# Electronic Supplementary Information (ESI) for "Insights into thermoelectric properties of SnSe from *ab initio* calculations"

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## Methodology to calculate transport properties

As a preliminary step, the BoltzWann code requires the input files from Wannier90, with extensions .amn, .chk., .eig, .mmn and .nnkp. Detailes information about the content of these files can be found in the Wannier90 user's guide (http://www.wanier.org/doc/user_guide.pdf).

The control parameters to calculate transport properties are included in a .win file. These are the relaxation time and the chemical potential, the latter around (and usually referred to) the Fermi energy. The chemical potential is set from calculations of the Seebeck coefficient, which is independent on the relaxation time so that this parameter is irrelevant. For instance, the particular cases of a calculation of the Seebeck coefficient with $\tau = 10^{-14}$ s (arbitrarily chosen) at 300 K and 600 K are shown in Fig. S1 below.

If there are experimental data at different temperatures, one can proceed by searching the $S$ value which fits those experimental data.
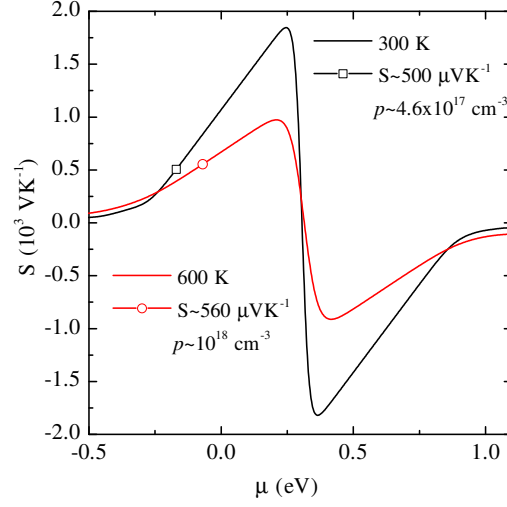
Fig. S1: Example of theoretical $S(\mu)$ curves calculated at 300 K and 600 K to yield the best fit to the experimental data (individual symbols). The respective carrier concentrations are calculated from the corresponding chemical potentials.

Symbols and lines in Fig. S1 illustrate this procedure, which yields the variation of the chemical potential with temperature (shown, for the data in the main text, in Fig. S2 below). Subsequently one may calculate the carrier concentration for the corresponding chemical potential, if desired. If there are not experimental data, a possible approximation consists on keeping the carrier concentration constant with temperature.

In the next step one compares the electrical conductivity calculated with the values of chemical potential found in the previous step (shown for our data in Fig. S2), which were set by using an arbitrary relaxation time because $S$ does not depend on $\tau$. As an example, Fig. S3 plots the theoretical $\sigma(\mu)$ curves calculated for $\tau = 10^{-14}$ s (the same relaxation time used for Fig. S1).

Notice that the electrical conductivity, unlike the Seebeck coefficient, does depend on the relaxation time. One then sets properly this parameter so as to optimally fit the experimental data; the procedure to set the relaxation times from experimental data can be checked in Ref. [58] of the main paper. If one does not have experimental data, the relaxation time can be estimated from the several models proposed in the literature. For the particular case
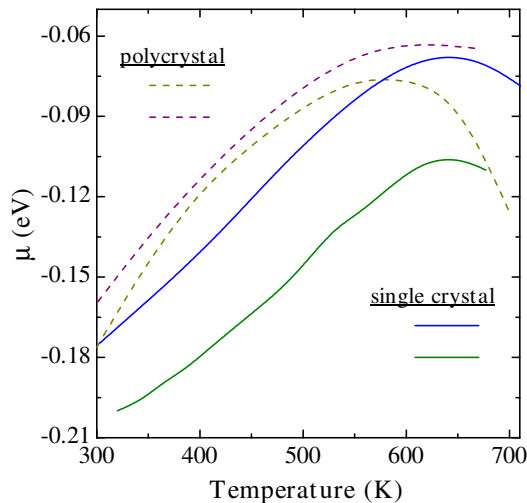
Fig. S2: Variation of the chemical potential with temperature for SnSe single crystals and polycrystals. This plot shows that the chemical potential for pure SnSe is negative, as one expects given its $p-$type character, and varies with temperature similarly for single crystals as for polycrystals. The maximum is reached at different temperatures, roughly 550 K and 600 K for polycrystals and single crystals, respectively.

of electron-phonon interactions, one of these models appears in Sec. 3.4 of the main paper, Ref. [60] containing additional details about this issue.

