Ab initio and molecular dynamics predictions for electron and phonon transport in bismuth telluride

Bao-Ling Huang and Massoud Kaviany*
Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan 48109-2125, USA
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Phonon and electron transport in Bi₂Te₃ has been investigated using a multiscale approach, combining the first-principles calculations, molecular dynamics (MD) simulations, and Boltzmann transport equations (BTEs). Good agreements are found with the available experimental results. The MD simulations along with the Green-Kubo autocorrelation decay method are used to calculate the lattice thermal conductivity in both the in-plane and cross-plane directions, where the required classical interatomic potentials for Bi₂Te₃ are developed on the basis of first-principles calculations and experimental results. In the decomposition of the lattice thermal conductivity, the contributions from the short-range acoustic and optical phonons are found to be temperature independent and direction independent, while the long-range acoustic phonons dominate the phonon transport with a strong temperature and direction dependence (represented by a modified Slack relation). The sum of the short-range acoustic and optical phonon contribution is about 0.2 W/m K and signifies the limit when the long-range transport is suppressed by nanostructure engineering. The electrical transport is calculated using the full-band structure from the linearized augmented plane-wave method, BTE, and the energy-dependent relaxation-time models with the nonparabolic Kane energy dispersion. Temperature dependence of the energy gap is found to be important for the prediction of electrical transport in the intrinsic regime. Appropriate modeling of relaxation times is also essential for the calculation of electric and thermal transport, especially in the intrinsic regime. The maximum of the Seebeck coefficient appears when the chemical potential approaches the band edge and can be estimated by a simple expression containing the band gap. The scatterings by the acoustic, optical, and polar-optical phonons dominate the electrical conductivity and electric thermal conductivity.

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I. INTRODUCTION

Efficient solid state energy conversion devices based on the thermoelectric (TE) effects, i.e., the Peltier effect for cooling and the Seebeck effect for power generation, have great application potential and economic benefits in many areas. However, present TE devices have a very low efficiency, which is directly limited by the performance of TE materials. The search into the fundamentals and improvement in TE transport phenomena continues. The performance of TE materials is presented by the dimensionless figure of merit (ZT),

\[ ZT = \frac{\alpha^2 T}{\kappa_e + \kappa_l}, \]  

(1)

where \( \alpha \) is the Seebeck coefficient, \( \kappa_e \) is the electrical conductivity, \( T \) is the temperature, and \( \kappa_e \) and \( \kappa_l \) are the electric and lattice thermal conductivities, respectively. Identifying and designing materials with high ZT has proven to be very challenging. Currently, the best bulk commercial TE materials for applications near room temperature are still the compounds based on Bi₂Te₃, with ZT near 1. Bi₂Te₃ exhibits many typical features of a good room-temperature TE material, such as a narrow band gap, high density of states near the band edges, and low total thermal conductivity. Understanding phonon and electron transport in Bi₂Te₃ is important in the design and optimization of TE materials.

Bulk Bi₂Te₃ has a rhombohedral lattice structure that belongs to the space group \( D_{3d}^1 (R\bar{3} m) \) and contains five atoms along the trigonal axis in the sequence of Te₁-Bi-Te₂-Bi-Te₁ (Fig. 1). At 293 K, the rhombohedral unit-cell parameters \( a = 10.473 \) Å and \( \theta = 24.159^\circ \), and the corresponding hexagonal unit-cell parameters \( a = 10.473 \) Å and \( c = 30.487 \) Å. In the rhombohedral structure, the fractional coordinates for Te₁ atoms are designated as \( (\pm u, \pm u, \pm u) \) and

![FIG. 1. (Color online) Crystal structure of Bi₂Te₃ showing both the rhombohedral and hexagonal unit cells. The first Brillouin zone for the rhombohedral cell and some symmetry axes and \( k \) points are also shown. The hexagonal structure is made of Te₁-Bi-Te₂-Bi-Te₁ five-layer blocks.](image-url)
those for Bi as $(±v, ±v, ±v)$, where $u$ and $v$ at 293 K have been found\cite{2} to be 0.4001 and 0.2095. In the hexagonal unit cell (Fig. 1), it is apparent that Bi$_2$Te$_3$ has a lamella structure made of Te1-Bi-Te2-Bi-Te1 blocks. The bond length of the Te1-Bi bond is 3.07 Å shorter than that of the Bi-Te2 bond (3.25 Å), indicating that they may be of different bond types; the Te1-Te1 bond is the longest (3.64 Å) and is believed to be a van der Waals interaction, which responds to the ease of cleavage along the planes.\cite{12} We denote the direction along the c axis (cross-plane direction) as “$\perp$” and the in-plane direction as “$\parallel$.”

Significant experimental characterization efforts\cite{3–9} on Bi$_2$Te$_3$ and some \textit{ab initio} calculations and theoretical treatments\cite{35, 310} have been reported. However, theoretical treatments for both the phonon and electron transport in Bi$_2$Te$_3$ are rare, especially for the lattice thermal conductivity. The difficulty has been due to the different physical features of phonon and electron transport, and a multiscale approach is required for such investigations.

In order to systematically study the relationship between the TE properties and the structural features and to understand the transport mechanisms in TE materials, we develop a comprehensive strategy to calculate all the TE transport properties ($\alpha_S$, $\sigma_\tau$, $k_\tau$, and $k_\rho$). In this strategy, first-principles calculations based on density functional theory (DFT), molecular dynamics (MD) simulations, and Boltzmann transport equation (BTE) are combined to calculate the TE transport properties of Bi$_2$Te$_3$. Below, we first report the classical interatomic potentials for Bi$_2$Te$_3$ developed on the basis of DFT energy calculations. With these potentials, the lattice vibrations are analyzed using MD simulations. Then, the lattice thermal conductivity along the in-plane and cross-plane directions are calculated in a temperature range from 150 to 450 K using MD combined with the Green-Kubo (GK) autocorrelation decay method. For an electric transport, we start with the first-principles band structure calculations and the modeling for the chemical potential. Then, the electric transport properties ($\alpha_S$, $\sigma_\tau$, and $k_\rho$) are determined using BTE with the appropriate modeling of the relaxation time and chemical potential between 100 and 500 K. The calculated results are in reasonable agreement with the experiments, noting that the experiments inherently contain various defects.

II. PREDICTION OF PHONON CONDUCTIVITY

There are two common theoretical approaches in the investigation of phonon transport in solids. One is the continuum transport theory (or kinetic theory), such as BTE,\cite{11, 12} which is suitable for fast calculations of large systems. However, this normally needs some parameter input from experiments or other predictions; therefore, its application is limited. The other is the atomistic technique, such as MD simulations. Unlike BTE, MD only requires material structures and suitable interatomic potentials. In a sense, MD is more fundamental and can provide insight into the lattice dynamics at the atomic level. Also, MD allows for decomposing different transport mechanisms and is therefore chosen here.

A. Interatomic potentials

Suitable interatomic potentials are essential for modeling the lattice dynamics of Bi$_2$Te$_3$ in the MD simulations. Though there are already some simple harmonic potentials fitted using the experiments in the literature,\cite{35, 3} they are not suitable for the calculation of lattice conductivity due to the omitted anharmonic effects. Here, the interatomic potentials involving the anharmonic terms have been developed by fitting the energy surface from the \textit{ab initio} calculations. The \textit{ab initio} energy surface scan is normally carried out by considering only small isolated clusters. This approach is valid only when the interatomic interactions in a real crystal are mainly of short range. However, long-range interactions, e.g., van der Waals interactions, may be important in determining the structure and dynamics of Bi$_2$Te$_3$.\cite{3} Therefore, a crystal structure with a periodic boundary condition was adopted in the energy surface scan.

The \textit{ab initio} calculations were performed with the QUANTUM-ESPRESSO package\cite{13} within the DFT framework using a plane-wave basis set and pseudopotentials adopting the Ceperley-Alder local density approximation (LDA) with Perdew-Zunger data. A cutoff energy of 50 Ry was used, and the spin-orbit coupling was included. The energy surface of Bi$_2$Te$_3$ was scanned by changing the bond lengths and angles. Both a rhombohedral primitive cell and a hexagonal representation were used in the scan. The classical potentials with predetermined forms were first fitted to these data using the GULP code.\cite{14} Then, the crystal structure and other properties such as the elastic constants were calculated by implementing those potentials in the GULP package and compared with experimental results. Such procedures iterated until convergent results were achieved. Note that the DFT with the generalized-gradient approximation (GGA) or LDA cannot describe the true long-range van der Waals interactions.\cite{15} Though recent developments\cite{15} have seamlessly included van der Waals interactions in DFT, the solutions are not very simple and are unavailable in most present DFT codes. In this work, the van der Waals interactions were first parametrized by fitting the energy surface scanned by QUANTUM-ESPRESSO and subsequently refined by fitting to the structure and elastic constants. In the fitting with the energy surface, we adopted the atomic charges fitted by Kullmann \textit{et al.}\cite{5} The final forms of the interatomic potentials are listed in Table I.

It is interesting to note that the Te1-Bi bond has a higher bond energy and a higher force constant than the Te2-Bi bond. Also, its potential has a larger spatial variation than the Te2-Bi bond, showing a stronger bond anharmonicity. This indicates that the Te1-Bi bond is more ionic than the Te2-Bi bond. The Te1-Te1 bond, which is commonly considered as a van der Waals interaction, has a bond energy $\varphi_o$ = 0.0691 eV, lower than that of a typical ionic or covalent bond but much higher than the bond energy of the Xe-Xe or Kr-Kr van der Waals interaction (for Xe-Xe, $\varphi_o$ = 0.014 eV, and for Kr-Kr, $\varphi_o$ = 0.02 eV),\cite{16} which has a close filled-shell atomic radius. Also, the force constant $\Gamma$ of Te1-Te1 at the equilibrium site is 10.45 N/m, which is also much larger than those of Xe-Xe ($\Gamma$ = 0.96 N/m) and Kr-Kr ($\Gamma$ = 1.15 N/m).\cite{16} This value agrees well with the results of Jenkins \textit{et al.}\cite{3} ($\Gamma$ = 9.83 N/m) and Kullmann \textit{et al.}\cite{5}
the interatomic potentials (excluding the electrostatic interactions) for Bi$_2$Te$_3$. Here, $r$ and $\theta$ are the interatomic separation distance and bond angle, respectively. The cutoff radius of the electrostatic terms is 12 Å. The atomic charges of Te1, Bi, and Te2 are $-0.26$, 0.38, and $-0.24$, respectively (Ref. 5).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Potential Model</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te1-Bi (adjacent layers)</td>
<td>$\varphi_o[1-\exp(-a(r-r_o))]^2$-1)</td>
<td>$\varphi_o=0.974$ eV, $a=1.2848$ Å$^{-1}$, $r_o=3.10$ Å</td>
</tr>
<tr>
<td>Te2-Bi (adjacent layers)</td>
<td>$\varphi_o[1-\exp(-a(r-r_o))]^2$-1)</td>
<td>$\varphi_o=0.5801$ eV, $a=1.2537$ Å$^{-1}$, $r_o=3.235$ Å</td>
</tr>
<tr>
<td>Te1-Te1 (adjacent layers)</td>
<td>$\varphi_o[1-\exp(-a(r-r_o))]^2$-1)</td>
<td>$\varphi_o=0.0691$ eV, $a=2.174$ Å$^{-1}$, $r_o=3.64$ Å</td>
</tr>
<tr>
<td>Bi-Bi (same layer)</td>
<td>$\varphi_o[1-\exp(-a(r-r_o))]^2$-1)</td>
<td>$\varphi_o=0.085$ eV, $a=1.93$ Å$^{-1}$, $r_o=4.18$ Å</td>
</tr>
</tbody>
</table>

