Accelerated Screening of Thermoelectric Materials by First-Principles Computations of Electron–Phonon Scattering

Georgy Samsonidze and Boris Kozinsky*

Recent discoveries of new materials for thermoelectric energy conversion are enabled by efficient prediction of the materials’ performance from first-principles, without empirically fitted parameters. The novel simplified approach for computing electronic transport properties is described, which achieves good accuracy and transferability while greatly reducing complexity and computation cost compared to the existing methods. The first-principles calculations of the electron–phonon coupling demonstrate that the energy dependence of the electron relaxation time varies significantly with chemical composition and carrier concentration, suggesting that it is necessary to go beyond the commonly used approximations to screen and optimize materials’ composition, carrier concentration, and microstructure. The new method is verified using high accuracy computations and validated with experimental data before applying it to screen and discover promising compositions in the space of half-Heusler alloys. By analyzing data trends the effective electron mass is identified as the single best general descriptor determining material’ performance. The Lorenz number is computed from first principles and the universality of the Wiedemann–Franz law in thermoelectrics is discussed.

1. Introduction

Accelerated discovery of new materials requires accurate computation of fundamental physical properties and identification of performance-controlling design rules to enable rapid examination of candidates. In the field of thermoelectric (TE) materials this approach is hindered by the difficulty in both measuring and predicting high-temperature transport properties. Fully first principles computations of thermoelectric transport have largely remained out of reach for realistic TE materials. While the electronic and vibrational spectra can be computed using modern ab initio techniques, the main difficulty lies in being able to describe the interaction of the two spectra which governs electronic scattering, thus determining the key transport parameters. The goal of this work is to describe in detail the method that enabled recent computation-driven discovery of new materials,[1,2] demonstrating the power of first-principles design and laying the foundation for future discovery efforts. The path starts from developing an efficient numerical approach based on many-body perturbation theory of thermoelectric transport, with validation by experiment and higher-resolution methods. We then proceed to deploy it to screen materials in a wide composite range of alloys to identify promising compounds, general trends, and microscopic factors governing TE performance.

In order to connect materials’ transport properties to device efficiency, it is useful to compute the TE figure of merit

\[ ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_l} \]  

where \( \sigma \) is the electrical conductivity, \( S \) is the Seebeck coefficient, \( T \) is the absolute temperature, and \( \kappa_e \) and \( \kappa_l \) are the electronic and lattice components of the thermal conductivity. Several approaches have been described to compute the lattice thermal conductivity in TE materials from first principles,[4–6] while electronic transport computations so far were limited by computational complexity to simple model systems.[7–9] Electronic transport coefficients in semiconductors and metals are commonly computed by solving the semiclassical Boltzmann transport equation within the relaxation time approximation.[10–12] In good electrical conductors the electron energy relaxation time \( \tau \) varies weakly with the electron energy \( \epsilon \).[10,13,14] allowing the use of constant relaxation time (CRT) approximation in electronic transport calculations.[11,13,15–19] In this work we show that \( \tau \) is not a universal constant and depends strongly on the material composition and carrier concentration. Moreover, the \( \epsilon \) dependence of \( \tau \) can have a significant effect on their electronic transport properties. This implies that optimizing and screening materials cannot be accomplished on the CRT level of approximation, and requires the use of first-principles computations for predicting \( \tau (\epsilon) \).

The total scattering rate \( \tau^{-1} \) of electrons is approximately the sum of the rates associated with intrinsic (electron–electron, electron–phonon) and extrinsic (impurities, grain boundaries, alloy disorder) scattering mechanisms. In automotive TE power
generation, the relevant temperature is around 400°C at the hot side of the device, which determines device performance. At this temperature, electron–phonon (el–ph) interaction is the dominant scattering mechanism, compared to the others.\textsuperscript{3,8} First-principles studies of el–ph scattering rates in semiconductors and metals have been performed using either simplified models, such as the deformation potential (DP) approximation\textsuperscript{20–25} and Allen's formalism,\textsuperscript{26–28} or direct sampling of the el–ph coupling matrix elements over the first Brillouin zone (BZ)\textsuperscript{7,29–32} Due to the high computational cost of direct BZ sampling, interpolation schemes were introduced, where the couplings are calculated on a coarse grid in the BZ and mapped onto a fine grid using linear interpolation\textsuperscript{12} and Wannier interpolation (the electron-phonon Wannier (EPW) method).\textsuperscript{8,9,33–36} These methods either do not capture the full details of electron scattering or are prohibitively complicated to use for realistic materials.\textsuperscript{3} For instance, the EPW code\textsuperscript{34} fully describes the el–ph scattering, but it is challenging to apply for materials screening due to the multistep construction procedure for Wannier functions and the high computational cost and complexity of the subsequent calculations.

