Ab initio thermal conductivity of thermoelectric Mg₃Sb₂: evidence for dominant finite-size effects

Maria Barbara Maccioni, Roberta Farris, and Vincenzo Fiorentini
Department of Physics at University of Cagliari, and CNR-IOM, UOS Cagliari, Cittadella Universitaria, I-09042 Monserrato (CA), Italy
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The lattice thermal conductivity of the candidate thermoelectric material Mg₃Sb₂ is studied from first principles, with the inclusion of anharmonic, isotope, and boundary scattering processes. We find that the anomalously low observed conductivity is due to grain-boundary scattering of phonons, whereas the purely anharmonic conductivity is an order of magnitude larger. Combining ab initio values vs sample size with measured grain-size distributions, we obtain an estimate of κ vs T in nano-polycrystalline material in good agreement with typical experiments, and compute the ZT figure of merit in the various cases.

Thermoelectricity is emerging as a viable energy source for a number of applications that recycle thermal waste, and materials with a high thermoelectric figure of merit

\[ \text{ZT} = \frac{\sigma S^2}{\kappa T}, \]

where σ and κ are the electrical and thermal conductivities, S the Seebeck coefficient, and T the temperature, are currently in growing demand. Recently, Mg₃Sb₂ has been studied fairly extensively [1–7] as a prototype of a family of so-called Zintl phases that have emerged as interesting candidates. The main focus has been at first on electronic properties, as the Seebeck coefficient in this family is somewhat larger than usual due to its multi-valley conduction band manifold. Equally significant for ZT, however, is the thermal conductivity of Mg₃Sb₂ and its doped relatives, which is unusually low for a crystalline material, namely κ ≃ 1.5 W K⁻¹m⁻¹ around room T (with considerable experimental scatter). The thermal conductivity κ = κₗ + κₑ is the sum of lattice and electronic contributions; κₑ is often modest (of order 1 W K⁻¹m⁻¹ [8]) at the typical doping used in this material and generally in thermoelectric applications, and it can be phased out by reducing the doping density. Thus, the interesting anomaly must reside in the lattice contribution κₗ being unusually small.

At present, there is no theoretical estimate of κ based on direct state-of-the-art calculations. In particular, it is not obvious that intrinsic vibrational properties behave for the low κ. In this paper we provide an ab initio assessment of lattice thermal conductivity in Mg₃Sb₂, including third-order anharmonic scattering processes, isotopic scattering, and Casimir finite-size boundary scattering. We find that the low thermal conductivity is due to microstructure size effects, i.e. to grain boundary scattering of phonons due to polycrystallinity. Boundary scattering reduces the thermal conductivity due to anharmonic scattering by as much as an order of magnitude for relevant crystallite sizes; significant isotopic scattering (peculiar to the isotopic composition of Mg and Sb) and structural anisotropy (due to the hexagonal structure) further contribute to reducing κₗ. After exploring the effects of different ingredients, we estimate an average κₗ vs T in polycrystalline Mg₃Sb₂ with nanosized grains by combining ab initio values vs sample size with measured grain-size distributions. We finally use the calculated κₗ in a calculation of the figure of merit ZT. In all cases, results seem in fair to satisfactory agreement with typical experiments.

We use the Quantum Espresso suite [9] to optimize the structure of Mg₃Sb₂ and obtain the phonon spectrum, and the D3Q-Thermal2 codes [10] [11] for the anharmonic force constants, thermal conductivity, and q-dependent linewidths, including Casimir and isotopic-disorder scattering. We use generalized-gradient (GGA) density-functional theory (DFT) [12] for electron-electron interaction, and Hartwigsen-Goedeker-Hutter [13] norm-conserving pseudopotentials for electron-ion interaction. The plane-wave cut-off is set at 50 Ry, and the k-points grids are 8x8x6 for both structure optimization and phonon dynamical-matrix calculations, 4x4x4 for the third-order force constants, and 10x10x10 for the thermal conductivity. For the latter calculation the conjugate-gradient solution method is used, and δ functions are mimicked by Gaussians with a width of 5 cm⁻¹. Tests on grids, cutoff, and widths, suggest that the lattice thermal conductivity value is stable to within about 5%.

