Thermoelectric Properties of Complex Bandstructure Materials by Coupling DFT to Boltzmann Transport Equation Including All Energy Dependences

P. Graziosi, C. Kumarasinghe, N. Neophytou
School of engineering, University of Warwick, UK
Patrizio.Graziosi@warwick.ac.uk

Thermoelectricity has recently experienced a large growth due to the discovery of a large number of complex bandstructure materials with unprecedented performance. Performance prediction for thermoelectric (TE) materials requires extracting DFT bandstructures and computation of TE coefficients using Boltzmann transport (BTE). The constant relaxation time approximation is employed due to complexities in accurately computing scattering rates.

In this work, we describe the construction of an advanced simulator, which couples generic bandstructures (e.g. from DFT) with BTE, utilizing the full numerical energy/momentum/valley dependences of all states in the extraction of the relaxation times. We provide much more predictive capabilities and accuracy, but also consider all scattering mechanisms (phonons, ionized impurities (IIS), alloy, nanostructuring, etc.) independently. We start the simulation by interpolating the E(k) (if needed-using linear/quadratic/Fourier, etc. methods). We then sample the Brillouin zone using Delaunay triangulation (Fig. 1a) to extract the k-points at the transport used energy grid, i.e. k(E). Iso-energy surfaces are shown in Fig. 1b for Si and 1c for TiCoSb. We then compute the scattering rates using Fermi's Golden rule. In Fig. 2 we show validations of our code with measured data for Si and GaAs mobilities, and Si and the half-Heusler NbCoSn TE power factors (PFs). (PF discrepancies occur due to lack of experimental details).

In Fig. 3 we show the bandstructures of 4 half-Heuslers, typical promising TE materials. They possess multi-valleys with complex energy surfaces (Fig. 3e). To illustrate the importance of accurate treatment of the scattering rates, Fig. 4 shows the PF vs T of TiCoSb, under 3 different scattering rate scenarios: a) constant τ=20 fs – black line (matches mobility data at 300 K), b) scattering rate ~ 1/T (typical for ADP - acoustic phonon scattering), c) full energy dependence ADP+IIS (red line). In Fig. 5 we show the PF for the 4 half-Heuslers of Fig. 3, and in Fig. 6 we compare 2 of them using constant τ, and proper τ(E) with acoustic/optical phonons. Evidently in Fig. 4-6, the PF values, trends, and rankings between the materials are different.

Thus, our results indicate that proper scattering considerations can alter the outcomes of large efforts currently being undertaken in materials screening to rank the TE potential of hundreds of materials. The code we develop can significantly assist for proper materials evaluation.

[1] J. Zhou et al., Nature Comm. **9**, 1721 (2018); [2] G. Sun et al., J. Mater. Sci. Chem. Eng, **3**, 78 (2015); [3] T. Sekimoto et al. Materials Transactions, **47**, 1445 (2006); [4] M. A. Kouacou et al., J. Phys.: Condens. Matter, **7**, 7373 (1995); [5] He et al., APL Materials **4**, 104804 (2016).

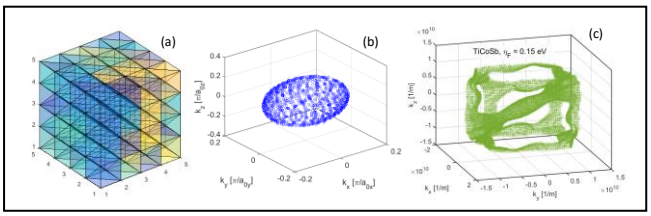

*Figure 1(a) 3D Delaunay triangulation sampling of the Brillouin Zone and extraction of the **k** points at each transport needed energy E for each band of an arbitrary bandstructure. Examples of iso-energy surfaces extracted using the code: (b) **k** points of an ellipsoid of the Si conduction band. (c) **k** points of an energy surface from the TiCoSb half-Heusler material. Strong deviations from parabolic/non-parabolic shapes are evident, indicating the need for full numerical description.*

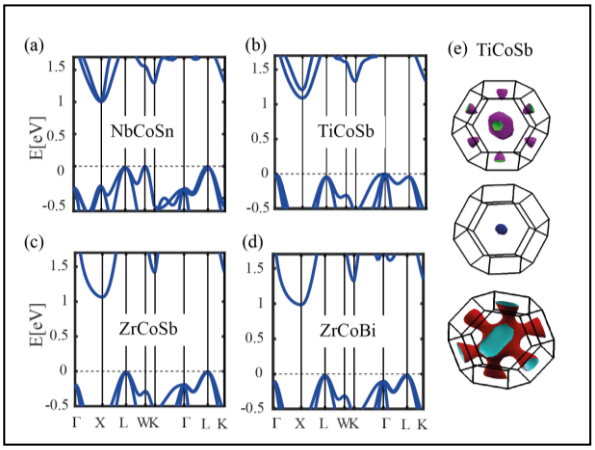

Figure 3: Bands and Fermi surfaces of representative half-Heulser alloys used in the study. Evidently, multi-band materials with complex energy surfaces call for full numerical implementation of details in transport rate description.

