Supporting Information

Thermoelectric Figure-of-Merit of Fully Dense Single-Crystalline SnSe

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To our best knowledge, the results displayed in Figure 4 represents the first theoretical study of the temperature dependent band structure of SnSe. First-principles density functional theory (DFT)[41] calculations were performed using the plane-wave-based VASP package[42,43] with the projector-augmented wave (PAW) method.[44,45] The lattice constants used for calculations are taken from the experimental values (cf. Figure 3B). For structural optimization, the temperature dependent experimental atomic positions were fully relaxed within the unit cell, and the exchange-correlation potential was estimated by the generalized gradient approximation (GGA).[46] The

kinetic energy cutoff was 300 eV, and the Monkhorst-Pack $4 \times 12 \times 12$ and $4 \times 6 \times 6$ *k*-point mesh were used to sample the Brillouin zone of the *Pnma* and *Cmcm* phases, respectively. However, the conventional DFT exchange-correlation approximation methods for describing the excited state properties are limited due to the self-interaction error.[47,48] To remedy this deficiency, the GW approximation[49] (including a proper many-electron screening effect and the Wannier90 code) was performed using VASP with the $2 \times 6 \times 6$ and $4 \times 6 \times 6$ Γ-centered grid for Brillouin zone sampling of *Pnma* and *Cmcm* phases to determine the energy band gap. The multi-band character and the temperature dependent variations of VB edge states help explain the weak temperature dependence of p. In addition, the calculated band gap value at 600 K agrees with the estimated value from the Goldsmid-Sharp relation.[32] However, the temperature dependence of the calculated energy band gap is not consistent with the temperature dependence of experimentally determined data of ρ, S and p below 600 K. In fact, our experimental data suggests that SnSe exhibits semiconducting behavior only between 600 K and 750 K. Thus, despite its strongly temperature-dependent band gap inferred from DFT calculations, SnSe behaves like a low-carrier-concentration multiband metal below 600 K due to the presence of a robust Fermi surface, above which it exhibits a semiconducting behavior.