 6-band model (6 valence valleys and 6 conduction valleys) for the unrelaxed Sb$_2$Te$_3$. We used identical parameters in the two calculations. The only difference between the two calculations is the slight variation in lattice parameters and scaled atom coordinates given in Table I. For both relaxed and unrelaxed Sb$_2$Te$_3$, Table IV lists the locations of those band edges and Table V gives the calculated effective mass tensor parameters at those band edges.

It appears that experimental measurements of the electronic structure of Sb$_2$Te$_3$ also yielded conflicting results. Schwartz et al. measured the Fermi surface of p-type Sb$_2$Te$_3$ by the de Hass–van Alphen effect and found six valence-band ellipsoids. In contrast, von Middendorff claimed that their data from the Shubnikov–de Hass effect in p-type Sb$_2$Te$_3$ crystals supported a 12 valence band model. Moreover, it was reported that for alloy Sb$_{1.5}$Bi$_{0.5}$Te$_3$, the value of ZT increases by at least a factor of 2 at about 2 GPa pressure from its value at ambient pressure. To explain that observation, electronic topological transition (Fermi surface topology change under compression) for Sb$_{1.5}$Bi$_{0.5}$Te$_3$ under pressure was suggested. Those previous works make us believe that our first-principles results for the band edge degeneracy (12 for the relaxed Sb$_2$Te$_3$ and 6 for the unrelaxed Sb$_2$Te$_3$) are reasonable and manifesting a possible electronic topological transition under the influence of lattice parameters and atomic positions for alloy Sb$_2$Te$_3$. Recently, Larson systematically examined the effect of uniaxial stresses on the electronic structures of Sb$_2$Te$_3$ crystals and also found the changes in the valence-band maximum (from 6 to 12) for Sb$_2$Te$_3$. In Ref. 35, Larson used a full-potential linear muffin tin orbital method within the local spin density approximation. In this work, we used the FLAPW-GGA method. Both of the two independent first-principles calculations predict a Fermi surface topology change in Sb$_2$Te$_3$ crystals when changing lattice parameters, so it is worthwhile to further experimentally investigate this phenomenon.

### C. Band gaps

Band gap is an important parameter when designing high-performance thermoelectric materials. The analysis in Ref. 23 points out that the thermoelectric semiconductors must have a band gap of at least 10k_B T (k_B is Boltzmann constant and T is the maximum operating temperature) in order to have an optimum thermoelectric performance. Unfortunately, DFT most often does not predict the band gap accurately. Our current calculations suffer the same problems. We calculated the band gaps for the relaxed and unrelaxed Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals by evaluating the energy difference between the lowest CBE and the highest VBE. Our results are

![Table III. Theoretical and experimental values of effective mass tensor parameters (in unit of m_e^{-1}, m_v is free-electron mass) for the holes associated with the valence-band edge and for the electrons associated with the conduction-band edge of Bi$_2$Te$_3$. The angle $\theta_{yz} = \frac{1}{2} \arctan[2\alpha_{yz}/(\alpha_{zz} - \alpha_{xy})]$ is the principal angle of the energy ellipsoid in the yz plane with respect to the bisectrix y axis.](image-url)
given in Table VI. Compared to experimental values, our predicted band gaps are significantly lower. We observe a slight improvement in the agreement between theory and experiment if we fully relax the crystals. However, the improvement is not pronounced.

### IV. DISCUSSIONS AND CONCLUSIONS

In this work, we calculated the electronic structure of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ crystals using first-principles method. We conducted our study for both the unrelaxed (with the experimental lattice parameters and scaled atom coordinates) and relaxed (with the lattice parameters and scaled atom coordinates from theoretical optimization) crystals.

We found six valence- and six conduction-band edges in the trigonal-bisectrix ($yz$) plane of the Brillouin zone for both relaxed and unrelaxed Bi$_2$Te$_3$. Our theoretical results are consistent with experimental measurements. Although the structural difference (lattice parameters and scaled atom coordinates) between the relaxed and unrelaxed Sb$_2$Te$_3$ crystals is quite small (see Table I), we witnessed a dramatic change in the topology of their Fermi surfaces. The relaxed Sb$_2$Te$_3$ crystal has 12 valence- and 12 conduction-band edges in the trigonal-bisectrix ($yz$) plane of the Brillouin zone, while the unrelaxed one has only 6 valence- and

<table>
<thead>
<tr>
<th>Band edges</th>
<th>Locations</th>
</tr>
</thead>
<tbody>
<tr>
<td>VBE1</td>
<td>[0.705,0.615,0.615]</td>
</tr>
<tr>
<td>VBE2$^a$</td>
<td>[0.534,0.341,0.341]</td>
</tr>
<tr>
<td>CBE1</td>
<td>[0.790,0.737,0.737]</td>
</tr>
<tr>
<td>CBE2$^b$</td>
<td>[0.703,0.612,0.612]</td>
</tr>
<tr>
<td>VBE</td>
<td>[0.695,0.613,0.613]</td>
</tr>
<tr>
<td>CBE</td>
<td>[0.690,0.605,0.605]</td>
</tr>
</tbody>
</table>

$^a$VBE2 is 4.9 meV lower than VBE1 in the highest valence band.