In this work we introduce a new approach, the electron–phonon averaged (EPA) approximation, that combines simplicity and speed with a fully first-principles treatment of the el–ph interaction. It is more predictive than the CRT and DP approximations, while allowing for automated rapid calculations for optimization of electronic transport quantities, not requiring complex interpolation procedures. Its accuracy suggests that energy-dependence of scattering is sufficient to quantitatively describe the physics of thermoelectricity in complex materials. We first describe the approach and validate it using in-depth investigation of electron scattering in state of the art TE materials, comparing to experiment and the CRT and EPW calculations. Then we deploy EPA to perform computational screening of the wide half-Heusler (HH) family of compounds\textsuperscript{37} for TE power generation applications, and examine the material descriptors that determine TE performance and can enable high-throughput design.

2. Theory of Electron Transport

Solving the semiclassical Boltzmann transport equation for electrons within the relaxation time approximation yields the following expressions for the electronic transport coefficients\textsuperscript{10,11}

\[
\sigma_{\alpha\beta}(\mu,T) = \kappa_{\alpha\beta}^{(0)}
\]

\[
S_{\alpha\beta}(\mu,T) = k_B T \sum_{i} \left( K_{\alpha\beta}^{(0)-1} i K_{\alpha\beta}^{(i)} \right)
\]

\[
\kappa_{\alpha\beta}(\mu,T) = k_B T \left[ K_{\alpha\beta}^{(0)} - \sum_{i} K_{\alpha\beta}^{(0)-1} i K_{\alpha\beta}^{(i)} \right]
\]

where \( \alpha, \beta, i, j \) are Cartesian components, \( \mu \) is the chemical potential of electrons (the Fermi level), \( T \) is the absolute temperature, \( k_B \) is the Boltzmann constant, \( \sigma_{\alpha\beta} \) is the electrical conductivity, \( S_{\alpha\beta} \) is the Seebeck coefficient (thermopower), \( \kappa_{\alpha\beta}^{(0)} \) is the electronic component of the thermal conductivity, and \( \kappa_{\alpha\beta}^{(i)} \)

is the \( p \)th order electronic transport coefficient. The latter is given by

\[
K_{\alpha\beta}^{(p)}(\mu,T) = \frac{g_e e^2}{(2\pi \hbar)^2} \sum_{\nu} \int_{BZ} d\mathbf{k} \kappa_{\alpha\beta}^{(0)} \tau_{\alpha\beta}(\mu,T) I^{(p)}(E_{\mathbf{k}},\mu,T)
\]

where \( g_e = 2 \) is the spin degeneracy, \( e \) is the elementary charge, \( n \) is the electron band index, BZ is the first Brillouin zone, \( \mathbf{k} \) is the electron wavevector, \( \mathbf{v}_\mathbf{k} \) is the electron group velocity, \( \tau_{\alpha\beta}(\mu,T) \) is the electron energy relaxation time, \( E_{\mathbf{k}} \) is the electron energy, and \( I^{(p)}(\epsilon, \mu, T) \) is the material-independent integrand factor

\[
I^{(p)}(\epsilon, \mu, T) = (\epsilon - \mu)^p f(\epsilon, \mu, T) \left[ 1 - f(\epsilon, \mu, T) \right]
\]

Here, \( f(\epsilon, \mu, T) \) is the Fermi–Dirac distribution function. The electron group velocity is defined by

\[
\mathbf{v}_{\mathbf{k}\alpha\beta} = \frac{1}{\hbar} \frac{\partial E_{\mathbf{k}}}{\partial \mathbf{k}_\alpha}
\]

where \( \hbar \) is the reduced Planck constant, and can be evaluated using the Fourier interpolation\textsuperscript{11,16} or the Wannier interpolation\textsuperscript{10} of \( E_{\mathbf{k}} \).

