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Molecular dynamics simulations of lattice thermal conductivity of bismuth telluride using two-body interatomic potentials

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Two-body interatomic potentials in the Morse potential form have been developed for bismuth telluride, and the potentials are used in molecular dynamics simulations to predict the thermal conductivity. The density-functional theory with local-density approximations is first used to calculate the total energies for many artificially distorted Bi$_2$Te$_3$ configurations to produce the energy surface. Then by fitting to this energy surface and other experimental data, the Morse potential form is parameterized. The fitted empirical interatomic potentials are shown to reproduce the elastic and phonon data well. Molecular dynamics simulations are then performed to predict the thermal conductivity of bulk Bi$_2$Te$_3$ at different temperatures, and the results agree with experimental data well.

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I. INTRODUCTION

There has been renewed interest on high-performance thermoelectric materials in the last decades. Thermoelectric energy conversion can convert waste heat to electricity without any moving parts, therefore it could play a significant role in addressing the energy challenge. The effectiveness of a thermoelectric material is characterized by its figure of merit $ZT$ given by $ZT=S^2\sigma T/\kappa$, where $S$, $\sigma$, and $T$ are the Seebeck coefficient, electrical conductivity, and absolute temperature, respectively. Here $\kappa$ is the thermal conductivity which contains both electronic and lattice contributions $\kappa_e$ and $\kappa_l$. High-performance thermoelectric materials with high $ZT$ require high $S$ and $\sigma/\kappa$ ratio.

Bi$_2$Te$_3$ as well as its alloys have long been the best thermoelectric materials at room temperature with a $ZT$ value of 1.4 at $T=100$ K was achieved in nanostructured bismuth antimony telluride bulk alloys, which are made using ball milling and hot pressing the nanoparticles into bulk ingots. And Bi$_2$Te$_3$/Sb$_2$Te$_3$ bulk nanocomposites with laminated structure was prepared by adopting a route involving hydrothermal synthesis and hot pressing to achieve $ZT$ values in these nanostructures is around 1. In the last decade significant enhancement of $ZT$ has been achieved using nanostructures. A $ZT$ value of 2.4 was reported in a $p$-type superlattice based on Bi$_2$Te$_3$ and Sb$_2$Te$_3$ when heat flows in the cross-plane direction. Bismuth telluride nanowires have been characterized for their enhanced thermoelectric materials at room temperature with a $ZT$ of 1.47 at $T=100$ K was achieved in nanostructured bismuth antimony telluride bulk alloys, which are made using ball milling and hot pressing the nanoparticles into bulk ingots. And Bi$_2$Te$_3$/Sb$_2$Te$_3$ bulk nanocomposites with laminated structure was prepared by adopting a route involving hydrothermal synthesis and hot pressing to achieve $ZT$ value of 1.47 around 450 K. The high $ZT$ values in these nanostructures is mostly attributed to the reduction in the lattice thermal conductivity.

Despite the rapid progress in experiments, theoretical studies on the thermal transport in both bulk and nanostructures of Bi$_2$Te$_3$ are rare, largely due to its heavy metal elements and complicated crystal structure. So far, common theoretical approaches for phonon thermal conductivity include Boltzmann transport equation (BTE), Monte Carlo simulations, and molecular dynamics (MD) simulations. BTE and Monte Carlo methods rely on relaxation-time models to describe phonon scattering and they generally require fitting of certain parameters to experimental data. Molecular dynamics does not need any prior knowledge of phonon transport from experiment—only the interatomic potentials are the inputs. However, the proper interatomic potentials are often difficult to obtain, which is the case for Bi$_2$Te$_3$. Only recently the first set of interatomic potentials for Bi$_2$Te$_3$ bulk crystal were developed by Huang et al. and then used in equilibrium molecular dynamics simulations to predict the phonon thermal conductivity. Their prediction results agree with experimental data quite well, although the three-body potential forms are quite complicated.