$^b$CBE2 is 1.6 meV higher than CBE1 in the lowest conduction band.

FIG. 5. Contour plots of the eigenvalues of (a) the highest valence band of relaxed Sb$_2$Te$_3$, (b) the lowest conduction band of relaxed Sb$_2$Te$_3$, (c) the highest valence band of unrelaxed Sb$_2$Te$_3$, and (d) the lowest conduction band of unrelaxed Sb$_2$Te$_3$ in the $yz$ plane, where $Z=[0.5,0.5,0.5]$ and $a=[0.64,0.43,0.43]$ in the basis vectors of the reciprocal lattice. In the figures, the locations of VBEs and CBEs are marked. In the plots, the energy difference is 10 meV between two neighboring lines.
6 conduction-band edges in the same \(yz\) plane. It appears that the degeneracy of band edges in Sb\(_2\)Te\(_3\) is sensitively influenced by the changes in its crystal structural parameters. Analysis in Ref. 23 suggests that ZT is a monotonically increasing function of the degeneracy of band edges of thermoelectric materials. Hence, our results for the topological change in the Fermi surface of Sb\(_2\)Te\(_3\) might be the explanation to the observations of a sharp increase in ZT by a factor of 2 in the compressed Sb\(_2\)Te\(_3\) Bi\(_{1.2}\)Bi\(_{0.5}\)Te\(_3\) alloys.\(^{33}\)

Tables II and IV show that both Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\) have VBEs and CBEs in the same \(yz\) plane of the Brillouin zone and the VBEs and CBEs of the two crystals (VBE1 and CBE2 for the relaxed Sb\(_2\)Te\(_3\)) are very close in \(k\) space. Therefore, the band edge degeneracy (six) of bulk Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\) could be well preserved in the Bi\(_2\)Te\(_3\)/Sb\(_2\)Te\(_3\) superlattices. This is helpful for the superlattices to behave like a pure crystal in conducting electrons and holes through its interfaces between different Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\) layers. High band edge degeneracy would lead to high carrier density and hence larger electrical conductivity.

The Bi\(_2\)Te\(_3\)/Sb\(_2\)Te\(_3\) superlattices were grown along the trigonal (\(z\)) axis,\(^\text{11}\) so the carrier (electron or hole) mobility in the two crystals along the \(z\) axis would determine the mobility of the carriers across the superlattice interfaces. In the theory of transport in semiconductors, the carrier is treated as a classical particle with momentum and effective mass.\(^\text{37}\) The smaller the effective mass, the higher the mobility of carriers. Within the envelope function approximation and when the offset potential is small, the effective mass for carrier motion parallel to the growth direction of the superlattices is written as:\(^\text{38}\)

\[
m_s = \frac{L_1}{L_1 + L_2} m_1 + \frac{L_2}{L_1 + L_2} m_2,
\]

where \(m_s\), \(m_1\), and \(m_2\) are the effective masses along the superlattice growth direction for the superlattice and its two component semiconductors, respectively. \(L_1\) and \(L_2\) are the layer thicknesses of the two components.

Effective mass \(m\) is equal to \(1/\alpha\). For Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\) crystals, the values of \(\alpha\) are given in Tables III and V. Our results indicate that the same carrier would have a less effective mass \(m_z\) (a larger \(\alpha_z\)) along the \(z\) axis in Sb\(_2\)Te\(_3\) than in Bi\(_2\)Te\(_3\). Here, we only include VBE1 and CBE2 of the relaxed Sb\(_2\)Te\(_3\) into comparisons since they are closer to VBE and CBE of Bi\(_2\)Te\(_3\) than VBE2 and CBE1 and hence contribute more significantly in conducting carriers in the Bi\(_2\)Te\(_3\)/Sb\(_2\)Te\(_3\) superlattices. Considering Eq. (3), the effective mass \(m_z\) of the carriers in the Bi\(_2\)Te\(_3\)/Sb\(_2\)Te\(_3\) superlattices will be reduced if there are more Sb\(_2\)Te\(_3\) than Bi\(_2\)Te\(_3\) in each period. In other words, the mobility of carriers in the cross-plane (\(z\)) direction would increase with more Sb\(_2\)Te\(_3\) component in the superlattice, agreeing excellently with the experimental results given in Fig. 2(c) of Ref. 9. In an early work, Mahanti et al. calculated the electronic structure of (Bi\(_2\)Te\(_3\))\(_n\)(Sb\(_2\)Te\(_3\))\(_n\) superlattices directly using first-principles method.\(^\text{39}\) Although they did not fully relax the internal structures in their calculations, their results still showed a clear reduction of the effective mass \(m_z\) in the superlattices compared to the corresponding value of Bi\(_2\)Te\(_3\). That agrees with our above prediction for Bi\(_2\)Te\(_3\)/Sb\(_2\)Te\(_3\) superlattices.

In conclusion, the electronic structures of the thermoelectric crystals can be accurately obtained from first-principles methods.
calculations. The main features of the theoretical electronic structure of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are consistent with experimental data. Furthermore, the electron-transmitting behavior across the interfaces of the Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices can be explained using the electronic structures of their component crystals. Therefore, the first-principles electronic structure calculations are very useful for designing semiconductor superlattices with high thermoelectric performance.

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