The inverse of the electron energy relaxation time induced by the el–ph interaction is given by\textsuperscript{12,13}

\[
\tau_{\alpha\beta}^{-1}(\mu,T) = \frac{\Omega}{(2\pi \hbar)^2} \sum_{\nu} \int_{BZ} d\mathbf{q} |g_{\nu\nu}(\mathbf{k}, \mathbf{q})|^2
\]

\[
\times \left\{ \left[ n(\omega_{\nu\nu}, T) + f(\epsilon_{\nu\nu}, \mu, T) \right] \delta(\epsilon_{\mathbf{k}} + \omega_{\nu\nu} - \epsilon_{\nu\mathbf{q}}) \\
+ \left[ n(\omega_{\nu\nu}, T) + 1 - f(\epsilon_{\nu\nu}, \mu, T) \right] \delta(\epsilon_{\mathbf{k}} - \omega_{\nu\nu} - \epsilon_{\nu\mathbf{q}}) \right\}
\]

where \( \Omega \) is the volume of the primitive cell, \( m \) is the electron band index, \( \nu \) is the phonon mode index, \( \mathbf{q} \) is the phonon wavevector, \( \omega_{\nu\nu} \) is the phonon energy, \( g_{\nu\nu}(\mathbf{k}, \mathbf{q}) \) is the el–ph coupling matrix element, \( n(\omega, T) \) is the Bose–Einstein distribution function, and \( \delta \) is the Dirac delta function.

The main element of the EPA approximation is to turn the complex momentum-space integration in Equation (8) into an integration over energies. This is accomplished by replacing momentum-dependent quantities in Equation (8) by their energy-dependent averages. We note that this may have implications for materials with strongly anisotropic effective masses (see the Supporting Information). First, el–ph coupling matrix elements are averaged over the directions of \( \mathbf{k} \) and \( \mathbf{k} + \mathbf{q} \) wavevectors

\[
|g_{\nu\nu}(\mathbf{k}, \mathbf{q})|^2 \mapsto \langle g_{\nu\nu}(\mathbf{k}, \mathbf{q}) \rangle
\]

Second, \( \mathbf{q} \)-dependent phonon energies are averaged over the cells of electron energy grids

\[
\omega_{\nu\nu} \mapsto \bar{\omega}_{\nu}(\mathbf{k}, \mathbf{q})
\]

At temperatures below the Debye temperature, electron scattering is dominated by acoustic phonons\textsuperscript{21,29,35,38} implying that very fine sampling of electron energies is required in Equations (9) and (10). However, in real doped semiconductor
samples, extrinsic scattering mechanisms are often dominant at low temperatures. At temperatures above the Debye temperature all the phonon modes are populated, which allows using much coarser sampling of electron energies in Equations (9) and (10) to reduce computational cost. If electron energy grid spacing is larger than the highest optical phonon energy, Equation (10) is reduced to the average phonon mode energy

\[ \omega_{\mathbf{q}} \rightarrow \bar{\omega}_{\mathbf{q}} \]  

(11)

This allows further simplification by performing the integration over \( \mathbf{q} \) and the summation over \( m \) in Equation (8) analytically, which yields

\[
\tau^{-1}(\epsilon, \mu, T) = \frac{2\pi \Omega}{\varepsilon_0 \hbar^2} \sum_{\mathbf{q}, \alpha} \{ g^2(\epsilon + \bar{\omega}, \mathbf{T}) n(\bar{\omega}, \mathbf{T}) \\
+ f(\epsilon + \bar{\omega}, \mu, T) \rho(\epsilon + \bar{\omega}) \\
+ g^2(\epsilon - \bar{\omega}, \mathbf{T}) n(\bar{\omega}, \mathbf{T}) + 1 - f(\epsilon - \bar{\omega}, \mu, T) \rho(\epsilon - \bar{\omega}) \}
\]  

(12)

Here, \( \rho(\epsilon) \) is the electron density of states defined as the number of electronic states per unit energy and unit volume. Consequently, Equation (5) is rewritten in the following form

\[
K^{(p)}_{\mathbf{q}}(\mu, T) = \frac{\hbar^2 e^2}{(2\pi)^2 (k_B T)^2} \int d\epsilon \nu^2_p(\epsilon) \rho(\epsilon) \tau^{-1}(\epsilon, \mu, T) f^{(p)}(\epsilon, \mu, T)
\]  