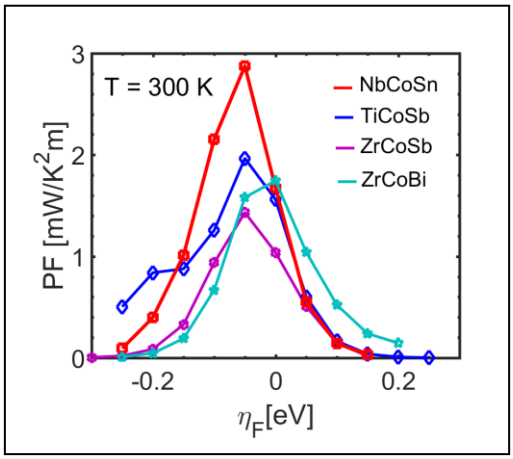

Figure 5: PF versus distance between the Fermi level and the band edge for selected p-type half Heuslers alloys, considering ADP and ODP energy dependent scattering rates. The results are shown for 300 K. Parameters are extracted from references [1]-[3].

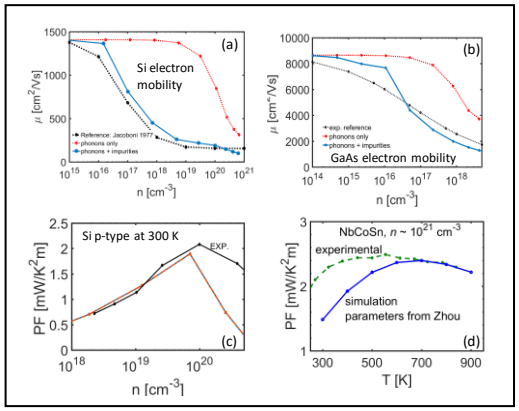

Figure 2: Validation of the simulator constructed for: (a) the mobility of Si conduction band, using phonon-limited and phonon plus ionized impurity scattering calculations. The black-dashed line is experimental data. (b) Same for GaAs. (c) TE power factor for Si (simulation vs experiment) and (d) NbCoSn, experimental data (green) from [5].

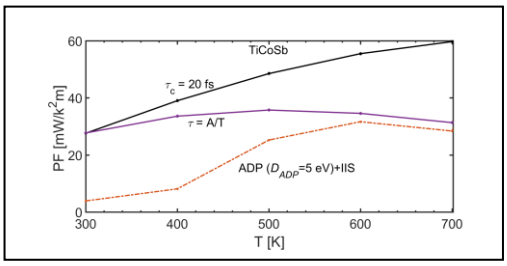

Figure 4: The PF of TiCoSb calculated using three different scattering rate considerations. a) Constant τ=20 fs (chosen to match the experimental mobility at 300 K [4])-black line, (b) a τ~1/T as in the ADP case (purple line) that matches the PF of (a) at 300 K, (c) energy dependent τ including ADP + impurities (IIS). Evidently, different scattering physics considerations give different values and trends.

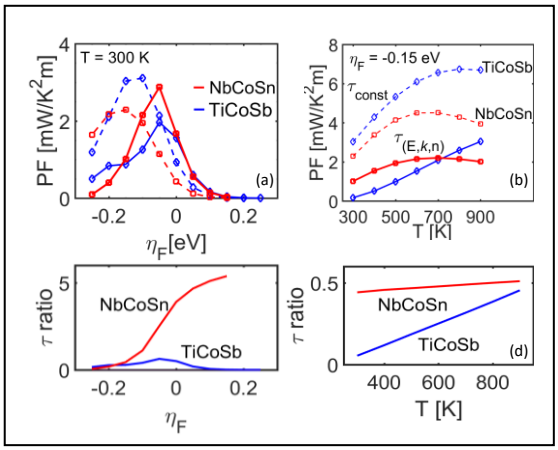

Figure 6: Comparison of constant τ (dashed lines) and τ(E) for the PF of Co-based half-Heuslers, (including ADP and ODP scattering-solid lines) versus (a) ηF, (b) T. (c, d) comparison of the constant τ needed in order to match τ(E) compared at each case. A constant τ leads to significant deviations among different materials, T, and carriers concentrations