In this work, we develop simple two-body interatomic potentials for Bi$_2$Te$_3$ using density-functional theory (DFT) and then use these potentials in molecular dynamics to predict the phonon thermal conductivity. We first perform ab initio calculations to obtain the ground-state energies of a series of distinct configurations. The energy surface data are then used to parameterize the Morse potential form through the least-square fitting. The obtained potentials are validated in lattice-dynamics calculations via reproducing the material’s lattice and elastic properties. Molecular dynamics simulations together with the Green-Kubo method are performed and the lattice thermal conductivities are predicted over the temperature range of 150–500 K.

II. ELECTRONIC STRUCTURE AND PHONON DENSITY OF STATES

Bulk Bi$_2$Te$_3$ belongs to the space group $D_{3h}^5(R\bar{3}m)$ with a rhombohedral lattice structure, along the trigonal axis of which atoms are in the sequence of Te1-Bi-Te2-Bi-Te1 (Fig. 1). The hexagonal conventional cell parameters are $a=4.369$ Å and $c=30.42$ Å and the corresponding rhombohedral unit-cell parameters are $a_0=10.45$ Å, $\theta_0=24.13^\circ$ with Te1 and Bi atoms sitting at $(\pm u, \pm u, \pm u)$ and $(\pm v, \pm v, \pm v)$, where $u=0.399$, $v=0.792$, respectively. To compute the electronic structure, ab initio calculations were performed employing the full-potential linearized augmented plane wave method based on DFT (Ref. 11) using the code WIEN2K. Due to the large atomic mass of Bi and Te atoms, the spin-orbit coupling effects should be considered. Also, as
suggested by Larson,\textsuperscript{13} the $p_{1/2}$ corrections which may significantly affect the electronic band structure have also been considered for the Bi 6$p$ and Te 5$p$ states. The calculated electronic band structure along high-symmetry lines is plotted in Fig. 1, where the band-structure profiles are similar to previous reports,\textsuperscript{13–17} indicating that our calculation can properly describe the ground state. On the other hand, the conduction-band minima and valence-band maxima for Bi$_2$Te$_3$ are off the high-symmetry lines, as pointed out in Refs. \textsuperscript{14, 16, and 17}. Although it is always favorable to accurately predict the band-gap value, we did not make an effort here since our molecular dynamics simulations will be performed at the ground state.

We adopt the ABINIT code\textsuperscript{18} to study the phonon properties of bulk Bi$_2$Te$_3$ and then to validate the obtained interatomic potentials by reproducing the phonon behaviors of Bi$_2$Te$_3$. By starting from the experimental structure, the Hartwigsen-Goedecker-Hutter pseudopotential is used with local-density approximation (LDA) approximation to fully relax the unit-cell structure, while the $4 \times 4 \times 4$ shifted $k$ grid in the first Brillouin zone is adopted based on energy convergence tests. The fully relaxed structure has rhombohedral unit-cell parameters $a_R=10.27$ Å, $\theta_R=24.49^\circ$ and atomic parameters $u=0.400$, $v=0.791$. From the fully relaxed structure, calculations based on vibrational density-functional perturbation theory\textsuperscript{19} are performed and the obtained phonon density of states (phonon DOS) is plotted in Fig. 2. As seen, the \textit{ab initio} calculations successfully reproduced the relative strength and positions of the peaks, as well as the cutoff frequencies in phonon DOS in comparison to experiments. Calculations at Gamma point also reveal that the frequency of $A_{1g}$ phonon mode is 1.94 THz, which is in good agreement with experimental values 1.88 THz.\textsuperscript{21}

Since \textit{ab initio} calculation can reproduce the phonon properties of Bi$_2$Te$_3$, it is used to generate total ground-state energy data to allow parameterizing classical interatomic potentials for phonon transport studies, as will be shown in detail in the next section.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.png}
\caption{(Color online) Left: Bi$_2$Te$_3$ hexagonal conventional cell structure; upper right: Bi$_2$Te$_3$ first Brillouin zone; lower right: Bi$_2$Te$_3$ electronic band structure along some high-symmetry lines.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure2.png}
\caption{(Color online) Normalized phonon density of states of Bi$_2$Te$_3$ with respect to frequency. Heavy solid curve: computed classical interatomic potentials; light dashed curve: computed \textit{ab initio}; dashed curve: experimental values from Ref. 20.}
\end{figure}

