Influence of thermal conductivity and of non-constant relaxation time on thermoelectricity in Mg$_3$Sb$_2$

R Farris, M B Maccioni, A Filippetti, V Fiorentini
Department of Physics, University of Cagliari, Cittadella Universitaria, I-09042 Monserrato (CA), Italy
E-mail: roberta.farris@dsf.unica.it

Abstract. We discuss the effects of different approximations to thermal conductivity and relaxation time on the thermoelectric figure of merit ZT in $n$-doped Mg$_3$Sb$_2$. We use density-functional electronic structure and Bloch-Boltzmann transport theory with an energy-dependent relaxation time. ZT is monotonically increasing with T in our range (300-700 K) with a maximum value of $\sim$1.5.

1. Introduction
Thermoelectrics make the recycling of thermal waste into usable energy a possibility. The material-specific thermoelectric figure of merit is

$$ ZT = \frac{\sigma S^2 T}{\kappa} = \frac{PT}{\kappa_e + \kappa_l}, $$

where $\sigma$ is the electrical conductivity, $\kappa$, $\kappa_e$ and $\kappa_l$ the total, electronic, and lattice thermal conductivities, $S$ the Seebeck coefficient, $P$ the power factor, and $T$ the temperature. Mg$_3$Sb$_2$ and related compounds have emerged as interesting candidates [1] due to their small [2] lattice thermal conductivity and appreciable power factor.

2. Results
We use density functional theory in the generalized gradient approximation [3] and the projector augmented wave method implemented in the VASP code [4, 5] to obtain electronic bands on a (24, 24, 18) k-point grid in the Brillouin zone; we then plug the band structure into the calculation of Onsager coefficients in the linearized Bloch-Boltzmann approximation [6, 7] as implemented in the BoltzTrap [8] code in the rigid band and constant-relaxation-time approximation. We further employ analytical energy-dependent expressions for the relaxation time $\tau$, including electron-acoustic phonon scattering, in the deformation potential approach; electron polar-optical scattering, in Ridley’s formulation; charged impurity scattering, via the Brooks-Herring formula [9, 10]. These formulas, implemented in BoltzTrap, were previously used with satisfactory results [11, 12, 13]. The relevant parameters needed in the various scattering terms have been either calculated or imported from the literature. We assume $n$-type doping of $3.2 \times 10^{19}$ cm$^{-3}$ with monovalent impurities. This is the optimal doping for thermoelectricity.
Figure 1. Power factor multiplied by T, computed with energy-dependent (●) and constant (△) scattering time.

as it maximizes ZT in this material [13]. We have previously calculated the lattice thermal conductivity [2], and we use the results below.

In Fig. 1 we show the power factor for energy-dependent and constant relaxation time. Clearly, due to the combination of effects on electrical conductivity and Seebeck coefficient, the power factor is significantly larger in the former case. The effect on ZT would be to lower it by about 20-25%. To determine ZT, we now consider the second key ingredient: thermal conductivity.

In Fig. 2, we display the total thermal conductivity obtained summing the electronic component calculated in the energy-dependent and constant time approximations to the lattice component [2], also displayed. It can be seen that a) the electronic component is as important as the lattice component, given the small size of the latter; and that b) the constant-time approximation overestimates significantly the thermal conductivity at high T, leading, in particular, to a sharp rise which is not observed in experiment [1]. Using this total κ, one eventually predicts a ZT about a factor 2 smaller. At this doping, the total κ still follows the downward trend in T of the lattice component.

The figure of merit ZT for our n-doped polycrystal, shown in Fig. 3 as filled blue squares, is essentially in agreement with experiment for the same kind of material (see Fig. 1a of Zhang et al., Ref.[1]), with a maximum ZT=1.5 at the top of our T range. ZT in the constant-time approximation is about a factor of 2 smaller, due to the larger increase in κe with T in that case. Using the lattice thermal conductivity of the crystal, which is ([2], [14]) nearly tenfold the polycrystal’s at room T, the figure of merit ZT is drastically suppressed.

3. Conclusions
In summary we examined the thermoelectric coefficients and figure of merit ZT in Mg3Sb2 with an energy-dependent scattering time. We find it is essential to include both the lattice and electronic components of thermal conductivity into the calculations, as they affect the final ZT significantly. In particular, we have demonstrated the effects of using the polycrystal vs the
Figure 2. Total thermal conductivity computed with energy-dependent (●) and constant scattering time △ for the polycrystal. The calculated lattice component [2] for the polycrystal is displayed for reference (□).

Figure 3. Various incarnations of the ZT figure of merit: full ZT with poly $\kappa_\ell$ and energy-dependent relaxation time (blue □), ZT with crystal $\kappa_\ell$ and energy-dependent relaxation time (orange ■) and ZT with constant scattering time and poly $\kappa_\ell$ (green △).

crystal $\kappa_\ell$. Our final ZT is in good agreement with experiment.
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