(13)

where \( \nu^2_p(\epsilon) \) is the energy projected squared velocity tensor\(^{(11)} \)

\[
\nu^2_p(\epsilon) = \sum_k \int d\mathbf{k} \nu_{\mathbf{k}p} \nu_{\mathbf{k}p} \delta(\epsilon - \epsilon_k)
\]  

(14)

### 3. Carrier scattering and transport

To verify our approximation and to compare available approaches, we use the CRT, EPA, and EPW methods to compute electronic transport properties for state-of-the-art TE materials from the family of HH compounds, the p-type HfCoSb\(^{(39,40)} \) and n-type HfNiSb\(^{(41)} \). Isovalent Zr–Hf alloying is used to reduce lattice thermal conductivity by mass disorder scattering\(^{(39–41)} \); and we neglect its effect in our computations of the electronic structure. Heterovalent Sn–Sb substitution is experimentally used to achieve p- and n-doping, which we treat within the rigid-band approximation\(^{(42)} \). The carrier concentrations are obtained from Hall measurements at room temperature: \( p = 0.06 \) per formula unit (1.1 × 10\(^{23} \) cm\(^{-3} \)) for Hf\(_0.5\)Zr\(_0.5\)CoSb\(_{0.8}\)Sn\(_{0.2}\)\(^{(39)} \) and \( n = 0.01 \) per formula unit (1.7 × 10\(^{23} \) cm\(^{-3} \)) for Zr\(_{0.99}\)Ni\(_{0.01}\)Sb\(_{0.01}\)\(^{(43)} \). The rigid-band approximation is applicable up to carrier concentrations of 3 × 10\(^{21} \) cm\(^{-3} \)\(^{(44–46)} \) and the carrier concentrations used in this work do not exceed 2 × 10\(^{21} \) cm\(^{-3} \).

We compare the EPA and EPW results for the electron energy relaxation time \( \tau \) as a function of the electron energy \( \epsilon \) on Figure 1 and see that the two approaches are in quantitative agreement and that \( \tau \) increases sharply near the band edges. This can be seen by extracting the \( \epsilon \) dependence from Equation (12)

\[
\tau^{-1}(\epsilon) = g^2(\epsilon) \rho(\epsilon)
\]  

(15)

Given a weaker \( \epsilon \) dependence of \( g \) than that of \( \rho \) (see Figure S1 in the Supporting Information), Equation (15) implies that \( \tau \) varies inversely as \( \rho \), in agreement with previous studies\(^{[3,8,28,49–51]} \). This allows \( g^2 \) to be calculated on a coarse grid in the BZ and mapped onto a coarse energy grid, while \( \rho \) is easily computed on a fine grid. As a result, the EPA approximation is computationally faster by orders of magnitude and simpler to apply than the direct BZ sampling and the EPW interpolation scheme (see the Experimental Section).

It is important to note that the values of \( \tau(\epsilon) \) that contribute the most to electronic transport coefficients, particularly conductivities, are selected by the corresponding transport integrands (Figure S2, Supporting Information) centered at \( \mu \), the electronic chemical potential that depends on the doping level (vertical lines in Figure 1). The electronic transport coefficients calculated with Equations (2–4) are shown in Figure 2 as a function of \( T \) and in Figure 3 as a function of \( p \) and \( n \). For comparison, the experimental data for single-crystal ingot and nanostructured samples\(^{(39–41)} \) are shown in Figure 2 by open and filled symbols, respectively. The constant values of the electron energy relaxation time, \( \tau = 4 \) fs for heavily doped HfCoSb \((p = 0.06) \) and \( \tau = 30 \) fs for less heavily doped HfNiSn \((n = 0.01) \), are obtained by fitting the calculated electrical conductivity \( \sigma \) to the experimental data of the ingot samples at \( T = 400^\circ \)C (see Figure 2a,b). The order of magnitude difference between the two \( \tau \) values indicates that \( \tau \) is sensitive to both the material composition and the carrier concentration. The ability to capture this dependence from first principles, which is absent in the CRT approach, is crucial for quantitative optimization and screening of materials.

