Improving the power factor of half-Heuslers through band convergence

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Half-Heuslers are known to possess complex bandstructures, having manifold band and valley degeneracies in the vicinity of conduction and valence band edges[1,2]. Band convergence is an effective strategy to improve their thermoelectric performance, but its benefits can be offset by increased inter-valley and inter-band scattering[3,4]. Theoretical calculations to identify the outcome of band convergence usually employ detailed density functional theory (DFT) for bandstructure calculations, but the transport calculations are kept simplistic using the constant relaxation time approximation due to the complications involved with detailed scattering calculations. This often leads to incorrect performance estimations[4,5].

In this work, we investigate benefits of band convergence for improving the thermoelectric power factor under different scattering scenarios.
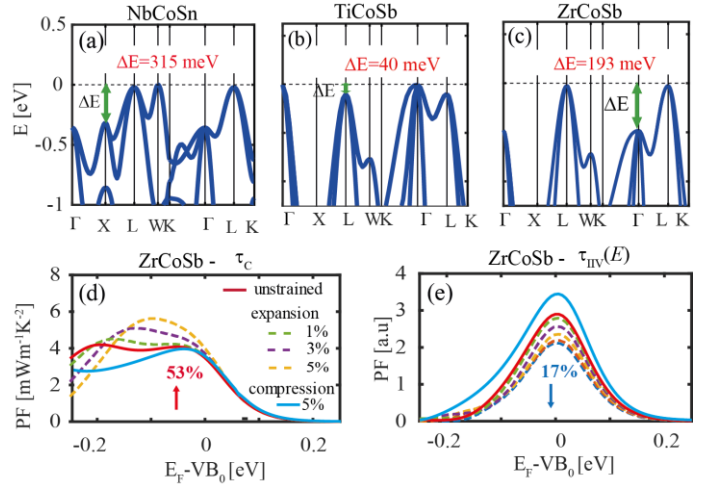

Fig. 1. (a)-(c) Bandstructures of half-Heuslers, NbCoSn, TiCoSb, and ZrCoSb. Power factor of ZrCoSb under different levels of strain, considering (d) constant rate of scattering and (e) inter- and intra-band scattering.

As a test case we consider the Co-based p-type half-Heuslers, TiCoSb, NbCoSn and ZrCoSb. We compute the electronic structure using ab-initio DFT calculations. For the thermoelectric coefficients we use semi-classical Boltzmann transport, going beyond the constant relaxation time approximation, by considering energy dependencies of the scattering rates, as well as intra- versus inter-valley scattering conditions. The valence bands of these materials are indicated in Fig. 1(a)-(c), where multiple bands appear near the valence band edge. First, by constructing non-parabolic effective mass models based on the DFT bandstructures, we extract band attributes for beneficial band convergence under i) the typically used constant scattering rate, ii) energy dependent intra-valley scattering and iii) energy dependent inter- and intra-valley scattering.

Next, we show that by applying isotropic strain, we can align the misaligned bands. Strain results in two changes in the bandstructures: 1) indeed, bands can be aligned (compressive strain aligns bands in TiCoSb and NbCoSn, whereas tensile strain aligns bands in ZrCoSb); 2) during alignment, band curvatures (and effective masses) also change. For each case, we then consider Boltzmann transport using the full DFT calculated bandstructure under the two scattering scenarios. We show that depending on the material and the scattering mechanism, the combined effect of band convergence and changes in the band curvature, can be advantageous or disadvantageous. More specifically, under a constant rate of scattering, the power factors of TiCoSb and NbCoSn improve with compressive strain and reduce with tensile strain, while the opposite happens for ZrCoSb (Fig. 1(d)). Under intra- plus inter-valley scattering, NbCoSn and ZrCoSb show an improvement in the power factor under compressive strain only, while interestingly, TiCoSb shows an improvement under both compressive and tensile strains. Even more interestingly, in the case of ZrCoSb, the power factor reduces with band alignment because of increased scattering (Fig. 1(e)), indicating that alignment degrades performance.

We conclude that in general, under constant rate of scattering, it is beneficial to align heavy bands, or bands that become heavier upon alignment. In the case of energy dependent scattering (proportional to the density of states), it is beneficial to align lighter bands, or bands that tend to become lighter upon alignment. Thus, our work illustrates the importance of going beyond the constant relaxation time approximation and considering the scattering details and the bandstructure specifics of the material, when considering band alignment. Finally, we elaborate on the construction of an advanced simulator that considers proper energy dependences of scattering rates and details for DFT-extracted bandstructures, for the extraction of thermoelectric properties of complex materials.

References

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