Angular

| Te1-Bi-Te1 (adjacent layers)       | $\frac{1}{2}\varphi_o(\cos \theta-\cos \theta_o)^2$                           | $\varphi_o=0.56$ eV, $\theta_o=90°$ |
| Bi-Te1-Bi (adjacent layers)        | $\frac{1}{2}\varphi_o(\cos \theta-\cos \theta_o)^2$                           | $\varphi_o=1.31$ eV, $\theta_o=90°$ |
| Te2-Bi-Te2 (adjacent layers)       | $\frac{1}{2}\varphi_o(\cos \theta-\cos \theta_o)^2$                           | $\varphi_o=1.47$ eV, $\theta_o=85°$ |
| Bi-Bi-Te2 (adjacent layers)        | $\frac{1}{2}\varphi_o(\cos \theta-\cos \theta_o)^2$                           | $\varphi_o=1.47$ eV, $\theta_o=85°$ |
| Te2-Bi-Te1 (three adjacent layers)  | $\frac{1}{2}\varphi_o(\cos \theta-\cos \theta_o)^2$                           | $\varphi_o=1.16$ eV, $\theta_o=92°$ |
| Bi-Te2-Bi (three adjacent layers)   | $\frac{1}{2}\varphi_o(\cos \theta-\cos \theta_o)^2$                           | $\varphi_o=1.18$ eV, $\theta_o=95°$ |

The large bond energy, the force constants, and the large spatial variation of the Te1-Te1 interaction indicates that the Te1-Te1 (excluding electrostatic interaction) interaction may be special. As will be discussed in Sec. III A, the interatomic bonds in each quintuple layer are primarily the $ppp$ interactions.

We applied these potentials in the GULP package to optimize the structure (energy minimization). The resulting $c$ and $a$ values at 0 K are listed in Fig. 2, compared with the values measured$^{17}$ at 4 K. Since structure parameters at low temperatures are unavailable, we also used MD to obtain the average bond lengths and angles in a freestanding structure at 300 K, and the comparisons with the experimental results measured$^{12-13}$ at 293 K are shown in Fig. 2. The overall agreement is good (the average deviation from the measured data is less than 1%). The calculated Te1-Te1 bond length at 0 K (not shown) in the crystal is 3.62 Å, shorter than the equilibrium bond length parameter 3.64 Å listed in Table I. This indicates that the repulsion between the adjacent two Te1 layers is overwhelmed by the electrostatic interaction between the distant Bi and Te1 layers in two neighboring blocks. However, at high temperature, as shown in Fig. 2, the attraction between the two adjacent Te1 layers originates from both the electrostatic interaction and the weak Te1-Te1 bonds. The combination of the electrostatic interaction and the strong van der Waals interaction makes the net Te1-Te1 interaction behave as an ionic bond.

The elastic constants (the elastic modulus $C_{\alpha\beta}$, bulk modulus $E_p$, and Young modulus $E_Y$) of the optimized structure are also calculated using the dynamical matrix approach implemented in the GULP package. In performing the lattice dynamical calculation, the Cartesian reference axis is chosen to be the same as that in Ref. 3. The calculated results apply to 0 K. Table II compares the elastic constants of the optimized structure with the experimental data at different temperatures.$^{35}$ Except for C13, our data for the optimized structure at 0 K agree quite well with the elastic constants at 0 K measured by Jenkins et al.$^{7}$ and the average deviation from the measured values is less than 10%. We also calculate the elastic constants of a freestanding structure at 300 K. As shown in Table II, the changes of the elastic constants $\Delta C_{\alpha\beta}$ vary quite well with the experiments. This indicates that these potentials can be used to describe the phonon behaviors of Bi$_2$Te$_3$ over a wide temperature range. Also, note that C11 is only slightly larger than C33 because of the high force constant of Te1-Te1 bonds, which shows weak anisotropy in the elastic properties of the layered Bi$_2$Te$_3$ structure.

The umklapp processes, in which the phonon momentum is changed by a reciprocal lattice vector, dominate the lattice.
thermal conductivity of crystalline materials at normal and high temperatures (typically above \(1/3\)–\(1/2\) of the Debye temperature). This intrinsic resistive process results from the anharmonicity of the interatomic potentials in solids. Its strength depends on both the available phonon phase and the anharmonicity of the interatomic potentials, respectively.\(^{18}\) Therefore, we calculate the volume of a hexagonal unit cell under different hydrostatic pressures \(p\) by minimizing the enthalpy of the system. With the resulting structure, the phonon frequency at each \(\mathbf{k}\) point was recalculated by diagonalizing the corresponding dynamical matrix (a \(6 \times 6 \times 6\) \(\mathbf{k}\) mesh was used). The Grüneisen parameter \(\gamma\) was then calculated from the changes in the phonon frequencies and listed in Table III.

The Grüneisen parameter \(\gamma_{G,\mathbf{k},s}\) describes the relative shift of phonon frequency of the mode \((\mathbf{k}, s)\) with the change of the volume and is defined as
\[
\gamma_{G,\mathbf{k},s} = -\frac{V}{\omega_s(\mathbf{k})} \frac{\partial \omega_s(\mathbf{k})}{\partial V},
\]
where the mode is denoted by the wave vector \(\mathbf{k}\) and the branch identifier \(s\), \(\omega\) is the angular frequency, and \(V\) is the volume. The overall Grüneisen parameter is defined as
\[
\gamma_{G} = \sum_{\mathbf{k},s} \gamma_{G,\mathbf{k},s} c_{v,s}(\mathbf{k}),
\]
\[
c_{v,s}(\mathbf{k}) = \frac{\hbar \omega_s(\mathbf{k})}{V} \frac{\partial}{\partial T} \left[ \frac{1}{e^{\hbar \omega_s(\mathbf{k})/k_B T} - 1} \right] = \frac{\beta E_p}{c_v},
\]
where \(c_{v,s}(\mathbf{k})\) is the contribution of the mode \((\mathbf{k}, s)\) to the volumetric specific heat \(c_v\), and \(\beta\) is the volumetric thermal expansion coefficient. To calculate the volume dependence of the phonon frequencies in Eq. (2), we used GULP to calculate the volume of a hexagonal unit cell under different hydrostatic potentials, respectively.\(^{18}\)

\[
\begin{array}{cccccc}
\text{Parameter} & \gamma_{G} & \gamma_{G,\parallel} & \gamma_{G,\perp} & \beta (10^{-6}/K) & \beta_{\parallel} (10^{-6}/K) & \beta_{\perp} (10^{-6}/K) \\
\text{Experiment} & 1.49^{+1} & 48.0^{a} & 44.0^{b} & 12.9^{+} & 13.0^{b} & 22.2^{+} \text{ and } 18.0^{b} \\
\text{Calculation} & 1.40 & 1.17 & 1.86 & 46.8 & 12.9 & 21.0 \\
\end{array}
\]

\(^{a}\)Reference 1.  
\(^{b}\)Reference 20.
\[ \gamma_{G,a} = \frac{3\beta_a E_p}{c_v}, \] (8)

which measures the anharmonicity along the \(a\) direction and equates to \(\gamma_G\) if the structure is isotropic \((\gamma_G = \sum_a \gamma_{G,a}/3)\).

Table III shows that the in-plane Grüneisen parameter \(\gamma_{G,\parallel}\) is close to the \(\gamma_G\) value of an ideal covalent material\(^{21}\) and is much smaller than the cross-plane Grüneisen parameter \(\gamma_{G,\perp}\), indicating that the in-plane anharmonic scattering is much weaker than the cross-plane anharmonic scattering. The calculated \(\gamma_{G,\perp}\), however, is a typical value of an ionic material, which confirms the conclusion about the Te1-Te1 ioniclike mixed bond.

B. Lattice vibrations

To further investigate the lattice vibrations of Bi\(_2\)Te\(_3\), we also used the MD simulations to calculate the normalized total phonon density of states (DOS) \([\text{Fig. 3(a)}]\) together with the atomic partial phonon density of states (PDOS) \([\text{Fig. 4}]\).

The normalized PDOS of the \(\beta\)th species in the \(a\) direction, \(D^{\beta}_{p,\beta,a}(\omega)\), is determined by taking the Fourier transform of the velocity autocorrelation function \(1800\) ps raw velocity data were used in the autocorrelation calculation.\(^{22,23}\)

\[
D^{\beta}_{p,\beta,a}(\omega) = \frac{\int \exp(-i\omega t)\langle u_{\beta,a}(t)u_{\beta,a}(0)\rangle dt}{\int \int \exp(-i\omega t)\langle u_{\beta,a}(t)u_{\beta,a}(0)\rangle dt d\omega},
\] (9)

where \(u_{\beta,a}\) denotes the velocity of an atom of the \(\beta\)th species in the \(a\) direction.

The normalized total phonon DOS is obtained by summing over the normalized partial DOS weighted with the species concentration \(c_p\).

\[
D^p(\omega) = \sum_{\beta,a} c_p D^{\beta}_{p,\beta,a}(\omega).
\] (10)

To obtain the DOS and PDOS, the MD simulations were run at 300 K, and \(1800\) ps raw velocity data were used in the

![Graph of normalized phonon density of states](image)

**FIG. 3.** (Color online) Predicted variation of the normalized phonon DOS for Bi\(_2\)Te\(_3\) with respect to frequency, and the comparison with the available DOS (Refs. 3 and 24).