Once the relaxation time for electrical conduction has been tuned, it can be use for calculations of the electron thermal conductivity, which also depends linearly on $\tau$. These data for our case appear in Fig. S4 below.

We must refer to the calculation of the $zT$ factor too. For an accurate calculation of this coefficient, one needs to calculate first the lattice thermal conductivity which, in turn, requires calculating the phonon spectrum of the system. This is a very time-demanding calculation, due in part to that they require a very strict convergence criterium for forces. Details about these calculations were originally reported in Ref. [46] of the main text.

Finally, we show below for completeness the mean lifetime for phonons calculated at 300 K, which are the inverse of the scattering rates of Fig. 11 of the main text.
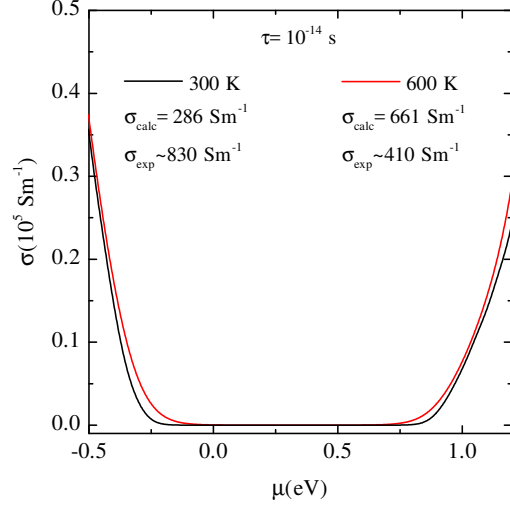
Fig. S3: $\sigma(\mu)$ curves calculated at 300 K and 600 K from the chemical potentials yielding the respective best fit of the Seebeck coefficient (Fig. S1). Both curves were obtained for $\tau = 10^{-14}$ s.
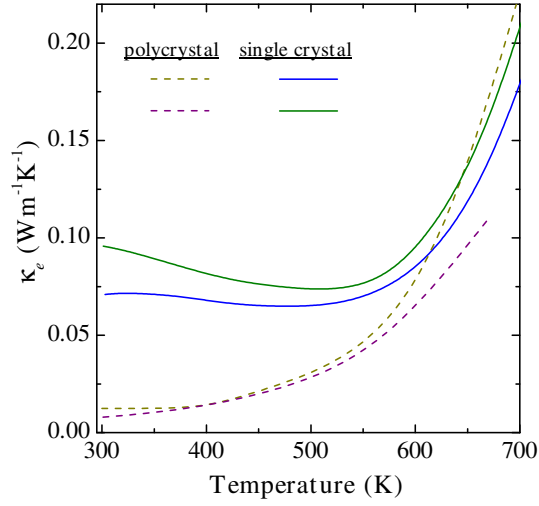


Fig. S4: Electron thermal conductivities for SnSe single crystals and polycrystals.
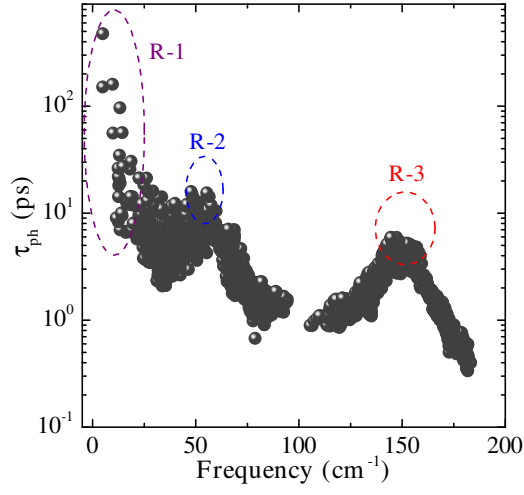
Fig. S5: Mean lifetime for phonons calculated at 300 K as a function of the frequency. The three frequency ranges (R-1, R-2 and R-3) are defined in Fig. 10.