Compared to measurements, EPA and EPW calculations overestimate \( \sigma \) at low temperatures, as seen in Figure 2a,b. This...
is caused by extrinsic scattering mechanisms (not included in our calculations) that decrease the overall $\tau$ at low temperatures. Agreement is much better at higher temperature where el–ph scattering is expected to dominate. EPA and EPW results agree well for $\tau$ and $\sigma$, which is remarkable given the significant reduction of complexity of the phase-space integral in the EPA scheme and strong anisotropy in the effective masses of these compounds (see Table S2 in the Supporting Information). The key implication is that only energy dependence of the el–ph scattering is sufficient for accurate description of the physics of electronic relaxation and conductivity.

For the Seebeck coefficient $S$ the agreement between EPA/EPW and experiment is good even in the lower temperature range. This is expected because $S$ is independent of $\tau$ to first order (e.g., on the CRT level of approximation\(^\text{(11)}\)), and is thus insensitive to extrinsic scattering mechanisms, and determined largely by the electronic band structure. The deviations from experiment at higher temperature are likely due to uncertainties in measured carrier concentrations and computed band structures, as well as their temperature dependence (e.g., thermal expansion, carrier activation). The agreement between EPW and EPA values of $S$ at high $T$ is notably better for HfCoSb than for HfNiSn. This is due to the narrower dispersion in el–ph coupling matrix element values in HfCoSb (see Figure S1 in the Supporting Information), and hence better results from replacing them with averages within the EPA scheme.

The first principles transport formalism provides access also to the electronic part of thermal conductivity $\kappa_e$ (Equation (4)), which is important to consider in designing high-performance TE materials, but at the same time is extremely challenging to measure directly by decoupling from the lattice contribution. The Wiedemann–Franz law is commonly used to estimate the $\kappa_e$ from measurements of $\sigma$. The Lorenz number\(^\text{(52)}\) $L = \kappa_e/(\sigma T)$ is typically set to the Sommerfeld value $L_0 = 2.44 \times 10^{-8} \text{ W} \Omega^{-1} \text{K}^2$ (valid for elastic scattering in degenerate electron gas\(^\text{(52,53)}\)), or $L$ can be derived from a single-parabolic-band model with acoustic phonon scattering.\(^\text{(54–56)}\) To investigate the validity of these approaches we compute $L$ with CRT and, for the first time, using full el–ph intrinsic scattering with EPA and EPW. As Figures 2 and 3 show, $L$ is far from being constant, deviates significantly from $L_0$, and the single-band model fails to consistently capture its variation. The calculated Lorenz numbers increase as $\mu$ approaches the band edge (Figure 3e,f), in agreement with previous observations.\(^\text{(57)}\) This occurs because the integrand factor of $\kappa_e$ (Equation (6)) is broader in energy than the integrand factor of $\sigma$ (see Figure S2 in the Supporting Information), and consequently $\kappa_e$ decreases slower than $\sigma$ as $\mu$ approaches the band edge. The same mechanism causes the well-known increase in $S$ near the band edges in semiconductors (Figure 3c,d). Due to the $T$ dependence of $\mu$ and the integrand factors, $L$ can significantly depend on $T$, as is the case for HfNiSn, and less so for HfCoSb. We note that this behavior is primarily a band structure effect and is captured
Importantly, we obtain significant differences between the CRT values of S and L and those computed from EPA and EPW, particularly in the case of HfNiSn (Figures 2 and 3), as also observed in other materials.[28] The deviation from the CRT results is due to the strong dependence of $\tau$ on $\varepsilon$ for HfNiSn in the range of energies where the integrand factors of $S$ and $\kappa_e$ are greatest, as seen by superimposing Figure S2 of the Supporting Information on Figure 1. In comparison, the $\tau(\varepsilon)$ variation in HfCoSb is an order of magnitude narrower, which leads to better agreement between CRT and EPA/EPW values for $S$ and $L$. The assumption of constant $\tau$ is often used as a justification for the CRT approach for computing $S$ and $L$ in TE materials, where these quantities become independent of the constant $\tau$, hence requiring only the knowledge of the easily computed electronic band structure. We caution that this approach may be simple but is not generally valid in realistic TE materials.