### III. CLASSICAL INTERATOMIC POTENTIALS

Appropriate classical interatomic potentials are crucial in MD predictions. The simplicity of the potentials is also important to ensure their better transferability. So far, few interatomic potentials exist in literature for Bi$_2$Te$_3$. Simple harmonic potentials were obtained by fitting to experiments\textsuperscript{22,23} but they are not suitable for the calculation of lattice thermal conductivity due to the omitted anharmonic effects. The three-body potentials developed by Huang \textit{et al.}\textsuperscript{5} can predict the thermal conductivity quite well but the potential form is quite complicated. In light of this, we develop simpler two-body interatomic potentials which include anharmonic interactions by fitting to the energy surface from the \textit{ab initio} calculations.

The two-body potential $\varphi(r_{ij})$ between atoms $i$ and $j$ separated by a distance $r_{ij}$ can be written in a form consisting of a short-range interaction $\varphi_s(r_{ij})$ and a Coulombic term for the long-range electrostatic interaction,

$$\varphi(r_{ij}) = \varphi_s(r_{ij}) + q_i q_j / r_{ij},$$

where $q_i$ and $q_j$ are effective charges of the ions in a partially charged model, which is more appropriate for partially covalently bonded solids such as Bi$_2$Te$_3$. For the Coulombic term, we have adopted the charge values obtained in Kullmann’s work,\textsuperscript{23} which are 0.38, −0.26, and −0.24 for Bi, Te1, and Te2 atoms, respectively.

For the short-range interactions, we chose to use the Morse potential form, which is known as a good approximation for vibrational structure of molecules

$$\varphi_s(r_{ij}) = D_s [1 - e^{-\alpha(r_{eq} - r_{ij})}] - 1].$$

Here, $D_s$ is the depth of the potential well, $r_{eq}$ is the equilibrium bond distance, and $\alpha$ is the measure of bond elasticity. Treated with care, by considering only the nearest neighbors for short-range interactions, we reached at a potential form with different cutoff distances for different pairs, while the long-range electrostatic interactions are treated by Ewald summation method\textsuperscript{24} with uniform cutoff radius. The parameters in the potential functions are obtained by fitting to the \textit{ab initio} calculated total-energy surface. The fitting is a mul-
tive fitting procedure done with GULP.25 Using the parameterized potentials, we optimize the crystal structure and predict the elastic properties, and then compare the results to experimental data. Such procedures iterate until the predicted results agree with experimental data well. The final optimized parameters are listed in Table I. First of all, it can be seen that Te1-Te1 bond has relatively small bond energy but intermediate force constant, which originates from the combined nature of van der Waals interactions across adjacent Te1-Te1 layers and covalent bonds within the same layer. The combination of Te1-Te1 bond with electrostatic repulsive interactions between Te1 atoms results in an ionic-like interaction as also observed by Huang and Kaviany.5 On the other hand, the bond energies of the cross plane Te1-Bi, Te2-Bi, and Te1-Te2 bonds are higher than other bonds, which indicates that these bonds are more ionic. However, the force constants of these bonds are generally smaller, which is consistent with the fact that the elastic constant $C_{33}$ is less than $C_{11}$. As a result, the vibrations in the cross-plane direction is expected to be weaker than the in-plane direction and so is the heat transport through phonon channels.