![Graph of directional phonon density of states](image)

**FIG. 4.** (Color online) (a) Predicted variation of the directional phonon DOS for Bi\(_2\)Te\(_3\) with respect to frequency. (b) Root mean square of the displacement for various atoms in Bi\(_2\)Te\(_3\).
calculation for the autocorrelation function. The obtained total phonon DOS is shown in Fig. 3. The generalized phonon density of states \( G(\omega) \) measured at 77 K by Rauh et al.\textsuperscript{24} using the inelastic neutron scattering and that calculated by Jenkins et al.\textsuperscript{3} with the assumed Born–von Karman model are also shown in Fig. 3. Note that the \( G(\omega) \) measured by Rauh et al.\textsuperscript{24} is not the conventional DOS because the difference of the weight factors is significant for Bi and Te. The cutoff frequency calculated by the MD simulation is 4.7 THz, larger than the value of 4.3 THz calculated by Jenkins et al.\textsuperscript{3} but agreeing well with the value of 4.7 THz measured by Rauh et al.\textsuperscript{24} and of 4.55 THz measured by Kullmann et al.\textsuperscript{3} Overall, our DOS results agree fairly well with that of Jenkins et al.\textsuperscript{3} In our DOS results, there is a gap between 2.5 and 2.9 THz, which is mainly determined by the weak Te1-Te1 bond and the Te2-Bi bond. Neither our model nor that of Jenkins et al.\textsuperscript{3} can reproduce the transversal eigenmode around 1.0 THz. This may be due to the simple nature of the “rigid-ion” model since the high polarizability of Te and Bi may significantly influence the dispersion behavior of the transverse optical mode. A suitable core-shell model may account for this problem, which will be investigated in the future.

Figure 4(a) shows the normalized in-plane and cross-plane phonon DOSs of the entire Bi\(_2\)Te\(_3\) structure and those of the different species. Overall, the in-plane and cross-plane phonon DOSs almost overlap, especially when \( f < 3 \text{ THz} \), and the difference only lies in the high-frequency regime (\( f > 3 \text{ THz} \)), where the cross-plane spectrum seems to shift a little toward a relative higher frequency regime. This rough identity indicates that there is only a minor difference between the in-plane and cross-plane vibration spectra, which is consistent with the fact that C11 differs only slightly from C33. The in-plane and cross-plane PDOSs of the different species provide more details about the lattice vibration. When \( f < 1.5 \text{ THz} \), where acoustic vibrations dominate, the three PDOSs for both directions are almost the same. The Bi atoms have more modes in the low-frequency regime (\( f < 2.6 \text{ THz} \)) of the PDOS for both directions, but less modes in the high-frequency regime (\( f > 3 \text{ THz} \)) than those of the Te1 and Te2 atoms. This is due to their larger mass. Overall, the in-plane PDOSs of Te1 and Bi match each other quite well, and the difference only exists in a narrow frequency regime (2.8 THz < \( f < 3.6 \text{ THz} \)). This is believed to directly result from the strong Te1-Bi bonds. However, most in-plane vibration modes of Te2 atoms concentrate in the high-frequency regime (2.8 THz < \( f < 4.6 \text{ THz} \)). The in-plane vibration spectrum of Te1 shows strong peaks between 2.8 and 3.6 THz, where Te1 and Bi have much less vibration modes. Te2 also has much less vibration modes than Bi and Te1 atoms in the regime between 1.5 and 2.6 THz. All these show that the correlation between the in-plane optical vibrations of Te2 and Bi/Te1 is weak, while the correlation between the in-plane vibrations of Bi and Te1 is strong. This may be due to the relatively weak Bi-Te2 bonds (compared with Bi-Te1 bonds) and the symmetric position of Te2 atoms in the five-layer sandwich structure. Similarly, the cross-plane PDOS of Te2 atoms mainly focuses on the high-frequency regime (\( f > 2.8 \text{ THz} \)). There are strong peaks between 3 and 3.6 THz in the cross-plane PDOS of Te2, but those peaks are rather weak in the PDOS of Te1 and Bi, indicating the energy localization of those modes. Also, there are large differences among the cross-plane PDOSs of neighboring Te1/Bi and Bi/Te2 layers, suggesting that phonon transporting across the planes will suffer from strong scattering. Those strong scatterings are mainly due to the mass difference and the large variation in the force constant and the bond-scaling parameter \( \gamma' \) in the neighboring bonds.\textsuperscript{24} Figure 4(b) shows the root mean square (rms) displacement of atoms. The rms’ of the Te2 atoms are isotropic, while the Bi atoms have the largest cross-plane rms and the Te1 atoms have the largest in-plane rms.

C. Molecular dynamics simulation procedure and GK autocorrelation

The thermal conductivity limited by the phonon-phonon scattering \( K_p \) is determined using the GK approach, in which the thermal conductivity is related to the decay of the heat current autocorrelation function (HCACF). The thermal conductivity \( K_p \) tensor is given by

\[
K_p = \frac{1}{k_B V T} \int_0^\infty \langle \dot{w}(t) \dot{w}(0) \rangle dt,
\]

where \( k_B \) is the Boltzmann constant, \( V \) is the volume of the simulation system, \( T \) is the system temperature, and \( \langle \dot{w}(t) \dot{w}(0) \rangle \) is the HCACF. A slow-decaying HCACF indicates that the heat current fluctuations can spread over a long time before vanishing, i.e., a long phonon relaxation time. The heat current \( \dot{w} \) is defined as

\[
\dot{w} = \frac{d}{dt} \sum_{i=1}^N r_i E_i,
\]

where \( r \) and \( E \) are the position vector and the energy of a particle (atom) (excluding the site energy), respectively.

The MD simulations were performed with a system consisting of \( 6 \times 6 \times 1 \) hexagonal unit cells and involving 540 atoms. The simulations with larger systems produced very similar results. The temperatures considered were from 100 to 400 K, with an interval of 50 K. The time step was chosen as 10 fs. The Verlet leapfrog algorithm was adopted for the calculation, while the Nose-Hoover thermostat and the Berendsen barostat were used to control the system temperature and pressure. The system was first simulated in an NPT (constant number of atoms, pressure, and temperature) ensemble for 100–200 ps until it reached a freestanding state at the desired temperature; then, it was switched into an NVE ensemble and ran for 200 ps to arrive in equilibrium. At each temperature point, 1700 ps raw heat current data were obtained for the calculation of HCACFs. After calculating HCACF, the direct integration method is used to obtain the thermal conductivity. The integral is averaged to smooth the behavior in a converged region. The final result is the average value over the converged region.

To speed up the calculations, the Wolf method\textsuperscript{25} was adopted for the calculation of the long-range electrostatic
interactions. The decay parameter $\beta$ is chosen to be 0.25 Å$^{-1}$, and the cutoff radius $R_c$ is chosen to be 10 Å.

### D. Phonon conductivities and its decomposition

Figure 5 shows the time variation of the normalized raw HCACF and the lattice thermal conductivity along the in-plane and cross-plane directions. The normalization factors $\langle \tilde{w}_\alpha(0) \cdot \tilde{w}_\alpha(0) \rangle$ for the two directions only differ slightly (<3%). The normalized raw HCACF curves in both directions involve high-frequency components caused by the high-frequency optical phonons. It is apparent that the fluctuations in the in-plane HCACF are much larger than those in the cross-plane one. Considering the identity of the normalized vibration spectrum along the two directions, the high-frequency vibrations along the cross-plane direction are more likely to be localized. Both HCACF curves consist of two stages, i.e., an initial rapid decay stage followed by a relatively slow decay stage, which have also been found for other crystals. It has been shown that the HCACF of a crystal with a multilayer unit cell can be decomposed into three parts by fitting the HCACF to a function of the form:

$$\langle \tilde{w}_\alpha(t) \cdot \tilde{w}_\alpha(0) \rangle = A_{A,sh,\alpha} \exp(-t/\tau_{pA,sh,\alpha})$$

$$+ A_{A,lg,\alpha} \exp(-t/\tau_{pA,lg,\alpha})$$

$$+ \sum_{O,i} B_{O,i,\alpha} \exp(-t/\tau_{pO,i,\alpha}) \cos(\omega_{pO,i,\alpha}t).$$

(13)

where $\tau_{p,\alpha}$ is a time constant, the coefficients $A$ and $B$ represent the strength of a given mode, and the subscripts $sh$, $lg$, $A$, and $O$ denote short-range, long-range, acoustic, and optical contributions, respectively. We used a Fourier low-pass filter (the cutoff frequency was set at 1.5 THz) to remove the high-frequency components of HCACF and fitted the low-frequency acoustic part using the two-term exponential functions. The fitting results are also shown in Fig. 5. At the beginning, the decay relaxation times for HCACF curves are almost the same, rather short (0.27 ps). However, for the long-range decay, the relaxation time for the in-plane HCACF is 10.62 ps, which is longer than that for cross-plane HCACF (7.88 ps), indicating that the lattice scattering along the cross-plane direction is stronger. The time variation of the lattice thermal conductivities shown in Fig. 5 also confirms this.

Figure 6 shows the temperature-dependent in-plane and cross-plane lattice conductivities of Bi$_2$Te$_3$ calculated by the MD simulations using the potentials listed in Table I. The available experimental results are also shown. Note that the calculated in-plane and cross-plane $k_{p,i}$, $k_{p,\perp}$ are higher than the experimental results. This is expected, considering the various defects (e.g., isotopes, displacements, lamellae, etc.) in a real Bi$_2$Te$_3$ crystal, which will reduce the thermal conductivity.

The lattice conductivities in both directions roughly follow the $1/T$ law, similar to insulators. The calculated cross-plane thermal conductivity $k_{p,\perp}$ is lower than the in-plane $k_{p,i}$. Since the average cross-plane sound velocity (1631 m/s) is very close to the in-plane sound velocity (1775 m/s), the difference between the two thermal conductivities is mainly due to the different anharmonicities along the two directions. This can be verified by the directional Grüneisen parameter $\gamma_{G,i}$ along the $i$ direction. For Bi$_2$Te$_3$, at 300 K, the in-plane Grüneisen parameter $\gamma_{G,i}$ is 1.17, while the cross-plane Grüneisen parameter $\gamma_{G,\perp}$ is 1.86. The large difference in the anharmonicity originates from the unique bond characteristics in the layered structure (Fig. 1), in which the intralayer bonds are mainly covalent but the interlayer bonds are the hybrids of the electrostatic interaction and the van der Waals interaction.

Figure 5 illustrates the different decay stages and components of HCACF. According to Eqs. (11) and (13), the lattice...
The thermal conductivity $K_p$ can then be decomposed into three parts as

$$K_p = K_{p,Ash} + K_{p,Alg} + K_{p,O}. \quad (14)$$

Here, $K_{p,Alg}$ is believed to be the contribution from the long-range acoustic phonons, with a mean-free path larger than one-half of their wavelengths; $K_{p,Ash}$ is the contribution from the short-range phonons, with their mean-free paths minimized (Kaburaki et al. attributed it to single-particle motions in a local environment), and $K_{p,O}$ is the contribution from the high-frequency optical phonons. We obtained $K_{p,Ash}$ and $K_{p,Alg}$ by fitting the low-frequency part of HCACF with the two-term exponential functions shown in Eq. (13) and obtained $K_{p,O}$ by directly integrating the high-frequency part of HCACF. The Fourier low-pass and high-pass filters were used to separate the different components. Further details about the decomposition can be found elsewhere.