4. Thermoelectric Materials Screening

Having validated the computational approach for well characterized compositions, we turn to the exploration of the wide chemical space of the HH family of alloys. The goal is twofold: to discover new promising compositions, and to use computed properties to identify broad fundamental design rules that can be used in wider discovery efforts. We start this study by narrowing down the list of all possible elemental combinations in the HH crystal structure, selecting only semiconducting compositions consisting of earth-abundant elements. The final selection of 28 p- and n-type compounds includes only basic 3-component compositions, expanding upon selections used in previous efforts.[37] Using the EPA formalism we compute the electronic transport coefficients $\sigma$, $S$, and $\kappa_e$ for the 28 HH compounds. $ZT$ (Equation (1)) depends also on the lattice contribution to the thermal conductivity $\kappa_l$, and there has been work on methodology of computing it from first-principles starting from anharmonic phonon scattering.[4–6] However, in many TE materials, specifically in HH alloys, $\kappa_l$ can be substantially reduced from its intrinsic value by isoelectronic alloying and nanostructuring.[40,41] This is possible due to rather short electron mean free paths in these materials, as we show below, and long phonon mean free paths. Using these processing techniques the intrinsic room temperature values of 22 W (m$^{-1}$ K$^{-1}$) for HfCoSb[6] and 20 W (m$^{-1}$ K$^{-1}$) for HfNiSn[6] are reduced to 3 W (m$^{-1}$ K$^{-1}$) for HfCoSb[40] and 4 W (m$^{-1}$ K$^{-1}$) for HfNiSn.[41] This reduction in $\kappa_l$ increases the predicted $ZT$ values of HfCoSb and HfNiSn by factors of 6 and 4, respectively. Consequently, we do not include computations of intrinsic values of $\kappa_l$. As a realistic assumption to explore upper limits of performance, we set $\kappa_l$ for all HH compounds in this work to have the value of 2 W (m$^{-1}$ K$^{-1}$) at $T = 400 ^\circ$C.[40,41]

As mentioned above, electronic transport coefficients depend strongly on the electronic chemical potential, and hence the carrier concentration $x$. For comparing materials of different compositions we identify the value of $x$ for each...
compound such that the power factor $\sigma S^2$ is maximized. We found that there is only 10% average difference in ZT at values of $x$ that maximize $\sigma S^2$ versus those that maximize ZT. Importantly, the EPA method enables us to perform sweeps in the $x$ values automatically and much faster than the EPW procedure (see the Experimental Section). This step is critical in identifying the maximum achievable performance for each composition in the screening. The resulting values of ZT and $x$ for the 28 HH compounds are shown in Figure 4a,b. One can see from Figure 4a that state-of-the-art TE materials HfCoSb\(^{40}\) and HfNiSn\(^{41}\) have some of the highest ZT values among p- and n-type compounds, respectively. The best p-type compound predicted in Figure 4a is NbFeSb. We note that this material was originally identified by our EPA calculations and suggested for experimental synthesis. A variant of this compound was synthesized and tested in devices, showing leading TE

**Figure 4.** a) The thermoelectric figure of merit ZT, b) the optimal carrier concentration $x$ (per formula unit), c) the electron energy relaxation time $\tau$, and d) the electron mean free path $l$ for the p- and n-type HH compounds (shown as red and yellow bars, respectively) calculated within the EPA approximation. Calculations are performed at temperature $T = 400^\circ C$ using the lattice thermal conductivity $\kappa_l = 2 \text{ W m}^{-1} \text{ K}^{-1}$. The values of $x$ are selected to maximize the power factor $\sigma S^2$. The error bars in (b) show the range where $\sigma S^2$ drops by 10% from its maximum value. The experimental values from literature for several compounds are shown by filled symbols.\(^{[1,2,18-41,43]}\)
performance as well as material-level cost and record thermal cycling reliability.\[1\] NbCoSn is another material predicted to have a moderate n-type performance (Figure 4a) which was recently synthesized and characterized.\[2\] We note that the experimentally determined values of ZT and $x$ for these compounds\[1,2,39–41,43\] (filled symbols in Figure 4a,b) somewhat differ from the predicted ones. The possible reasons behind this are that the experimental compositions are optimized to achieve the maximum performance at temperatures above 400°C, and the value of $\kappa_l$ used in our calculations is not fully realized in experimental compositions.