By employing the fitted classical potentials, the elastic constants and bulk modulus are obtained and compared to Huang’s results and experimental data as listed in Table II. It is seen that the computed elastic properties are in overall good agreement with experiments, indicating that the potentials can well describe the harmonic behaviors of Bi$_2$Te$_3$. Also, by computing the dynamical matrix in GULP package, the phonon DOS is predicted and shown in Fig. 2 in comparison with both the previously obtained phonon DOS from $ab$ initio calculations and the experiments.20 It is seen that the classical interatomic potentials successfully reproduced the lower-frequency acoustic portion of the phonon DOS as compared to both $ab$ initio calculations and experiments in both relative strength and positions. However, on the other hand, the predicted position for the second major peak is relatively higher than the experimental value while the relative strength of those peaks around the second major peak is in good agreement with $ab$ initio calculations. Also, the phonon cutoff frequency is higher than that from both $ab$ initio results and experiments. A closer look at the phonon dispersions, as shown in Fig. 3, shows the comparison between phonon dispersion computed from classical interatomic potentials and the experimental relations. It is seen that the acoustic-phonon modes of Bi$_2$Te$_3$ are well reproduced while optical-phonon modes are generally overestimated. Especially for higher-frequency modes, the overestimation is significant and results in a gap between 2.3 and 3 THz, which is not seen in either experiment or $ab$ initio calculations. This is probably due to the oversimplified rigid-ion model that ignores the polarization in Bi and Te atoms. This simplification might greatly affect the dispersion relation of optical-phonon modes, which should be considered as a limitation of our classical potentials model, and core-shell model might improve the phonon-dispersion relations. Despite the relatively poor capability of the interatomic potentials in reproducing optical-phonon dispersions, the dispersion of acoustic-phonon modes are well predicted. Therefore, we expect that the interatomic potentials can predict the lattice thermal conductivity of Bi$_2$Te$_3$ reasonably well since the thermal transport is dominated by acoustic-phonon modes while the optical-phonon contributions are generally negligible.

### IV. MOLECULAR DYNAMICS SIMULATIONS ON LATTICE THERMAL CONDUCTIVITY

Phonon thermal conductivity of solids can be effectively predicted using equilibrium molecular dynamics simulations...
For Bi$_2$Te$_3$, the contribution from acoustic phonons has been
range phonon and acoustic long-range phonon, respectively.
the
other hand, the lattice thermal conductivity can be defined as
cillations in HCACF do make the fitting to HCACF with
were performed with a system consisting of 6
average and minimize statistical fluctuations, while in each
semble and ran for 250 ps to arrive in equilibrium, after
desired temperature; then, it was switched into an NVE en-
constant number of atoms, volume, and temperature en-
Verlet leapfrog algorithm was adopted for the calculation
in larger simulation domain produced very similar results.
conductivity of Bi$_2$Te$_3$ is negligible, however, the huge os-
immersed in the optical-phonon oscillations while it has been
the HCACFs can be fitted to a sum of two exponential func-
account for the large oscillations in HCACFs and is tempera-
Here the subscripts $ac$, $sh$, and $lg$ denote acoustic short-
then the lattice thermal conductivity could be obtained by
performing direct integrals of these exponential functions. Here the
subscripts $ac$, $sh$ and $ac$, $lg$ denote acoustic short-
range phonon and acoustic long-range phonon, respectively.
For Bi$_2$Te$_3$, the contribution from acoustic phonons has been
immersed in the optical-phonon oscillations while it has been
shown that the contribution of optical phonons to the thermal
conductivity of Bi$_2$Te$_3$ is negligible, however, the huge os-
cillations in HCACF do make the fitting to HCACF with
exponential decay form very difficult. Fortunately, on the
other hand, the lattice thermal conductivity can be defined as the
$\omega \rightarrow 0$ limit of the Fourier transform of the HCACF,

$$\kappa_{\omega,\alpha} = \lim_{\omega \rightarrow 0} \frac{1}{k_B T^2} \int_0^\infty \langle S_{\alpha}(t) \cdot S_{\alpha}(0) \rangle e^{i\omega t} dt,$$

FIG. 4. (Color online) Typical HCACF with respect to time at
300 K before (insert) and after Fourier filtering.

Therefore, in order to better extract the acoustic-phonon sig-
als, a Fourier low-pass filter with the cutoff frequency 0.5
THz can be used to remove the high-frequency optical-
phonon components in the HCACF and fit the low-frequency
acoustic part using the two-stage exponential decay function.
Although, as pointed out by Volz and Chen,30 small cutoff
frequency will affect the accuracy of the outcomes due to the
fact that the finite size of the simulation domain does not
allow very long-wavelength phonons to physically present,
an appropriate choice of the cutoff frequency which allows
exponential decay fitting to HCACF is expected to give ac-
curate lattice thermal conductivity value. In the present stud-
ies, the scale of the simulation domain is $6a$, where $a$ is the
lattice constant. By assuming that the longest phonon wave-
length that can exist in the system is about the same scale of
the domain, then only phonon modes within $(1/6) \times 2 \pi/a$
about the Brillouin-zone center are inaccurate, which corre-
spond to phonon frequencies less than 0.2 THz. Thus, with
the choice of cutoff frequency 0.5 THz, the correctness of the
results obtained here is not expected to be affected. Indeed,
by testing different choices of cutoff frequencies from 0.5 to
1.5 THz, only less than 1% difference in the results is seen,
which falls into the standard error from the fitting.

