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Ab initio lattice thermal conductivity in pure and doped Half-Heusler thermoelectric materials.

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Abstract

Half-Heusler phases are promising intermetallics for applications in thermoelectric generators. Optimization of their thermal transport properties is essential to improve their overall conversion efficiency. Our goal is to perform a theoretical evaluation of thermal transport properties directly from first-principles calculations for various pure and doped half-Heusler compounds. The electronic structures are modeled in the framework of the density functional theory (DFT). The ab initio thermal properties are deduced from harmonic and anharmonic interatomic force constants calculations using finite size displacements method. Many-body perturbation theory is used for calculating the phonon-phonon interactions which yields the lifetime of phonons as function of momentum and band index. Finally, thanks to a direct solution to the phonons Boltzmann transport equation we computed the ab initio thermal conductivities, which are found in good agreement with the experimental data.

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Introduction

Improving the overall efficiency of motors and power generators is a prerequisite to evolve toward a more environmental friendly and sustainable world. The development of new thermoelectric materials (TE) for converting wasted heat into usable electric power can help this goal [1] (see figure 1). Equally important, the availability of these advanced technologies in a medium-long term is an obligation for maintaining the European competitiveness in the aerospace industry. Identifying high efficiency TE materials is a challenge residing in the combination of the physical properties involved. Best TE should have a phonon-glass electron-crystal behaviour. Phonon-glass describe the necessity for a low lattice thermal conductivity as in amorphous glasses, and electron-crystal because the best electrical properties (Seebeck coefficient and electrical conductivity) have been found in crystalline semiconductors. The recent enhancement of the field of thermoelectric is mainly due to the discovering of new methods that can synthesise materials close to the ideal phonon-glass electron-crystal structure. Half-Heusler (HH) compounds is a class of materials that can help those requirements [2, 5, 9]. Furthermore, these materials are more specific to the aerospace industry which requires high temperature materials that can sustain aggressive environments (mechanical stress, corrosion, oxidation). The main problem encountered is the phonon-glass behaviour. Indeed, pure HH possess a high thermal conductivity that thermalise the system too fast. Recently, many efforts are deployed to modify the basic HH structure to reduce the thermal conductivity without affecting the electrical transport properties. Experimentally, several routes are explored to achieve this goal. One route consist in doping the material with isoelectronic substitutions [3]. It generate mass fluctuations helping the diffusion of heat trough the material. This doping is widely used experimentally but, only few theoretical work is available. Our goal is to give a clear theoretical description of the mechanisms involved in the calculation of the thermal conductivity in order to find new pathways to improve the TE efficiency. In this document, we present the basic method to model the thermal transport properties in such materials. It consists in studying the phonons (see figure 2) and their interactions which are the main actors in the thermal transport. The lattice thermal conductivity has been calculated for various pure undoped HH structures, including ZrCoSb which is in good agreement with the experimental work. A method to account for isoelectronic doping is presented and preliminary results applied on one HH structures are shown.

Ab initio modelling of the lattice thermal conductivity

Pure structures

To compute the thermal conductivity, the standard approach consists in solving the Boltzmann transport equation (BTE) describing the evolution of the lattice vibrations (the phonons) out of equilibrium, for instance when a temperature gradient is applied. The Boltzmann equation represent the evolution of distribution function which measure the phonon occupation number, and is written :

$$\frac{\partial n_{qp}^{(1)}}{\partial t} + \frac{\partial n_{qp}^{(0)}}{\partial T} \frac{\partial T}{\partial \vec{v}_{qp}} + \vec{v}_{qp} = C(qp; n_{qp}^{(1)}) + \frac{1}{2} D(qp; n_{qp}^{(1)})$$
Thermoelectricity

Figure 1: When a temperature gradient is applied to a metal or a semiconductor, the charge carriers (electrons $e^-$ and holes $h^+$, respectively for n-type and p-type semiconductors) are diffusing from the hot to the cold side. This produces a charge difference inducing an electrostatic potential between the two sides. The system evolve towards an equilibrium between the electrical repulsion of charge carriers and the chemical potential. This is known as the Seebeck effect. The produced voltage $V$ is proportional to the temperature difference $\Delta T$ between the two sides, where the proportionality constant $\alpha$ is the Seebeck coefficient: $V = \alpha \Delta T$. To maximise the Seebeck coefficient, single type of carriers is needed. Indeed, if both type of carriers are present (mixed p-type and n-type) and moving to the cold end, the Seebeck coefficient cancels out. The efficiency of TE materials is characterised by their figure of merit $ZT$: $ZT = \frac{\sigma S^2 T}{\kappa}$ where $\sigma$ is the electrical conductivity, $S$ the Seebeck coefficient, $T$ the temperature and $\kappa$ the thermal conductivity. To maximise $ZT$, large electrical conductivity, low thermal conductivity and high Seebeck coefficient are required. Since these transport properties rely on inter-depend material properties, a set of parameters need to be optimised. Real TE device are a collection of n-type and p-type semiconductors (not mixed) assembled in parallel. This figure shows a setting where both type of semiconductors are used to maximise the TE efficiency.
Figure 2: In a gas, every molecule behaves almost independently from each other. The temperature effect resides in the velocities of the molecules that are allowed to move freely and collide with each other. In a crystalline solid, atoms are localized around specific positions and bonded together. To retrieve the effect of the temperature, the same treatment as for the gases is no more valid. In this case, the phonon description is used. Phonons are quantized vibrations of the atomic lattice. Instead of moving randomly, the atoms are oscillating coherently around their equilibrium positions. Those oscillations, the phonons, are carrying heat and can propagate through the material. This figure shows a linear chain of atoms where the atoms are allowed to move in the perpendicular direction. The first drawing shows the atoms at their equilibrium positions. The second drawing shows the oscillation of the atoms around their equilibrium positions. The red arrows show the displacement of the atoms from their equilibrium positions. For a given crystalline structure, thermal properties are retrieved via analyzing the phonons and their collisions.