Having validated our computational and screening methodology, we proceed to analyze the computed dataset in order to distill physical trends in the given materials space. We first consider the variation of $\tau$ across the space of compositions, testing the validity of the common fixed-value CRT approximation for materials discovery. In order to simplify the comparison between materials, we integrate over the energy dependence to define for each compound a single effective value for the electronic relaxation time

$$\tau_{\text{eff}} = \frac{\sigma_{\text{epa}}}{\sigma_{\text{CRT}}},$$

where $\sigma_{\text{epa}}$ and $\sigma_{\text{CRT}}$ are electrical conductivities computed within the EPA and CRT approximations, respectively, and $\tau_{\text{CRT}}$ is the constant relaxation time. Each quantity is computed at optimal value of $x$ at $T = 400°C$. Note that $\tau_{\text{eff}}$ does not depend on $\tau_{\text{CRT}}$ because $\sigma_{\text{CRT}} \propto \tau_{\text{CRT}}$ by definition. We also define the effective electron mean free path (MFP),

$$\ell = \frac{v}{\tau_{\text{CRT}}},$$

where $v$ is the electron group velocity calculated at the value of $\epsilon$ at which $\tau(\epsilon) = \tau_{\text{CRT}}$. The resulting values of $\tau_{\text{eff}}$ and $\ell$ for the 28 HH compounds are shown in Figure 4c,d. The values of $\tau_{\text{eff}}$ vary in the range of 1–100 fs for different HH compounds (see Figure 4c). This implies that a single value of $\tau$ cannot be used for different materials. Similarly, the values of $\ell$ vary in the range of 1–100 nm for different HH compounds (see Figure 4d). Interestingly, these values are too small to be affected by typical nanostructuring, given that the average grain size in nanostructured HH compounds is greater than 200 nm.\[40,41\] This explains why the nanostructuring approach is so effective for improving TE performance of HH compounds. It does not negatively impact $\sigma$ while at the same time it reduces $\kappa_l$\[40,41\] and consequently increases ZT. Our findings also suggest that decreasing the average grain size below 100 nm may have limited potential for increasing TE performance.

A computation discovery effort would be greatly facilitated by identifying simple physical descriptors that can be used to predict TE performance of materials. Rapid screening calculations using the EPA method provide a path to this goal by yielding the relationships between electronic and atomic structures and TE properties for a wide set of materials without empirical bias. We analyzed the results of EPA computations on our set of 28 HH compounds by evaluating statistical correlations between transport coefficients at optimal doping and basic characteristics of electron and phonon spectra, such as acoustic phonon velocities, optical phonon frequencies, carrier effective masses (Figure 5), and electronic band gaps (Figure 6). The strongest trend we found is that the electron density-of-states (DOS) effective mass $m^*$ is...
the single best descriptor of overall performance at optimal doping, as illustrated in Figure 5. We can explain the trends in the transport properties using arguments based on the single parabolic band model. In this model the density of states is \( \rho \propto m^{3/2} \varepsilon^{1/2} \) and the electron group velocity is \( v \propto m^{-1/2} \varepsilon^{1/2} \), where \( \varepsilon \) is the electron energy relative to the band edge. Using Equation (15) we obtain \( \tau \propto m^{-3/2} \varepsilon^{-1/2} \). The relevant values of \( \varepsilon \) are determined by the chemical potential of electrons \( \mu \) (Figure 5b) and are thus mostly independent of \( m \) (Figure 5b). The power law fit to \( m \)-dependence of \( \tau \) (solid line in Figure 5a) instead gives a close value of \(-1.30\) for the exponent. The electrical conductivity \( \sigma \) (Figure 5c) is an integral of \( \varepsilon^3 \tau \) times the \( \mu \)-dependent integrand factor (Equation (13)). We thus obtain \( \sigma \propto m^{-1} \) times an \( m \)-independent integral. Indeed, the envelope of \( \sigma \) distribution in Figure 5c decreases with \( m \). The Seebeck coefficient \( S \) (Figure 5d) is a ratio of two integrals with the same \( m \) dependence (Equation (3)). Although \( S \) increases near the band edge (Figure 3c), it is independent of \( m \) if the band is parabolic. Increasing \( S \) requires changing the shape of \( \rho(\varepsilon) \) rather than simply increasing \( m \).\([50,58]\) Accordingly, the \( \sigma \) distribution at optimal values of \( x \) in Figure 5d shows no overall significant dependence on \( m \). Consequently, \( ZT \) (Figure 5e) carries the \( m^{-1} \) dependence from \( \sigma \). As expected, the envelope of \( ZT \) distribution in Figure 5e decreases with \( m \). The carrier concentration \( x \) (Figure 5f) is an integral of \( \rho \) times the \( \mu \)-dependent Fermi–Dirac distribution function. We thus obtain \( x \propto m^{1/2} \) times an \( m \)-independent integral. The power law fit (solid line in Figure 5f) gives a slightly lower value of \(-0.92\) for the exponent. We can thus rationalize the trends in transport quantities in terms of the physics of the simple parabolic band model, even though material-specific deviations certainly require accurate computations. Figure 5e shows that low \( m \) is a necessary but not a sufficient requirement for high \( ZT \), but not highly correlated with it, which agrees with previous studies that used semiempirical methods.\([15,59]\) Note that according to Figure 5f, the low-\( m \) materials generally achieve optimal TE performance at low carrier concentrations. Interestingly, \( S \) at optimal \( x \) is not found to be a good descriptor, since it varies in a rather narrow range of values (Figure 5d), thus having weak predictive power. In summary, we are able to understand and even quantitatively anticipate the trends in computed transport properties as a function of the effective mass \( m \) across a wide set of compositions. Despite the fact that this study was limited to one structural family of half-Heusler alloys, we believe that the trends hold generally for other classes of materials.