Figure 7 shows the variation of the different components of the in-plane and cross-plane lattice thermal conductivities with respect to temperature. The results shown are the average for several data sets. The difference between the sum and the phonon DOS at different temperatures is due to the fact that $k_{p,Ash}$ and $k_{p,O}$ are almost temperature independent. On the other hand, $k_{p,Alg}$ decreases with increasing temperature. A power-law fit yields $k_{p,Alg} \propto T^{-1.03}$ and $k_{p,Ash,\perp} \propto T^{-1.25}$, and the stronger temperature dependence of $k_{p,Ash,\perp}$ may be due to the larger thermal expansion along the cross-plane direction. In other words, in both the in-plane and cross-plane directions, $k_{p,Ash}$ roughly follows the normal $T^{-1}$ law for high-temperature lattice thermal conductivities.

In Fig. 7, the lattice conductivity calculated by the Cahill-Pohl model is also shown, which is given by

$$k_{p,CP} = \left( \frac{\pi}{6} \right)^{1/3} \kappa Bn^{3/2} \sum_{i=1}^{3} u_{p,i} A_i \left( \frac{T}{T_D} \right)^2 \int_0^{T_D/T} \frac{X^2 e^x}{(e^x - 1)^2} dx,$$  \quad (15)

where $n$ is the number density of atoms. The lattice conductivity predicted by Eq. (15) has been interpreted as the minimum solid phase thermal conductivity. In Fig. 7, $k_{p,CP,\perp}$ is only slightly higher than $k_{p,CP}$ and both are almost temperature independent in the temperature range between 150 and 450 K. The sum of $k_{p,Ash}$ and $k_{p,O}$ is about 60% of $k_{p,CP}$ or $k_{p,CP,\perp}$. The behaviors of $k_{p,Ash}$ and $k_{p,O}$ are actually quite similar. If they are both mainly affected by a local environment, their sum seems likely to be independent of different scattering mechanisms unless the local environment (with a dimension of the order of the interatomic spacing) is changed. In other words, this provides a lower limit of the phonon conductivity for structure engineering, which is 0.2 W/m K at 300 K.

By assuming that heat was mainly carried by the acoustic phonons scattered via the three-phonon processes, Slack proposed a simple relation for the thermal conductivity of crystals with constant volume at high temperatures

$$k_{p,S} = \frac{3.1 \times 10^9 (\langle M \rangle N_e)^{1/3} \delta T_{D,\infty}}{T(G)},$$  \quad (16)

where $\langle M \rangle$ is the mean atomic weight of the atoms in the primitive cell, $\delta$ is the average volume per atom, $N_e$ is the number of atoms in a primitive cell, and $T_{D,\infty}$ is defined from the phonon DOS $D_p$ i.e.,

$$T_{D,\infty} = \frac{5\hbar^2}{3k_B} \int_0^f \rho D_p(f) df,$$  \quad (17)

where $\hbar$ is the Planck constant and $f$ is the phonon frequency. Note that the integral is only over the acoustic portion of the phonon spectrum. $T_{D,\infty}$ is generally close or slightly lower than the Debye temperature for the acoustic branches $T_D N_e^{1/3}$ ($T_D$ is the Debye temperature).

Slack mainly applied this relation for isotropic crystals with a cubic structure. However, as discussed in Ref. 21, if the long-range phonons dominate the heat transfer, their contribution may still have a form very similar to Eq. (16);
therefore, it is possible to modify this relation and apply it for anisotropic crystals. Assuming that the scattering of phonons along the \( \alpha \) direction is only related to the elastic and anharmonic properties along this direction, that is, the transport of phonons along this direction is similar to the transport in an isotropic structure with the same elastic and anharmonic properties, then we extended Eq. (16) as

\[
k_{p,s,\alpha} = \frac{3.1 \times 10^4 (M)N_\infty^{1/3} \delta I_{\alpha}^3}{T \gamma_{G,\alpha}^2}, \quad \alpha = \perp \text{ or } ||.
\]  

(18)

Here, \( T_{D,\alpha} \) is given by Eq. (17) while replacing \( D_p(\nu) \) with \( D_{p,\alpha}(\nu) \). As discussed in Sec. II B, the total in-plane and cross-plane PDOSs are almost the same, and the calculation according to Eq. (17) provides \( T_{D,\alpha ||} = 76 \) K and \( T_{D,\alpha \perp} = 75 \) K. Using \( \gamma_{G,\perp} = 1.17 \) and \( \gamma_{G,||} = 1.86 \) calculated in Sec. II A, the in-plane and cross-plane long-range components [denoted as \( k_{p,A,\perp,\perp} \) (Slack) and \( k_{p,A,\perp,\perp} \) (Slack)] were calculated by Eq. (18) and are also shown in Fig. 7. Overall, these results are in reasonable agreement with those decomposed from the MD simulations in both directions (the average deviations from the MD results are within 30% for \( k_{p,A,\perp,\perp} \) and 20% for \( k_{p,A,\perp,\perp} \)).

E. Role of phonon-electron scattering in phonon conductivity

In semiconductors, phonons are scattered by grain boundary, defects, other phonons, and carriers. According to the Matthiessen rule, the total thermal resistivity can be represented as

\[
\frac{1}{k_p} = \frac{1}{k_{p,b}} + \frac{1}{k_{p,d}} + \frac{1}{k_{p,U}} + \frac{1}{k_{p,c}},
\]  

(19)

where \( k_{p,b}, k_{p,d}, k_{p,U}, \) and \( k_{p,c} \) are the thermal conductivity limited by the scattering of grain boundary, defects,phonon-phonon \( U \) process, and carriers, respectively.

The thermal conductivity limited by phonon-carrier scattering \( k_{p,c} \) can be estimated using the electrical resistivity \( \rho_e \). Their relations have been derived by ignoring the difference between the \( N \) and \( U \) processes between carriers and phonons,33,34 as in

\[
\frac{1}{k_{p,c}} = \frac{A}{N_L T} \left( \frac{T_D}{T} \right) I_5 \left( \frac{\sigma_e^2 z_e}{27 I_5^2} \right),
\]  

(20)

\[
\rho_e = A \left( \frac{T}{T_D} \right)^5 I_5,
\]  

(21)

where

\[
I_5 = \int_0^{T_D/T} \frac{x^6 e^x}{(e^x - 1)^2} dx.
\]  

(22)

In the above relations, \( z_e \) is the number of free electrons per atom, \( N_L \) the Lorenz constant, and \( A \) is a constant (for metals, \( A = 3.7 \)). Then, we have

\[
\frac{1}{k_{p,c}} = \frac{\rho_e (T_D/T)^6}{N_L T} \left( \frac{\pi^2 \sigma_e^2 z_e}{27 I_5^2} \right).
\]  

(23)

When \( T/T_D \) increases from 0.1 to 10, \( (T_D/T)^6/I_5(T_D/T)^2 \) decreases from 97 to 9. Also, for a normal dopant concentration \((<10^{19} \text{ cm}^{-3})\), \( z_e \) is of the order of \( 10^{-3} \). Then, for a wide temperature range \((0.1 \equiv T/T_D \equiv 10)\), \( 1/k_{p,c} \) is only about \( 10^{-4} \) of the electrical thermal resistivity \( 1/k_\epsilon \) found from the Wiedemann-Franz law; therefore, it is negligible for most semiconductors (including Bi\(_2\)Te\(_3\)).

III. PREDICTION OF ELECTRONIC PROPERTIES

The thermoelectric transport properties can be derived from BTE with the relaxation time approximation. The general form of the relations for TE properties is35

\[
\sigma_{e,\alpha \beta}(E_e) = \frac{1}{N} \sum_{i,\mathbf{k}} e^2 \tau_{e,i,\mathbf{k}} \mu_a(i, \mathbf{k}) \mu_{\beta}(i, \mathbf{k}) \frac{\delta(E_e - E_{e,i,\mathbf{k}})}{dE_e},
\]

\[
\sigma_{e,\alpha \beta} = \frac{1}{V} \int \sigma_{e,\alpha \beta}(E_e)(E_e - \mu) \left( \frac{\partial f_\mu(T;E_e)}{\partial E_e} \right) dE_e,
\]

\[
v_{\alpha \beta} = \frac{1}{\epsilon_e T V} \int \sigma_{e,\alpha \beta}(E_e)(E_e - \mu) \left( \frac{\partial f_\mu(T;E_e)}{\partial E_e} \right) dE_e,
\]

\[
\alpha_{c,\alpha \beta} = (\alpha_{e}^{-1})_{\alpha \beta} v_{\epsilon,i,\beta}
\]

\[
k_{e,\alpha \beta} = \frac{k_e}{\epsilon_e T V} \int \sigma_{e,\alpha \beta}(E_e)(E_e - \mu)^2 \left( \frac{\partial f_\mu(T;E_e)}{\partial E_e} \right) dE_e,
\]

\[
k_{e,\alpha \beta} = k_{\epsilon,\alpha \beta} - T v_{\alpha,i \beta} (\alpha_{e}^{-1})_{\alpha \beta} v_{\epsilon,i,\beta}.
\]  

(24)

where \( \alpha_e \) is the Seebeck coefficient, \( \sigma_e \) is the electrical conductivity, \( k_e \) is the electrical thermal conductivity, \( i \) is the band index, \( \tau_e \) is the relaxation time, \( \epsilon_e \) is the charge of electron, \( \mathbf{k} \) is the wave vector, \( u \) is the group velocity, \( f = [e(E_e - \mu)/(k_B T)] + 1 \) is the equilibrium Fermi-Dirac distribution function, \( \mu \) is the chemical potential, and \( E_e \) is the total energy of electron. Accordingly, the band structure \( E_e(i, \mathbf{k}) \), chemical potential \( \mu \), and relaxation times \( \tau_e \) are required inputs for the electronic property calculations.

A. Electronic band structure of Bi\(_2\)Te\(_3\)

The band structure calculation for Bi\(_2\)Te\(_3\) was carried out in the DFT framework. The WIEN2K Program,36 which employs the full potential, linearized augmented plane-wave and local orbital methods, was chosen for this investigation. The GGA as proposed by Perdew et al.37 was used for the exchange and correlation potential. The experimental rhombohedral cell parameters of \( a = 10.48 \) Å and 24.16° and the atomic parameters12 \( u = 0.4001 \) and \( v = 0.2095 \) at \( T = 300 \) K were used in the calculations. The radii of both Bi and Te atoms were set at 2.8 a.u. An \( R \cdot \mathbf{k} \) max value of 9 and a \( G \) max value of 14 were adopted, and a nonshifted mesh with 10 000 \( \mathbf{k} \) points were used. The energy cutoff between the
gap is evaluated as the high-symmetry lines with spin-orbit coupling. The solid and dashed lines are the results with and without the p$_{1/2}$ corrections included.

core and valence states was set at −6 Ry. Because of the significant spin-orbit (SO) effects on the band structure of Bi$_2$Te$_3$, the eigenstates below 10 Ry were considered in the SO calculations. As suggested by Larson, the p$_{1/2}$ corrections may significantly affect the band structure; therefore, the p$_{1/2}$ corrections have also been considered for the Bi 6p and Te 5p states.