The calculated lattice thermal conductivity κₗ in a vibrationally-harmonic crystal is infinite. Phonophonon interactions due to anharmonicity cause it to become finite, with a roughly ~1/T behavior above the Debye temperature, and still diverging as temperature goes to zero. If the finite size of the crystal is accounted for [15] [17], κₗ becomes finite at zero T and generally decreases at all T’s. In addition, if different isotopes of the constituents exist, ionic mass disorder further reduces κₗ.

Figure 1 presents the computed lattice thermal conductivity κₗ in several different variants. In all cases (see below for the lowest curve), we plot the inverse average of the tensor components (which are κₗzz = κₗyy ≃ 1.1 κₗxx; there is no off-diagonal component in zero magnetic
FIG. 1. Temperature dependence of $\kappa_\ell$ in Mg$_3$Sb$_2$. From top: anharmonic; anharmonic and isotopes; anharmonic, isotopes and Casimir ($L=50$ nm). The lowest curve (diamonds) is the average conductivity over an experimental grain-size distribution in Mg$_3$Sb$_2$ polycrystals (see text and Figure 2).

The anharmonic scattering processes result in a $\kappa_\ell$ (upper curve in the Figure) of over 10 at room $T$, which is typical of crystals, but nearly a factor 10 larger than most experimental reports. Isotopic disorder scattering reduces $\kappa_\ell$ (second curve from top), as expected from the significant naturally-occurring isotopic diversity of Mg and Sb [14], but the effect is not nearly enough to cure the discrepancy. We then include Casimir boundary scattering. We choose isotropic shape and, for demonstration purposes, a size of $L=50$ nm. The result is the third curve from top in Figure 1, which shows that finite-size scattering at this length decreases $\kappa_\ell$ by a factor of about 3 at room temperature, to somewhere around a factor 2-3 the experimental value. In all calculations including Casimir scattering we have assumed the correction factor [11] for shape and roughness [15–17] to be $F=1$, which we deem appropriate to isotropic grains with rough surfaces and separated by sizable disordered regions, such as those found in this material [7]. We checked, at room temperature, that the often-used [11, 18] value $F=0.5$ would in fact reinforce our conclusions, reducing $\kappa_\ell$ by a further 15-20%.

Now we consider that the average value of $\kappa_\ell$ in polycrystalline samples will be determined by the grain size distribution and shape. We thus investigate the size dependence of $\kappa_\ell$, and set up a simple estimate based on actual grain distributions [6]. Figure 2 reports the size-dependent $\kappa_\ell(L)$ at 300 K (squares, left vertical axis), and the distributions (from Ref. [6], normalized; right vertical axis) of grain sizes vs $L$ in Mg$_3$Sb$_2$ and Mg$_3$Sb$_{1.8}$Bi$_{0.2}$.

Evidently, the grain distribution is quite localized over small values (about 20 nm on average) and becomes negligible at larger values. To average over the grains, we assume that thermal transport will occur “in series” across randomly-oriented grains of size $L$ with abundance given by the normalized distribution $n_L$, so that

$$\bar{\kappa}_\ell = 1/\left[ \sum_L n_L \kappa_\ell(L) \right].$$

The result at 300 K is $\bar{\kappa}_\ell \approx 1.65$, which is in line with typical experiments. (We note that the specifics of averaging are not crucial; one could argue instead that $\bar{\kappa}_\ell = \kappa_\ell(L_{\text{ave}})$ for an average grain size, say at the peak of the distribution, and still get essentially the same value.)

FIG. 2. $\kappa_\ell(L)$ at 300 K (squares, left vertical axis), and the distributions (from Ref. [6], normalized; right vertical axis) of grain sizes vs $L$ in Mg$_3$Sb$_2$ and Mg$_3$Sb$_{1.8}$Bi$_{0.2}$.

Repeating the $L$-dependent calculations at other temperatures, we finally obtain the lowest curve (diamonds) in Figure 1, which is indeed as close to the experimental...
data (e.g. Figure 5c of Ref. [6]) as the intrinsic variability of grain sizes and shapes will reasonably allow. This indicates that polycrystallinity is the likely cause of the low thermal conductivity, and is therefore an essential ingredient of thermoelectric efficiency in Mg$_3$Sb$_2$.

