Thermoelectric Properties Modeling of Bi$_2$Te$_3$

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Overview

• Introduce EZTB a modeling tool for thermoelectric properties using a tight-binding model and the Boltzmann transport equation.

• Introduce the fitting process of tight-binding parameters to a first-principles band structure using a genetic algorithm.

• Present the accuracy of the fitting with the tight-binding parameters for Bi₂Te₃.

• Present the accuracy of the modeling tool with the thermoelectric properties of Bi₂Te₃.
EZTB: Thermoelectric Properties Modeling

Material Parameters: Electron and Lattice Structure

First principles electronic structure

First principles equations of state

Model Parameter Fitting

Force fields model

Tight binding model

Boltzmann transport equation

Electron contribution:
- $S$: Seebeck coefficient
- $\sigma$: Electrical conductivity
- $\kappa_e$: Thermal conductivity

Lattice contribution:
- $\kappa_{ph}$: Thermal conductivity

Figure of Merit: $ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_{ph}}$
Model Parameter Fitting

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Figure of Merit: $ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_{ph}}$
• Tight-binding model maps the electron Hamiltonian onto couplings between atomic orbitals.
• The coupling parameters are fitted to a first-principles band structure using a genetic algorithm.

\[ H = \sum_i \varepsilon_i |i\rangle \langle i| + \sum_{ij} t_{ij} |i\rangle \langle j| \]

| Atomic Orbital: \( |i\rangle \) | Parameter: \( \varepsilon_i, t_{ij} \) | Band Structure |

**Objective:** Fit the tight-binding band structure to a first-principles band structure
A genetic algorithm is inspired by the natural selection and sexual reproduction process of living organisms.

The genetic algorithm is known to be efficient in finding a global optimum in a high-dimensional, multi-modal search space.
Some of the band structure values are more important than others.
- The highest conduction and the lowest valence bands are responsible for thermoelectric properties (10X).
- The location, energy, and effective mass of the band edge are critical (100X).

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| i ⟩: atomic orbital
| Band Structure

**Objective**: Fit the tight-binding band structure to a first-principles band structure
Bi$_2$Te$_3$

- Bi$_2$Te$_3$ is a narrow-gap semiconductor with the gap of ~160 meV.
- Bi$_2$Te$_3$ has a rhombohedral crystal structure with five atoms per unit cell.
- Bi$_2$Te$_3$ is the basic constituent of currently best thermoelectric materials.
- Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices exhibit a high thermoelectric figure of merit: $ZT \approx 2.4$. [R. Venkatasubramanian, et al., Nature 413, 597 (2001)]
Bi$_2$Te$_3$ First-principles Band Structure

- Recently, a first-principles band structure is obtained with the screened-exchange local density approximation [Kim, Freeman, and Geller, PRB 72, 035205 (2005)].
- The band edges are located off the high symmetry lines and on the y-z mirror plane.

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Bi$_2$Te$_3$ Tight-binding Band Structure

Tight-binding method with sp$^3$d$^5$s$^*$ orbitals, nearest-neighbor int., spin-orbit coupling.

- Tight-binding parameters are fitted to a recent screened-exchange LDA (sX-LDA) calculation [Kim, Freeman, and Geller, PRB 72, 035205 (2005)].
- Conduction and valence band edge parameters are fitted within 4% error.

![Graph showing band structure comparison between TB and sX-LDA models]

<table>
<thead>
<tr>
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<th>TB CBE</th>
<th>TB VBE</th>
<th>sX-LDA CBE</th>
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n-Doped Bi$_2$Te$_3$ Thermoelectric Properties

constant relaxation time = $2.2 \times 10^{-14}$ s
experimental value $\kappa_{ph}$ = 1.5 W m$^{-1}$K$^{-1}$

Experimental data from Thermoelectric refrigeration, H.J. Goldsmid (1964)
Summary

Current Work

- Developed a modeling tool for thermoelectric properties.
- Found the tight-binding parameters for Bi$_2$Te$_3$, which fit the first-principle band structures: the band edge characteristics within 4% error.
- Calculated the thermoelectric properties of Bi$_2$Te$_3$ with the tight-binding model and the Boltzmann transport equation.
- The resulting figure of merit is in good agreement with experiments.

Future Work

- Model the thermoelectric properties of Bi$_2$Te$_3$ quantum wires and wells.
- Optimize the Bi$_2$Te$_3$ nanostructure geometry to maximize the figure of merit.
- Fit tight-binding parameters for Sb$_2$Te$_3$.
- Calculate the thermoelectric properties of Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice.
- Optimize the superlattice geometry to maximize the figure of merit.