The calculated band structures along some high-symmetry lines is plotted in Fig. 8. The solid and dashed lines show the results with and without the p$_{1/2}$ corrections, respectively. When the p$_{1/2}$ corrections are not included, our results are consistent with the results of Scheidemantel et al. The band gap is evaluated as $\Delta E_{c,g} = 0.13$ eV (Scheidemantel et al. reported $\Delta E_{c,g} = 0.11$ eV), which is slightly smaller than the zero-temperature experimental results (0.16 eV). The band edges were found in the mirror plane and off the high-symmetry lines, yielding six highest valence bands and six lowest conduction bands (LCBs). The conduction band edge (CBE) is found at (0.667, 0.571, 0.571), close to those of previous investigations. The secondary LCB edge is found at (0.238, 0.238, 0.238) with a 10 meV higher energy. The valence band edge (VBE) is also found at (0.667, 0.571, 0.571), the same k position of the LCB edge. This result is close to (0.652, 0.579, 0.579) reported by Scheidemantel et al., but different from (0.546, 0.383, 0.383) found by Youn and Freeman and (0.555, 0.397, 0.397) by Kim et al. These comparisons are listed in Table IV.

As shown in Fig. 8, the addition of p$_{1/2}$ lowers the CBE but elevates the VBE, resulting in a decrease in $\Delta E_{c,g}$ from 0.13 to 0.07 eV. The positions of the band edges are still off the high-symmetry lines. The CBE remains at the same position (0.667, 0.571, 0.571), but VBE shifts to (0.571, 0.571, 0.429). Figure 8 also illustrates this shift.

The effective masses of electrons and holes for a single valley near the band edge $m^*_i e$ = $(m^*_i e, o, x, y, z) / (i= e, h)$, where $m^*_i e$ = $h^2 / [\partial^2 E_i / \partial k_i \partial k_i]$, were calculated by choosing a small region around the band extrema. As shown in Table IV, the addition of the p$_{1/2}$ corrections significantly reduces $m^*_i e, o, x, y, z$. Figure 9(a) also shows that the addition of the p$_{1/2}$ corrections lowers the slope of the electron density of states near the band edge. The band structure without the p$_{1/2}$ corrections seems to agree better with the experiments.

The total electron density of states $D_e$ with and without the p$_{1/2}$ corrections are shown in Fig. 9(a). It is apparent that $D_e$ of both the valence bands and conduction bands are nonparabolic. However, we find that the Kane band structure model, with $\Delta E_{c,g}$ and $m^*_i e, o, x, y, z$ calculated from WIEZK (listed in Table IV), gives a good approximation for $D_e$ near both the conduction and valence band edges.

Many semiconductors with narrow band gap exhibit significant nonparabolicity of their energy bands. The two-band Kane model, which has been used successfully to describe many real narrow gap materials, was adopted to account for the theoretical calculations of transport coefficients. The Kane model assumes that the band extrema for the conduction and valence bands are located at the same k point. The energy separation from other bands is greater than the main energy gap, and the momentum operator has nonzero matrix elements between the states corresponding to the extremal points. The dispersion relation of the bands of a valley is of the form

![FIG. 8. (Color online) Electronic band structure of Bi$_2$Te$_3$ along the high-symmetry lines with spin-orbit coupling. The solid and dashed lines are for the results with and without the p$_{1/2}$ corrections included.](image)

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\Delta E_{c,g}$ (eV)</th>
<th>CBE</th>
<th>VBE</th>
<th>$m^*_i e, o, x, y, z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Youn and Freeman (Ref. 39)</td>
<td>0.06</td>
<td>(0.663, 0.568, 0.568)</td>
<td>(0.546, 0.383, 0.383)</td>
<td></td>
</tr>
<tr>
<td>Larson (Ref. 38)</td>
<td>0.05</td>
<td>(0.381, 0.5, 0.5)</td>
<td>(0.546, 0.383, 0.383)</td>
<td></td>
</tr>
<tr>
<td>Scheidemantel et al. (Ref. 10)</td>
<td>0.11</td>
<td>(0.663, 0.568, 0.568)</td>
<td>(0.652, 0.579, 0.579)</td>
<td></td>
</tr>
<tr>
<td>Kim et al. (Ref. 40)</td>
<td>0.154</td>
<td>(0.646, 0.549, 0.549)</td>
<td>(0.555, 0.397, 0.397)</td>
<td>0.07 0.11</td>
</tr>
<tr>
<td>Experiment (Refs. 4, 8, and 9)</td>
<td>0.16</td>
<td></td>
<td></td>
<td>0.07 0.09</td>
</tr>
<tr>
<td>This study (no p$_{1/2}$ correction)</td>
<td>0.13</td>
<td>(0.667, 0.571, 0.571)</td>
<td>(0.667, 0.571, 0.571)</td>
<td>0.06 0.08</td>
</tr>
<tr>
<td>This study (with p$_{1/2}$ correction)</td>
<td>0.07</td>
<td>(0.667, 0.571, 0.571)</td>
<td>(0.571, 0.571, 0.429)</td>
<td>0.02 0.03</td>
</tr>
</tbody>
</table>
FIG. 9. (Color online) (a) Dimensionless electronic density of states \(D_e\) of Bi\textsubscript{2}Te\textsubscript{3} with and without the \(p_{1/2}\) corrections. The inset is for the band edge; also shown is \(D_e\) calculated by the Kane model. (b) Total \(D_{e,\beta}\) for individual species \(\beta\) (partial \(D_e\) of each species times its multiplicity). (c) Decomposed, partial \(D_{e,\beta,l}\) for each species.

\[
E_e \left(1 + \frac{E_e}{\Delta E_{e,g}}\right) = \frac{\hbar^2 \kappa^2}{2m_{e,o}}, \tag{25}
\]

where \(m_{e,o}\) is the density of state effective mass at the band edge, \(\Delta E_{e,g}\) is the energy gap, and \(\kappa\) is the wave vector. Note that here \(E_e\) is measured from the band edge. Then, the density of states \(D_e\) can be explicitly written as

\[
D_e(E) = \frac{2^{1/2}Nm_{e,o}^3}{\pi^2 \hbar^3} E_e^{1/2} \left(1 + \frac{E_e}{\Delta E_{e,g}}\right)^{1/2} \left(1 + \frac{E_e}{2\Delta E_{e,g}}\right). \tag{26}
\]

Here, \(N\) is the multiplicity of the valleys. However, for Bi\textsubscript{2}Te\textsubscript{3}, it is \(D_e\) calculated by the Kane model using \(N=12\) instead of \(N=6\) that can match the results near the band edge from \textsc{wien2k} [shown in Fig. 9(a)]. This is believed to result from the secondary band edges, of which the energy only slightly differs from that of the band edges. This also leads to the total effective masses \(m_{e,o}=h^2/m_{e,o}=0.31m_e\) and \(m_{h,o}=0.42m_e\) (\(m_e\) is the mass of a free electron), which agree well with \(m_{e,o}=0.32m_e\) and \(m_{h,o}=0.46m_e\) measured by Harman et al.\textsuperscript{45} Also note that the energy regime in which the Kane model can provide a good approximation for \(D_e\) is within 0.1 eV around the band edges. Since only the states with an energy within \(3k_B T\) about the chemical potential are important for the transport properties, the Kane model is believed to be a good approximation for \(D_e\) over a wide temperature range.

The total density of states without the \(p_{1/2}\) corrections for each species (a product of the partial \(D_e\) of each species and its multiplicity) is shown in Fig. 9(b). For a comparison of the contributions of different orbitals, the orbital-decomposed \(D_e\) (without the \(p_{1/2}\) corrections) are also shown in Fig. 9(c).

As shown in Fig. 9(b), for the valence bands, Te1 atoms contribute the most to the electronic density of states \(D_e\) near the band edge, while the contributions from Bi and Te2 atoms are less and nearly the same. This indicates that the Te1 atoms are probably going to lose electrons and be a donor in the structure. In contrast, for the conduction bands, the Bi atoms contribute the most to the density of states near the band edge, indicating that they are probably going to receive an electron and be an acceptor. Note that the contributions from Te1 atoms are only slightly less than those from the Bi atoms. This is consistent with the slightly ioniclike bond between the Bi and Te1 atoms. Te2 atoms contribute the least to
the density of states at both the valence and conduction band edges, indicating that they are relatively inert in determining the electronic transport properties of Bi$_2$Te$_3$. Figure 9(c) shows that for Te1 and Te2 atoms, p-type orbitals predominate in both valence and conduction bands. Bi atoms, however, have a strong s+p orbital contribution at the valence band edge, but the wave function at the conduction band edge is mainly p type. Considering the layer sequence Te1-Bi-Te2-Bi-Te1, it seems that the bonds between the nearest-neighboring atoms in each quintuple layer are primarily the p$p$ interactions, as suggested by Mishra et al.\textsuperscript{44}

**B. Chemical potential**

In a thermal equilibrium system, chemical potential $\mu$ is an essential parameter to describe the equilibrium distribution of carriers and their concentrations. All the electronic transport coefficients, in fact, are functions of the band structure $E_i(\kappa)$, $\mu$, and temperature.