where $n_{qp} \approx n_{qp}^{(0)} + n_{qp}^{(1)}$ is the phonon occupation function for a phonon with wave vector $q$ in the branch $p$. $n_{qp}^{(0)}$ is the equilibrium value and $n_{qp}^{(1)}$ is the first order deviation from equilibrium. $T$ is the temperature, $\vec{r}$ the position, $\vec{v}_{qp}$ the velocity. $C(qp; n_{qp}^{(1)})$ account for the collision processes and $D(qp; n_{qp}^{(1)})$ for the decay processes, both depending on the phonon lifetime $\tau_{qp}$. The lifetime is driven by the amount of interactions of the phonons. The solution of the BTE is usually found either by applying an iteration scheme [12] or in the relaxation time approximation which consists in fixing a constant lifetime. In this work, to retrieve the ab initio thermal conductivity, we aim at overcoming these two approximations with a direct solution to the phonon BTE [8] where the main input, the phonons lifetimes, were deduced thanks to perturbation theory and ab initio density functional theory (DFT).

The phonons have a wide panel of interactions driving their lifetimes. Indeed, they can interact strongly with other phonons, with isotopes, boundaries, electrons, photons etc [4, 6, 7]. For the calculation of pure structures, we have considered interactions with isotopes, boundaries and between phonons. Every interactions add a contribution to the lifetime $\tau_{pure}$ of the pure structure, this is encoded thanks to the Matthiessen’s rule:

$$\frac{1}{\tau_{pure}} = \sum_{i} \frac{1}{\tau_{i}} = \frac{1}{\tau_{phonon/phonon}} + \frac{1}{\tau_{isotopic}} + \frac{1}{\tau_{boundary}},$$
where the phonon/phonon interaction lifetime term $\tau_{\text{phonon/phonon}}$ is dominating over isotopic and boundary contribution $\tau_{\text{isotopic}}, \tau_{\text{boundary}}$ at high temperature, while the boundary scattering dominate in the low temperature regime. To access to the phonon/phonon interaction contribution, the phonons are defined in the periodic electronic potential of the lattice. The Taylor expansion of the electronic potential $E$ with respect to the displacements $\eta$ from the equilibrium position gives,

$$E = E_0 + \sum_l \sum_\alpha \frac{\partial E}{\partial \eta_\alpha(l)} \eta_\alpha(l) + \frac{1}{2} \sum_{ll'} \sum_{\alpha \beta} \frac{\partial^2 E}{\partial \eta_\alpha(l) \partial \eta_\beta(l')} \eta_\alpha(l) \eta_\beta(l') + \frac{1}{6} \sum_{ll'l''} \sum_{\alpha \beta \gamma} \frac{\partial^3 E}{\partial \eta_\alpha(l) \partial \eta_\beta(l') \partial \eta_\gamma(l'')} \eta_\alpha(l) \eta_\beta(l') \eta_\gamma(l'') + O(\eta^4)$$

The sums over $l, l'$ and $l''$ run over all the lattice atomic positions and the sums over $\alpha, \beta$ and $\gamma$ run over the spatial directions $x, y$ and $z$. The first order vanishes because the development is made around the equilibrium positions. Expanded up to second order, the potential energy give rise to the harmonic contribution, which assume the role of a collection of independent quantum harmonic oscillators, the phonons. This allow us to compute basic thermodynamic quantities, such as constant volume specific heat or entropy. However, this approach is not sufficient to access to the thermal conductivity. Higher order expansions are needed to introduce an anharmonic contribution representing the phonon-phonon interactions. We use density functional theory to retrieve the harmonic and anharmonic contribution of the interatomic force constants with high accuracy. Harmonic computations are reasonably available without the necessity of high performance computing, the bottleneck resides in the anharmonic computations. Indeed, third order development of the potential energy drastically increase the total calculation time. From the DFT calculations, we can deduce the total lifetime $\tau_{\text{total}}$ and solve the BTE. When the solution to the BTE is found, the total lattice conductivity $\kappa$ can be deduced by,

$$\kappa = C_p v^2 \tau$$

Where $C_p$ is the heat capacity, $v^2$ the squared velocities and $\tau$ the relaxation time.