5. Conclusions

We presented a simplified computational method for first-principles prediction of transport properties that achieves good accuracy and transferability at a greatly reduced complexity and computation cost. Our new approach is suitable for performance optimization and design of next-generation materials for waste heat recovery, exemplified by our computational screening of half-Heusler compounds and identification of a new composition with leading cost, TE performance, and thermal cycling. We are able to show for the first time from first principles that in TE materials the energy dependence of the electron relaxation time can have a significant effect on their transport properties, including the Seebeck coefficient and the Lorenz number which are generally assumed to be independent of the relaxation time. By directly computing electrical and thermal part of the thermal conductivities, we find deviations from the Wiedemann–Franz law in these materials at high temperatures and low carrier concentrations. This suggests potential risks in the common procedures used to interpret results of electronic and thermal transport measurements. We demonstrate that the entire complexity of electron–phonon coupling matrix is not needed for accurately calculating electron relaxation times and electronic transport coefficients in TE materials. In addition, we identify the electron effective mass as a useful qualitative descriptor of TE performance, which can be used to screen and prioritize materials. In conclusion, we demonstrate a pathway to wide computational discovery, optimization and understanding of realistic TE materials using first-principles calculations of electronic and vibrational spectra and their coupling. This methodology opens opportunities for understanding intrinsic transport properties of complex semiconductors and enables wide computational materials design in a wide range of technological applications.

6. Computational Methods

The structural, electronic, and vibrational properties were obtained from density functional theory\([66]\) and density functional perturbation theory\([61]\) calculations using the Quantum ESPRESSO\([62]\) code. The electron energy relaxation times and the electronic transport coefficients were calculated within the CRT and EPA approximations and the EPW method using the BoltzTraP\([11]\) and EPW\([14]\) codes. The EPA method was imple-
mented in Quantum ESPRESSO and BoltzTraP. Calculations were performed using the generalized gradient approximation in the PBE form [63] for the exchange-correlation functional, ultrasoft pseudopotentials [64] from PSLibrary [65, 66] for the core–valence interaction, and a plane wave basis set with 80 and 700 Ry kinetic energy cutoffs for wavefunctions and charge density. [67] Spin–orbit coupling was shown to have a minor effect (Figure S3, Supporting Information). The Debye temperature corresponding to \( \omega_{\text{max}} \) was calculated for all HH compounds studied in this work. The resulting value of \( \omega_{\text{max}} \) was lower than 200 meV energy grid spacing (Figure S1, Supporting Information). The Debye temperature corresponding to \( \omega_{\text{max}} \) was also lower than the temperature at the hot side of the device used for automotive TE power generation (400°C). This justified the application of the EPA approximation to HH compounds.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

charge transport, electronic processes, semiconductors, structure–property relationships, thermoelectrics

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