In Figure 5 we assess qualitatively the behavior of $\tau_\ell$ in a low-concentration Mg$_3$Sb$_{1.8}$Bi$_{0.2}$ alloy. We calculate $\kappa_\ell(L)$ with Bi acting as a fictitious Sb isotope of 10% relative abundance in the isotope scattering term; in addition, we import the size distribution of the nanocrystalline alloy with the same composition from Figure 3d of Ref. [7] (also displayed in Figure 4 above) and calculate the average. The two effects reduce $\tau_\ell$ by roughly equal amounts; both the temperature trend and the change in conductivity values are in fair agreement with experiment [1]. The predicted conductivity would be probably further lowered if the actual phonon spectrum and anharmonic scattering in a Bi-containing alloy were included, due to the softer Bi-related modes. In any event, polycrystallinity remains a dominant factor in the conductivity reduction.

The figure of merit ZT of Mg$_3$Sb$_2$ is reported in Figure 4, for both the perfect crystal and the polycrystal, for three $n$-type doping levels. Clearly, the poly and crystal situations are quite different, very possibly setting apart thermoelectrically useful vs useless material. ZT vs doping density has a maximum near $10^{19}$ cm$^{-3}$ for the poly case, while it increases monotonically for the crystal case, due to the different ratio of the electrical and lattice components of $\kappa$, and the different $T$-behavior of the two $\kappa_\ell$'s (due to the very definition of ZT). Overall, ZT for our model of a $n$-doped Mg$_3$Sb$_2$ polycrystal is essentially in the experimental ballpark (see Figure 1a, Ref. [1]).

All electronic transport coefficients used to produce Figure 4 are obtained with the Bloch-Boltzmann transport code BoltzTrap [19] including phonon and impurity scattering via an energy- and temperature-dependent relaxation time $\tau_\ell$ [20], which was tested in previous applications [21]. The electronic structure is again obtained within GGA-DFT, using the projector augmented wave method as implemented in the VASP code [22]. Full details are reported elsewhere [8]. We use the total thermal conductivity $\kappa=\kappa_\ell+\kappa_e$, since the electronic thermal conductivity $\kappa_e$ is not generally negligible. The lattice part is either the crystal value, or the grain-average $\tau_\ell$ discussed above. For all the electronic transport coefficients we use the crystal values, since we found that, within the model of Ref. [7], the effects of grain boundaries on electrical quantities are marginal (of order 0.5-1%) at our typical doping, with ZT even increasing slightly in the poly case due to a compensation of the decrease in $\sigma$ and $\kappa_e$, and the increase in $S$.

![FIG. 4. ZT vs T in a Mg$_3$Sb$_2$ for three $n$-type doping levels using the perfect crystal (empty symbols) and polycrystal (filled symbols) lattice thermal conductivity.](image)

![FIG. 5. Phonon linewidths vs energy with and without Casimir scattering, $L=20$ nm, T=300 K.](image)

We close with a brief discussion of the phonon-phonon and finite-size phonon scattering linewidths. Figure 5 shows linewidths vs energy for the entire spectrum. The central region between 100 and 150 cm$^{-1}$ clearly dominates the linewidths; as pointed out in Ref. [23] this spectral region is the only one involving significantly the octahedrally-coordinated Mg cation, which has much longer bonds to Sb (as well as an anomalous effective dynamical Born charge of 3.6 vs about 2 of the other two, tetrahedrally-coordinated, Mg's).

Casimir scattering mainly affects lower-energy modes, as borne out by Figure 5 depicting the phonon dispersion (inclusive of the quasiparticle interaction shift) with superimposed linewidths for the lower part of the spectrum at $T=300$ K. Both anharmonic and Casimir scattering are especially significant along the $\Gamma$-$A$-$L$-$M$-$\Gamma$ circuit, with the $A$ and $M$ points being the most significant region of scattering overall. This agrees with the identification of Ref. [23] (see in particular Figure 5 thereof) of the shearing transverse-acoustic mode as a significant locus of anharmonicity and scattering in this material.

In closing, we acknowledge a very recent phenomenological estimate of $\kappa_\ell=2.5$ W/(K m) at room temperature [24], obtained by a simplified phenomenological expres-
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In summary, we demonstrated that the lattice thermal conductivity (and hence, by and large, the total conductivity in typical thermolectric applications) of Mg$_2$Sb$_2$ is not anomalously small for intrinsic reasons, but rather because of Casimir grain-boundary scattering. While the bulk thermal conductivity is around 11 at room T, it drops to about 1.5 or less for a typical experimental distribution of grain sizes. The final prediction for $\kappa_t$, as well as the figure of merit ZT, in a nano-polycrystal is in good agreement with experiment.

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