Generally, $\mu$ can be determined from

$$n_{d,h} - n_{d,e} = n_b + n_{h,b} - n_e - n_{e,b},$$

(27)

where $n_{d,h}$ and $n_{d,e}$ are the concentrations of acceptors and donors, $n_b$ is the hole concentration, $n_{h,b}$ is the concentration of holes bound on the acceptors, $n_e$ is the electron concentration, and $n_{e,b}$ is the concentration of electrons bound on the donors. For modest doped semiconductors, $n_{h,b}$ and $n_{e,b}$ are normally negligible at normal and high temperatures ($>100$ K). Therefore, we can rewrite Eq. (27) as

$$n_{d,h} - n_{d,e} = \int_{-\infty}^{0} D_c(E_e) \frac{1}{\sqrt{\epsilon(E_e - \mu) + i\hbar \gamma}} dE_e$$

$$- \int_{\Delta E_{e,g}}^{0} D_c(E_e) \frac{1}{\sqrt{\epsilon(E_e - \mu) + i\hbar \gamma}} dE_e.$$  

(28)

Given $n_{d,h} - n_{d,e}$ and using the $D_c$ calculated by the Kane model, we obtain the carrier concentrations and the chemical potentials at each temperature point. Figure 10 shows the temperature dependence of the calculated carrier concentrations and chemical potentials, compared with the experimental results\textsuperscript{45} for $p$-type Bi$_2$Te$_3$ single crystals, where $n_{d,h} - n_{d,e} = 1.1 \times 10^{19}$ 1/cm$^3$. Both a constant $\Delta E_{e,g}$ and a temperature-dependent $\Delta E_{e,g}(T)$ were adopted in the calculation. As shown in Fig. 10, a constant $\Delta E_{e,g}$ gives a much lower carrier concentration compared to the experiments\textsuperscript{45} at high temperatures ($T>300$ K) when the thermal excitation of carriers becomes important. A good overall agreement can only be achieved by using a temperature-dependent band gap $\Delta E_{e,g}=0.13–1.08 \times 10^{-4} T$. The different $\Delta E_{e,g}$ produce two chemical potential $\mu$ curves. The deviation between them is small under 200 K but becomes more prominent when $T \geq 250$ K, especially when $T \geq 500$ K. Below 300 K, $\mu$ resides within the valence band, and the sample is in the extrinsic regime. For $T>300$ K, increasingly more carriers are thermally excited, leading $\mu$ into the band gap, and the crystal becomes intrinsic. At even higher temperatures, $\mu$ tends to move toward the middle of the band gap. In the following electrical transport calculations, we use $\mu$ calculated from

![Diagram](image-url)

**FIG. 10.** (Color online) Temperature dependence of the calculated carrier concentrations and chemical potentials, compared with the experimental results (Ref. 45). Both a constant band gap $\Delta E_{e,g}=0.13$ eV and a temperature-dependent band gap $\Delta E_{e,g}=0.13–1.08 \times 10^{-4} T$ were used.

Eq. (28) with the temperature-dependent $\Delta E_{e,g}$ by shifting the conduction band.

**C. Relaxation-time models**

The relaxation-time models simplify the calculation of BTE but condense all the complexities into the relaxation time $\tau_e$. In principle, the scattering relaxation time can be obtained using the Fermi golden rule and the perturbation theory. The scattering of electrons is related to the perturbation of the Hamiltonian for an electron,\textsuperscript{36,46}

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 + \frac{e^2}{4\pi \varepsilon_0} \int \left[ \frac{n_i g_i(r')}{|r - r'|} \right] \left[ n_i g_i(r') + 2 + \right] \frac{\hbar^2}{\kappa^2} \cdot \overline{p} \cdot \overline{r} +$$

$$\frac{1}{4\pi \varepsilon_0} \left( \nabla \cdot \left( \nabla \psi_{c,\kappa} \right) \right)$$

(29)

$$H' = H'_{\text{e-p,\kappa}} + H'_{\text{e-p,\alpha}} + H'_{\text{e-p,\beta}} + H'_{\text{e-p,\gamma}} + H'_{\text{e-p,\delta}} + H'_{\text{e-p,\epsilon}} + \cdots$$

$$= \nabla \cdot \left( \nabla \psi_{c,\kappa} \right) + \frac{\kappa}{\kappa^2 + \lambda^2} \left( i Q_{\kappa} e^{i\kappa \cdot r} \right) + \psi_{c,\kappa}$$

$$+ \frac{2e^2}{\kappa} \nabla \cdot \left( \nabla \psi_{c,\kappa} \right) + \cdots$$

(30)

where $g_i(r)$ is the electron radial distribution function, $\psi_{c,\kappa}$ is the exchange-correlation energy, $\psi_{e,\kappa}$ is the external potential excluding the perturbation, $H'$ is the perturbation Hamiltonian due to scatterings, $H'_{\text{e-p,\alpha}}$, $H'_{\text{e-p,\beta}}$, $H'_{\text{e-p,\gamma}}$, $H'_{\text{e-p,\delta}}$, and $H'_{\text{e-p,\epsilon}}$ are the perturbation Hamiltonian for the acoustic phonon scattering, nonpolar-optical phonon scattering, polar-optical phonon scattering, short-range scattering by impurity, and scattering by Coulomb potential, respectively. Here, $\phi_{\kappa,\alpha}$ and $\phi_{\kappa,\beta}$ are the deformation potentials for the acoustic and optical phonons, $q$, is the effective charge, and $\psi_{e,\kappa}$ is the scattering potential of impurity. $d = n^{-1} \sum_{\kappa} Q_{\kappa} S_{\kappa} \exp(i\kappa \cdot R)$ ($N$ is the number of unit cells.
and $s_{np}$ is the polarization vector) is the normal coordinate form of lattice displacement, $\mathbf{K}_p$ is the phonon wave vector, $Q_{\mathbf{K}_p}$ is the normal coordinate, $\lambda$ is the screening length, and $Z\varepsilon_c$ is the effective charge of impurity. The electron relaxation time $\tau_e$ for mode $\mathbf{K}$ can be represented as:

$$\frac{1}{\tau_e} = \sum_{i} \frac{1}{\tau_{e,i}} = \int \frac{d\mathbf{K}'}{(2\pi)^3} \frac{1}{\gamma_{\mathbf{K},\mathbf{K}',j}} (1 - \frac{g_{\mathbf{K}} f^e_{\mathbf{K}}}{g_{\mathbf{K}} f^o_{\mathbf{K}'}}),$$

(31)

where $f^e_{\mathbf{K}}$ is the carrier equilibrium distribution, $g_{\mathbf{K}} = f_{\mathbf{K}} - f^o_{\mathbf{K}}$ is the perturbation of the distribution, and $\gamma_{\mathbf{K},\mathbf{K}',j}$ is the transition rate from state $\mathbf{K}$ to $\mathbf{K}'$ by the $i$th scattering, which can, in turn, be given by the Fermi golden rule as:

$$\gamma_{\mathbf{K},\mathbf{K}',j} = \frac{2\pi}{h} \delta [E_e - E_e(\mathbf{K}')] |M_{\mathbf{K},\mathbf{K}',j}|^2,$$

(32)

where $H'_i$ is the perturbation Hamiltonian for the scattering mechanism $i$ and $\psi(\mathbf{k}, r)$ is the wave function for mode $\mathbf{k}$. The Bloch wave function corresponding to the electron wave vector $\mathbf{k}$ can be written as:

$$\psi(\mathbf{k}', r) = \frac{1}{V^{1/2}} \sum_{C,J} C'_J \sum_{G} C^G_{J} e^{ik'G'r},$$

(33)

where $V$ is the volume, $C$ and $C'$ are coefficients, and the subscripts $J$ and $G$ denote the different orbitals and reciprocal lattice vectors, respectively. Therefore,

$$M_{\mathbf{K},\mathbf{K}'} = \frac{1}{V^{1/2}} \sum_{J} \sum_{G} C^J_{J} C'^J_{J} \sum_{G'} e^{i(\mathbf{K}' - \mathbf{K}'')G'r} e^{i(\mathbf{K}' - \mathbf{K}'')G'r}.$$

(34)

If the wave function and the perturbation potential can be obtained from the first-principles calculation, $\tau_{e,i}$ can be directly determined. This calculation is very challenging, and here we just introduce an analytical relaxation-time model, which is also based on the Fermi golden rule and incorporates the nonparabolic Kane model for energy dispersion.

Five common electron scattering mechanisms are considered in this work, namely, the deformation potential of the acoustic phonons $\tau_{e,p,A}$, deformation potential of the optical phonons $\tau_{e,p,O}$, polar scattering by the optical phonons $\tau_{e,p,PO}$, short-range deformation potential of vacancies $\tau_{e-v,d}$, and Coulomb potential of vacancies $\tau_{e-v,C}$. According to the Matthiessen rule, the total scattering relaxation time $\tau_e$ is expressed as:

$$\frac{1}{\tau_e} = \frac{1}{\tau_{e-p,A}} + \frac{1}{\tau_{e-p,O}} + \frac{1}{\tau_{e-v,d}} + \frac{1}{\tau_{e-v,C}}.$$

(35)

Using the Kane model, the expressions for the different scattering mechanisms are given as follows:

(i) Scattering by deformation potential of acoustic phonons $\tau_{e-p,A}$. The relaxation time for electrons dispersed on the deformatonal potential of acoustic phonons, when using the Kane model of dispersion and assuming an elastic procedure, can be given as:

$$\tau_{e-p,A} = \frac{2\pi^2 C_l}{\varphi_{d,A,e} k_B T (2m_{e,c})^{3/2}},$$

(36)

where $\varphi_{d,A,e}$ is the acoustic deformation potential coupling constant for the conduction band, $C_l$ is the combination of elastic constants, $a_A$ is the ratio of the acoustic deformation potential coupling constants for the valence and conduction bands, and $m_{e,c}$ is the density of state effective mass for a single ellipsoid.

(ii) Scattering by deformation potential of optical phonons $\tau_{e-p,O}$. The relaxation time for electrons dispersed on the optical phonon potential, when using the Kane model of dispersion and assuming an elastic procedure, can be given as:

$$\tau_{e-p,O} = \frac{2\pi^2 C_l}{\varphi_{d,O,e} k_B T (2m_{e,c})^{3/2}}.$$

(37)

where $\varphi_{d,O,e}$ is the optical deformation potential coupling constant for the conduction band, $C_l$ is the combination of elastic constants, $a_o$ is the ratio of the optical deformation potential coupling constants for the valence and conduction bands. The expression for the relaxation time for electrons dispersed on the polar-optical phonons $\tau_{e-p,PO}$ is obtained in a simple isotropic parabolic model, the relaxation time for po-
where vacancies permitivities, BAO-LING HUANG AND MASSOUD KANVIAN PHYSICAL REVIEW B

Inclusion of nonparabolicity and screening effects will lead to

\[ \tau_{\text{e-p,PO}} \sim \frac{1}{u_{e}\kappa} \int_{0}^{2\pi} qdq, \]  

where \( u_{e} \) is the velocity of electrons. When the integral takes into account all phonons, we have

\[ \tau_{\text{e-p,PO}} = \frac{\hbar^{2}u_{e}}{2k_{B}Tc_{s}^{2}[(\epsilon_{o},\epsilon_{e,s})^{-1}-(\epsilon_{o},\epsilon_{e,\infty})^{-1}]} \]  

Inclusion of nonparabolicity and screening effects will lead to

\[ \tau_{\text{e-p,PO}}^{1} = \frac{\hbar^{2}u_{e}}{2k_{B}Tc_{s}^{2}[(\epsilon_{o},\epsilon_{e,s})^{-1}-(\epsilon_{o},\epsilon_{e,\infty})^{-1}]} \]  

\[ F = 1 - \delta \ln(1 + \delta^{-1}) - \frac{2}{1 + 2E_{e}/\Delta E_{c,s}} \left( 1 + \frac{E_{e}}{\Delta E_{c,s}} \right)^{2} \times [1 - 2\delta + 2\delta^{2} \ln(1 + \delta^{-1})] \]  

\[ \delta = (2\kappa\lambda_{o})^{-2}, \]  

where \( \epsilon_{cs} \) and \( \epsilon_{c\infty} \) are the static and high-frequency relative permittivities, \( \kappa \) is the carrier wave vector, and \( \lambda_{o} \) is the screening length of the optical phonons.