Figure 4 shows the typical HCACF obtained as function of
time before (inset of Fig. 4) and after applying Fourier
filter. As it is seen, after fast Fourier transform, the large
oscillations are greatly removed and exponential decay be-
havior of the HCACF has emerged, which allows for the
two-stage exponential decay fitting mentioned earlier. From
the fitting, the typical relaxation time for short-range acoustic
phonons in cross-plane direction is 0.4 ps while in in-plane
direction is 0.8 ps, and they are temperature independent.
Since the short-range acoustic-phonon contributions corre-
spond to energy transfers between neighboring atoms, the
difference in the relaxation times is consistent with the fact
that bond length in in-plane direction is generally larger than
in cross-plane direction. The long-range acoustic-phonon
contributions dominate the lattice thermal conductivity and

$$\kappa_{\omega,\alpha} = \lim_{\omega \rightarrow 0} \frac{1}{k_B T^2} \int_0^\infty \langle S_{\alpha}(t) \cdot S_{\alpha}(0) \rangle e^{i\omega t} dt.$$
FIG. 5. (Color online) Computed temperature-dependent in-plane and cross-plane lattice thermal conductivity compared with the experimental data (Ref. 31).

roughly exhibit $T^{-1}$ dependence in both directions, indicating that the dominant phonon-scattering mechanism should be three-phonon Umklapp process in the temperature range of interest in both directions, which limits the thermal conductivity of the bulk Bi$_2$Te$_3$. The relaxation times for long-range acoustic phonons in cross-plane direction are generally smaller than in in-plane direction over the temperature range, indicating Umklapp scattering is larger in the cross-plane direction. In Fig. 5, the plot of $\kappa_T$ vs. temperature is shown and compared to experiments, good overall agreement is seen in both directions. Compared to Huang and Kaviany’s results, the lattice thermal conductivity predicted from their temperature dependence in both directions, indicating Umklapp scattering is larger in the cross-plane direction. As a result, the lattice thermal conductivities in the cross plane is smaller than in the in-plane values, indicating that the lattice scattering in the cross plane is larger. This is due to the different anharmonicities originated from different bonding natures along the two directions (as can be seen in the fitted potentials) and difference in mass of Bi and Te atoms which can result in large mismatch of available phonon modes of different atoms in the cross plane, which induces stronger lattice scattering.

V. DISCUSSIONS AND CONCLUSIONS

In conclusion, we use the pseudopotential method based on density-functional theory with LDA to characterize the electronic structures of Bi$_2$Te$_3$. We then develop the two-body interatomic potentials based on which the calculated elastic constants and phonon DOS agree well with the experiments and ab initio calculations, indicating that the developed potentials are suitable in describing the harmonic behaviors of Bi$_2$Te$_3$ and can well capture the phonon transport nature within. By utilizing this fitted potential, molecular dynamics simulations are performed and the lattice thermal conductivities are reproduced over a temperature range from 150 to 500 K using Green-Kubo method, which generally reveal an Umklapp process for the bulk. Close agreement with experiment is seen. The obtained results suggest that the low lattice thermal conductivity of Bi$_2$Te$_3$ is a result of weak bondings among Bi and Te atoms while the anisotropic phonon transport in Bi$_2$Te$_3$ stems from the difference in elastic and anharmonic properties along in-plane and cross-plane directions. Besides the success of our simple two-body interatomic potential form in reproducing thermal transport process in bulk, it can also allow for further phonon transport studies in Bi$_2$Te$_3$-based nanostructures and alloys, which will be reported in subsequent works.

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