The presented method works well and do not demand excessive computing power if the system studied is highly symmetric. It has been applied to many well known structures such as silicium, diamond etc. The \emph{ab initio} lattice thermal conductivity retrieved fits well with the experimental results.

**Doped structures**

When a structure is doped, the symmetry of the crystal changes. Most of the time, inserting defects causes a symmetry breaking where there are less symmetry operations that can be used to simplify the equations. A colossal computing power would be needed to access the thermal conductivity. Based on perturbation theory, we developed a method that can retrieve the effect of localised defects on the lattice thermal conductivity without high computing power. It consist in adding two perturbative terms to the hamiltonian,

$$H = H_0 + \sum_{jl} \sum_\alpha \frac{\eta_\alpha^2(jl)}{2} \delta \frac{1}{M(jl)} + \frac{1}{2} \sum_{jl'j''l'} \sum_{\alpha \beta} \delta A_{\alpha \beta}(jl; j'l') \eta_\alpha(jl) \eta_\beta(j'l')$$
Where $H_0$ is the unperturbed hamiltonian, the second term stands for mass fluctuations induced by the doping and the third term stands for the local fluctuations of the force constants. Those two contributions participate in reducing the phonons lifetimes and therefore also reducing the total lattice conductivity. The same way as before, both mass and force constant fluctuations add a contribution to the total lifetime \( \frac{1}{\tau_{\text{total}}} \) and

\[
\frac{1}{\tau_{\text{total}}} = \sum_i \frac{1}{\tau_i} = \frac{1}{\tau_{\text{pure}}} + \frac{1}{\tau_{\delta\text{mass}}} + \frac{1}{\tau_{\delta\text{force}}},
\]

Those supplementary contributions diminish the total lifetimes and therefore reduce the lattice thermal conductivity. This has the overall effect of increasing the TE efficiency.

**Results**

**Pure half-Heusler**

The method described here above has been applied to few pure HH structures, including ZrCoSb which is widely studied. The lattice thermal conductivity with respect to the temperature is plotted in figure 3 for the ZrCoSb HH structure. The observed shape and value of \( \kappa \) is in well agreements with the experimental data. The phonon band structure decorated with the inverse phonon lifetimes is also shown figure 3. For the three lower phonon branches, we observe that the lifetimes are increasing. From this observation one can deduce that those phonons are the main actors in the thermal conduction. Indeed, if the lifetime of a phonon is large, its mean free path is also large. The phonon can travel long distances in the material and therefore easily transfer heat. We can also see that the three higher phonon branches possesses small lifetimes and therefore have a less important contribution to \( \kappa \). Thanks to our method we are able to compute the spectral representation of all quantities involved in the calculations of the lattice thermal conductivity. This gives us useful informations about the most participating frequencies. Figure 4 shows the spectral lattice thermal conductivity as a function of frequency and temperature for the HH ZrCoSb. It shows the contribution of all frequencies. From this graph we can observe that the most participating range of frequency is located between 1 and 4 THz. This also confirm the high conductivity of the three lower phonon branches which are low frequency phonons. From this graph, one can also see a gap where the spectral lattice thermal conductivity is vanishing. It shows us that certain frequencies within that gap are not participating to the lattice thermal conductivity.

**Doped half-Heusler, Ni\textsubscript{4}Ti\textsubscript{3}ZrSn\textsubscript{4}**

We applied our method to a doped HH structure. Compared to the previous calculations for pure structures, we added the contribution of the defects trough their mass and force constant fluctuations. As a first step, we studied the effects of an isoelectronic substitution to an HH structure. The isoelectronic substitution have the advantage of not disturbing much the electronic structure, in order to not deteriorate the electronic properties. Figure 5 shows the contribution of the mass fluctuations, the force constant fluctuations in the lattice conductivity compared to the pure structure. We can observe that the main contribution is due to the mass fluctuations. Which is coherent
Figure 3: The first plot shows the lattice thermal conductivity of the HH ZrCoSb as a function of temperature. The phonon band structure decorated by the inverse lifetime is shown on the second plot. The error between experimental data and our method is below 5%.

with our description since the isoelectronic substitution do have a light influence on force constants.

Conclusion

We presented the main method to calculate the thermal properties of a crystalline structure. It has been applied to one HH structure, ZrCoSb where good agreements with the experimental work. Useful informations on frequencies contributions have been retrieved thanks the spectral representation. We also presented our technic that account for isoelectronic substitutions trough mass and force constant fluctuations. We observed that the mass fluctuation is the main effect that reduce the lattice thermal conductivity and therefore increase the overall thermoelectric efficiency for the HH Ni$_4$Ti$_3$ZrSn$_4$ structure. The next steps of our study will be concentrated on the effect of disorder and nanostructure inclusions on the lattice thermal conductivity.
Figure 4: Spectral lattice thermal conductivity of the HH ZrCoSb. The z axis represents the effect of the temperature. The colours stands for differentiating the temperature.

Figure 5: Lattice thermal conductivity for a doped HH structure Ni$_4$Ti$_3$ZrSn$_4$. Every contribution are plotted separately and jointly.
Bibliography