(v) Scattering by short-range deformation potential of vacancies \( \tau_{\text{e-v,d}} \). \( \tau_{\text{e-v,d}} \) also has a form similar to the relaxation time of electron-acoustic phonon scattering due to a similar deformation potential, which is

\[ \tau_{\text{e-v,d}} = \frac{\pi\hbar^{4}}{\varphi_{e,v}^{2}m_{e,v,d}(2m_{e,v,d})^{2}n_{v}}, \]  

where \( n_{v} \) is the vacancy density and \( a_{v} \) is the ratio of the short-range deformation potential coupling constants of vacancies for valence and conduction bands.

(v) Scattering by Coulomb potential of vacancies \( \tau_{\text{e-v,c}} \)

\[ \tau_{\text{e-v,c}} = \frac{\varphi_{e,v}^{2}(m_{e,v,c})^{2}E_{c}^{2}(2m_{e,v,c})^{2}}{\pi(\varepsilon_{e}^{2})^{2}n_{v}\ln(1 + \xi - \xi(1 + \xi)) \left( 1 + 2E_{e}/\Delta E_{c,s} \right)}, \]  

\[ \xi = (2\kappa\lambda_{o})^{2}, \]  

where \( \varepsilon_{e} \) is the vacancy charge and \( \lambda_{o} \) is the screening radius of the vacancy potential and is given as

\[ \lambda_{o}^{-2} = \frac{4\pi\varepsilon_{e}^{2}}{D_{s}(\mu), \mu = E_{F}}, \]  

\[ D_{s}(\mu) = \left( \frac{1}{\pi^{2}\hbar^{3}} \right) \left( \frac{\mu^{2}}{\Delta E_{c,s}} \right)^{1/2} \left( 1 + 2\mu/\Delta E_{c,s} \right), \]  

where \( D_{s}(\mu) \) is actually the density of states at the Fermi level.

Figure 11 shows the temperature dependence of the calculated average relaxation times described above. The parameters used in the calculation are listed in Table V. Some parameters, e.g., the deformation potentials, are obtained by fitting the electrical conductivity with experimental results at 100 K. Overall, the scatters by acoustic and optical phonons dominate the electrical transport of Bi2Te3. On the other hand \( \langle \tau_{\text{e-p,PO}} \rangle \) and \( \langle \tau_{\text{e-p,d}} \rangle \) are orders of magnitudes larger than \( \langle \tau_{\text{e-p,d}} \rangle \) and \( \langle \tau_{\text{e-p,d}} \rangle \). Therefore, the scatters by the short-range deformation potential of vacancies and Coulomb potentials are unimportant for the electrical transport of Bi2Te3. Note that \( \langle \tau_{\text{e-p,PO}} \rangle \) is comparable with \( \langle \tau_{\text{e-p,d}} \rangle \) and \( \langle \tau_{\text{e-p,d}} \rangle \). Therefore, the polar scatters by optical phonons is also important.
TABLE V. Parameters used in the relaxation-time models for Bi$_2$Te$_3$, from fit to experimental results (Ref. 45).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Magnitude</th>
<th>Parameter</th>
<th>Magnitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{h,e,o}/m_e$</td>
<td>0.08</td>
<td>$m_{e,o}/m_e$</td>
<td>0.06</td>
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<tr>
<td>$n_o$ (1/m$^3$)</td>
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<td>$\rho$ (kg/m$^3$)</td>
<td>$7.86 \times 10^3$</td>
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<tr>
<td>$\epsilon_{e,o}$</td>
<td>400</td>
<td>$\epsilon_{e,\infty}$</td>
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<tr>
<td>$C_l$ (N/m$^2$)</td>
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<td>$\hbar\omega_o$ (eV)</td>
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</tr>
<tr>
<td>$z$</td>
<td>0.1</td>
<td>$\varphi_{d,A,c}$ (eV)</td>
<td>35</td>
</tr>
<tr>
<td>$\varphi_{d,A,c}$ (eV)</td>
<td>40</td>
<td>$\varphi'_e$ (J/m$^3$)</td>
<td>$1.2 \times 10^{-46}$</td>
</tr>
<tr>
<td>$a_A,a_O,a_v$</td>
<td>1.0</td>
<td>$a$ (Å)</td>
<td>10.45</td>
</tr>
<tr>
<td>$\Delta E_{e,g}$ (eV)</td>
<td>$0.13-1.08 \times 10^{-4}T$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

D. Seebeck coefficient

Figure 12 shows the variation of calculated $\alpha_{S,i}$ of Bi$_2$Te$_3$ with temperature using Eq. (24). The calculation was carried out using BOLTZTRAP, a software package adopting BTEs. Both the energy-dependent relaxation-time models (Sec. III E) and the constant relaxation-time model were used. We modified the BOLTZTRAP code and incorporated the relaxation-time model into the integration since BOLTZTRAP assumes a constant relaxation time. The corresponding Fermi energy at each temperature is determined by Eq. (28) along with the Kane band model for $D_e$. To incorporate the temperature dependence of the band structure, we assume that the band structure does not change with temperature and shifts the conduction band in the calculation to include the temperature dependence of the band gap $\Delta E_{e,g}$. Figure 12 shows that the constant $\Delta E_{e,g}$ leads to much higher values for $T>300$ K (intrinsic regime), while results calculated with

![Figure 12](image-url)

FIG. 12. (Color online) Variation of the calculated Seebeck coefficient for $p$-type Bi$_2$Te$_3$ with respect to temperature, compared with the available experimental results (Ref. 45). Both a temperature-dependent band gap $\Delta E_{e,g}=0.13-1.08 \times 10^{-4}T$ eV and a constant $\Delta E_{e,g}=0.13$ eV are used. Also shown are the predictions using the energy-dependent relaxation times and the constant relaxation-time model.

![Figure 13](image-url)

FIG. 13. (Color online) Variation of the calculated Seebeck coefficient of Bi$_2$Te$_3$ at $T=300$ K with respect to the chemical potential $\mu$.

The temperature-dependent $\Delta E_{e,g}=0.13-1.08 \times 10^{-4}T$ agree quite well with the experimental results. However, in the extrinsic regime ($T\leq300$ K), there is only minor difference between the results with the two different settings for $\Delta E_{e,g}$. As shown in Fig. 12, with the same temperature-dependent $\Delta E_{e,g}=0.13-1.08 \times 10^{-4}T$ eV, the two relaxation-time models give very similar results in the extrinsic regime since one kind of carriers dominates the electrical transport. However, some deviation appears in the intrinsic regime, where the concentrations of the holes and electrons become comparable, and it increases with increasing temperature. This phenomenon indicates that the temperature dependences of the mobilities of holes and electrons are different.

The band structure calculated with the experimental lattice parameters at 300 K was used in the above calculations for $\alpha_S$. Temperature changes not only the carrier concentrations but also the lattice parameters. However, the band structure calculations adopting the lattice parameters under different temperatures show that the thermal expansion has negligible effects on the band structure. The change of lattice parameters from 0 to 300 K only results in a less than 2% change in the band gap. Compared with the actual temperature dependence of band gap, it seems that the temperature variation of the band gap is mainly due to lattice vibration.

Figure 13 shows the variation of $\alpha_S$ along the $||$ and $\perp$ directions, with respect to the chemical potential $\mu$, at 300 K. Apparently, the two curves are very similar, indicating the isotropy of $\alpha_S$. Figure 13 shows that for $p$-type Bi$_2$Te$_3$, the $\alpha_S$ peaks along the $||$ and $\perp$ directions almost overlap. However, for $n$-type Bi$_2$Te$_3$, the absolute peak value $\alpha_S$ along the $||$ direction is larger than that along the $\perp$ direction, though the peak positions are identical. In Figs. 13, $\mu_0$ is the chemical potential value at which $\alpha_S=0$. It is useful to rewrite the relation for $\alpha_S$ in Eq. (24) as

$$\alpha_S = \frac{k_B \langle F_e - \mu \rangle J_{e,(F_e,\mu)}}{e_c k_B T},$$

where $k_B$ is the Boltzmann constant, $\mu$ is the chemical potential, and $\langle F_e - \mu \rangle$ is the average of the Fermi energy $F_e$. The $J_{e,(F_e,\mu)}$ is the current density at the Fermi level $F_e$. This equation shows that $\alpha_S$ is inversely proportional to the temperature $T$.
Here, $\langle E_e - \mu \rangle_{\sigma_e(E_e, \mu)}$ is the $\sigma_e(E_e, \mu)$-averaged energy deviation from the chemical potential. Then, we have

$$\mu_0 = \langle E_e \rangle_{\sigma_e(E_e, \mu)}$$

which is the $\sigma_e(E_e)$-averaged energy close to the middle of the band gap. Therefore,

$$\alpha_s = \frac{k_B (\langle E_e \rangle_{\sigma_e(E_e, \mu)} - \langle E_e \rangle_{\sigma_e(E_e, \mu)} - (\mu - \mu_0))}{e_c k_B T}.$$ (46)

$\langle E_e \rangle_{\sigma_e(E_e, \mu)}$ has a simple form if the nondegenerate approximation may be used, that is,

$$\langle E_e \rangle_{\sigma_e(E_e, \mu)} \approx \frac{\sigma_{e,c}\Delta E_{e,g}}{\sigma_{e,c} + \sigma_{e,h}} = \frac{1}{1 + be^{-2e(k_BT)\Delta E_{e,g}}}.$$ (47)

where $\sigma_{e,c}$ and $\sigma_{e,h}$ are the electrical conductivity contributed by electrons and holes, $b = (\mu_h/\mu_e) (m_{e,h}/m_{e,c})^{3/2}$ ($\mu_h$ and $\mu_e$ are the mobilities of electrons and holes), and $\Delta E_{e,g} = \mu - \Delta E_{e,g}/2$ is the separation of the chemical potential above the middle of the band gap. Apparently, for semiconductors with a large band gap (e.g., $\Delta E_{e,g} > 10k_BT$), the absolute value of the maximum $\alpha_s$ can be estimated as

$$|\alpha_{s,\text{max}}| = \frac{k_B \Delta E_{e,g}}{|e_c| 2k_B T}.$$ (48)

For small $2\Delta E_{e,c}/k_BT$, we have

$$\langle E_e \rangle_{\sigma_e(E_e, \mu)} \approx \frac{\Delta E_{e,g}}{1 + b} \left[ \frac{2b\Delta E_{e,c}/(k_BT)}{1 + b} \right].$$ (49)

Therefore,

$$\alpha_s \approx \frac{k_B}{e_c} \left( \frac{2b\Delta E_{e,g}}{(1 + b)^2k_B T} - 1 \right) (\mu - \mu_0).$$ (50)

For narrow band-gap semiconductors, as shown in Fig. 13, Eq. (50) is a good approximation for $\alpha_s$ when $|\mu - \mu_0| < \Delta E_{e,g}/2$. When $\mu$ moves toward the band edge, the effects of opposite changes become close; when $\mu$ moves further into the band edge, $\langle E_e \rangle_{\sigma_e(E_e, \mu)}$ will become closer to $\mu$. Therefore, $\alpha_s$ will achieve the maximum near the band edge, and the maximum value can be estimated from Eq. (50). Assuming that $b = 1$ and the maximum is achieved at the band edge for $\text{Bi}_2\text{Te}_3$ at 300 K, $|\alpha_{s,\text{max}}| \approx 320 \mu V/K$, close to the maximum in Fig. 13.

E. Electrical conductivity and electric thermal conductivity

Figure 14 shows the calculated electrical conductivity of $\text{Bi}_2\text{Te}_3$ along with the $\parallel$ and $\perp$ directions, wherein the Kane band model based relaxation times are used. The temperature-dependent band gap $\Delta E_{e,g} = 0.13-1.08 \times 10^{-4} eV$ and the corresponding chemical potential calculated in Sec. III B are adopted in the calculation. The parameters for the relaxation-time models are listed in Table V. Below 300 K, the ratio

![FIG. 14. (Color online) Variation of calculated directional electrical conductivity for $\text{Bi}_2\text{Te}_3$ with respect to temperature using the Kane band model and energy-dependent relaxation times, and comparison with the available experimental results (Ref. 45).](125209-16)

The deviation is caused probably by neglecting the directional dependence of the effective masses.

We also used a constant band gap $\Delta E_{e,g} = 0.13 eV$ for the calculation of $\sigma_{e,l}$ using the above energy-dependent relaxation-time models. The same parameters in Table V are used, and the results are also plotted in Fig. 14. Below 300 K, the $\sigma_{e,l}$ calculated with a constant $\Delta E_{e,g}$ is fairly close to those results with a temperature-dependent $\Delta E_{e,g}(T)$. However, in the intrinsic regime, the larger band gap suppresses the thermal excitation of carriers and thus leads to lower $\sigma_{e,l}$ values. Note that with a constant $\Delta E_{e,g}$, $\sigma_{e,l}$ continues to decay without any rebound shown in the experimental results. However, a temperature-dependent $\Delta E_{e,g}(T)$ yields a much better agreement with the experiments at high temperatures, indicating that the temperature dependence of the band gap is important in predicting the temperature dependence of the electrical conductivity.

Traditionally, the Wiedemann-Franz Law, $k_e = N_e \sigma_c T$, where $N_e$ is the Lorenz number, is used to calculate the electric thermal conductivity $k_e$ on the basis of $\sigma_c$. However, for semiconductors, $N_e$ may not be the values used for metals [$(N_e = (\pi^2/3)k_B^2/\epsilon_s^2)$], especially when the chemical potential is near the center of the band gap. Figure 15(a) shows the variation of the directly calculated Lorenz number $N_e$ (scaled with $N_{e,0}$) for $\text{Bi}_2\text{Te}_3$ (along $\parallel$ and $\perp$) at 300 K, with respect to the chemical potential. The results are similar to those found by Chaput et al. for doped skutterudites. When the sample is heavily doped (the chemical potential is deep inside the valence or conduction band), $N_e/N_{e,0}$ is close to 1.0. However, for intermediate doping, $N_e/N_{e,0}$ can be smaller than 1.0, and the minimum is around 0.7. For small doping
FIG. 15. (Color online) (a) Variation of the calculated scaled Lorenz number for Bi$_2$Te$_3$ (along \( \parallel \) and \( \perp \) ) with respect to the chemical potential. Both the constant relaxation-time model and the energy-dependent relaxation-time model (with the Kane band dispersion) results are shown. (b) Variation of the calculated \( k_e \) along the \( \parallel \) and \( \perp \) directions with respect to temperature. The results calculated using the constant \( N_{L,o} \), i.e., \( N_{L,o}\sigma_e T \), are also shown.

corrections or intrinsic regime, \( N_L/N_{L,o} \) may be much larger than 1.0. Figure 15(a) also shows that the constant relaxation-time model will lead to a larger \( N_L \), compared to that for the energy-dependent relaxation-time model discussed above. For both relaxation-time models, \( N_L \) along the \( \parallel \) direction is slightly larger than that along the \( \perp \) direction. Figure 15(b) shows the temperature dependence of the electric thermal conductivity calculated according to Eq. (24) and that calculated from \( N_{L,o}\sigma_e T \). The results from Eq. (24) show that \( k_e \) for both directions increase with increasing temperature, while \( N_{L,o}\sigma_e T \) results show valleys near the room temperature. Due to the significant changes of \( N_L \) in the intrinsic regime, \( N_{L,o}\sigma_e T \) underestimates \( k_e \) at high temperatures.

**F. Figure of merit**

Figure 16 shows the variation of the figure of merit \( ZT \) for the \( p \)-type Bi$_2$Te$_3$ specimen of experiment\(^{45} \) along the \( \parallel \) and \( \perp \) directions, with respect to temperature. The lower two curves are based on the directly (MD) calculated \( k_p \). Since \( k_p \) and \( \sigma_e \) are very sensitive to defects, which are always present in fabricated specimens, for comparison between the calculated and measured \( ZT \), we used a modified \( k_p \), and the results are shown with the top two curves. Due to the difficulty in modeling various defects, the modified \( k_p \) was obtained by fitting the total thermal conductivity to the experimental results\(^{45} \) at 300 K and then by using the \( 1/T \) law at other temperatures. The experimental results are also shown in Fig. 16. The \( ZT \) with a modified \( k_p \) is higher than experimental results above 200 K, mainly due to the overestimation of \( \sigma_e \). The calculated \( ZT \) reaches its maximum at around 250 K. \( ZT \) along the \( \parallel \) direction is higher than that along the \( \perp \) direction between 200 and 400 K due to the larger ratio \( \sigma_{e,\parallel}/\sigma_{e,\perp} \) compared to \( k_{p,\parallel}/k_{p,\perp} \). Note that the experimental \( \sigma_{e,\parallel}/\sigma_{e,\perp} \) is larger than the calculated results (discussed above), so the difference in the figure of merits along the \( \parallel \) and \( \perp \) direction is expected to be even larger.

**IV. SUMMARY AND CONCLUSION**

The interatomic potentials for Bi$_2$Te$_3$ have been developed, and the calculated elastic constants and thermal expansion coefficients agree well with the experimental data, indicating that the proposed force field is suitable in describing both the harmonic and anharmonic behaviors of Bi$_2$Te$_3$. The interaction between two Te1 atoms in the neighboring layers is a mixture of the electrostatic interaction and the van der Waals interaction and behaves like an ionic bond. The force constant difference between the Te1-Te1 and Te2-Bi bonds leads to a phonon band gap near 2.5 THz. There is only a small difference between the in-plane and cross-plane vibrations, and no significant two-dimensional elastic behavior has been found in this layered structure. However, the anisotropy in the polarized Grüneisen parameter shows much
stronger anharmonicity along the cross-plane direction, which is mainly due to the high anharmonic Te1-Te1 interaction.

The temperature dependence of the in-plane and cross-plane lattice thermal conductivities \( k_{p,A,i} \) and \( k_{p,A,\perp} \) has been calculated in a temperature range from 150 to 450 K. The ratio \( k_{p,A,i}/k_{p,A,\perp} \) varies from 1.55 to 2.17 in this temperature regime. Since the elastic properties along the two directions are nearly the same, the difference between \( k_{p,A,i} \) and \( k_{p,A,\perp} \) is believed to be mainly due to the different inharmonicity along the two directions. The calculated in-plane thermal conductivity roughly follows the \( 1/T \) law, while the calculated cross-plane lattice thermal conductivity seems to have a slightly stronger temperature dependence (i.e., \( 1/T^{1.23} \)), which may be due to the larger thermal expansion effects along that direction. The decomposition of the lattice thermal conductivity shows that the long-range acoustic phonons dominate the heat transfer in both the in-plane and cross-plane directions. The contribution from the long-range acoustic phonons \( k_{p,A,lg} \) has a strong temperature dependence; in contrast, the contribution from the short-range acoustic phonons \( k_{p,A,sh} \) and that from the optical phonons \( k_{p,O} \) are also temperature-independent. Also, at each temperature point, \( k_{p,A,sh} \) and \( k_{p,O} \) along the in-plane and cross-plane directions are almost identical. Therefore, \( k_{p,A,sh} \) and \( k_{p,O} \) are not sensitive to the inharmonicity. The sum of \( k_{p,A,sh} \) and \( k_{p,O} \) provides a lower limit for the doped bulk Bi2Te3, which is about 0.2 W/m K at 300 K. By using direction-dependent \( T_{D,\alpha} \) and \( \gamma_{\alpha} \), the Slack model was also extended for anisotropic materials. The extended Slack model gives a good estimation for both the in-plane and cross-plane lattice thermal conductivities, indicating that the phonon transport along a given direction is only affected by the elastic and inharmonic properties along that direction.

We have also calculated the temperature dependence of \( \alpha_S \), \( \sigma_e \), and \( k_e \) over the temperature range from 100 to 500 K. These calculations are based on the band structure, \( \mu \), and \( \tau_e \).

The Kane band model is found to be appropriate in describing the nonparabolicity of the Bi2Te3 band structure. The fitting with the carrier concentration and \( \mu \) shows that the temperature dependence of the band gap is important to give a good prediction. The thermal expansion has negligible effects on the relationship between \( \alpha_S \) and \( \mu_e \); therefore, the effects of temperature on \( \alpha_S \) are mainly through changing the distribution function and \( \mu \). Both the constant relaxation-time model and the analytic relaxation-time model with the nonparabolic Kane model for energy dispersion have been used in the calculations for \( \alpha_S \). The results show that \( \alpha_S \) is sensitive to the temperature dependence of the band gap and the relaxation time models in the intrinsic regime.

The fitting for \( \sigma_e \) using the relaxation-time model also shows that the polar scattering by optical phonons and the scattering by the deformation potential of acoustic and optical phonons predominate the electron transport in Bi2Te3. The scatterings by the short-range deformation potential of vacancies and the Coulomb potentials are negligible. The comparison of the temperature dependence of different scattering mechanisms also shows that the temperature dependence of the band gap is important in describing the temperature dependence of \( \sigma_e \). It is also found that the Lorenz number can be smaller than the value for metals for intermediate doping and will become much larger in the intrinsic regime. In the relaxation-time models used, some parameters are found by fitting to the experimental data on \( \sigma_e \). Further work will use the first-principles methods (e.g., \( \text{Eq. (32)} \)) to calculate the scattering rates by acoustic and optical phonons.

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*aivanyst@umich.edu*

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