THERMAL CONDUCTIVITY OF CAGE-LIKE STRUCTURES

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ABSTRACT

A two dimensional toy model is developed to study thermal transport in cage like structures such as skutterudites and clathrates. The model consists of host atoms on a rectangular lattice with fillers in the center of each rectangle. The thermal conductivity is calculated by using Green-Kubo equilibrium molecular dynamics simulations. It is generally believed that the smaller and the heavier the filler, the lower is the thermal conductivity. We show that the thermal conductivity decreases with atomic displacement parameter while it has local minima versus filler mass. Our study shows that it is very important to include the correct band dispersion to get the right features of the thermal conductivity. We show that by having a double well potential one can further reduce the thermal conductivity.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>area</td>
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<tr>
<td>ADP</td>
<td>atomic displacement parameter</td>
</tr>
<tr>
<td>( \varepsilon_i )</td>
<td>site energy of atom i</td>
</tr>
<tr>
<td>( \vec{F}_{ij} )</td>
<td>force exerted by atom j on atom i</td>
</tr>
<tr>
<td>( \vec{j}(t) )</td>
<td>heat current at time t</td>
</tr>
<tr>
<td>K</td>
<td>spring constant</td>
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<tr>
<td>( K_B )</td>
<td>Boltzmann Constant</td>
</tr>
<tr>
<td>( m_i )</td>
<td>mass of the atom i</td>
</tr>
<tr>
<td>( r_{eq} )</td>
<td>equilibrium distance between atom pairs i and j</td>
</tr>
<tr>
<td>( \vec{r}_i )</td>
<td>position vector of atom i</td>
</tr>
<tr>
<td>( \vec{r}_{ij} )</td>
<td>vector distance between atoms i and j</td>
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<tr>
<td>T</td>
<td>temperature</td>
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Greek

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( \kappa^{\alpha\beta} )</td>
<td>thermal conductivity tensor</td>
</tr>
<tr>
<td>( \phi_{ij} )</td>
<td>pair potential between atoms i and j</td>
</tr>
<tr>
<td>( \vec{v}_i )</td>
<td>velocity of atom i</td>
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INTRODUCTION

Cage-like structures such as skutterudites and clathrates have applications in thermoelectrics. The significance of such structures is the presence of a vacancy. The void space is large and can accommodate other atoms (fillers). The fillers have large thermal vibrations because of their weak bonding to the cage and the available space for vibration. The introduction of such filler atoms can be an effective method to reduce the thermal conductivity because the "rattling" atom will strongly scatter the propagating phonons, which are responsible for most of the heat transport [1]. The reduction of thermal conductivity by incorporating filler was demonstrated by many groups experimentally [2-5]. The rattling picture is widely used for these materials. However, the “rattling” induced phonon scattering in filled skutterudites has not been proven [6]. The rattling behavior is associated with a weak bonding of the filler to the cage, introducing the possibility of an independent, non-correlated vibration of the guest [7]. To model thermal conductivity within this picture, a Debye model is assumed for the host lattice and independent Einstein oscillators are assumed for vibrating fillers. In another approach for thermal conductivity calculations, partially filled skutterudites were accepted as solid solutions of completely filled and unfilled end members [8]. In this picture, the chemical disorder in the occupancy of the transition-metal sites is the main mechanisms for the reduction of thermal conductivity [9]. Recently, few groups calculated the
thermal conductivity of filled skutterudites with molecular dynamics based on first principle calculations [10,11]. In this work, we introduce a simple model, which was developed to help us understand the relationship between the thermal conductivity of cage-like structures and their crystal structure parameters. The aim is to distinguish between the contributions of different types of atoms, when one type is strongly interacting while the other is weakly bounded. We will discuss several parameters including atomic displacement parameter, mass ratio of the filler to the cage and off center parameter.

**MODEL**

The model consists of a two dimensional rectangular centered lattice as indicated in Fig. 1. Host atoms form a rectangular lattice with the width to the length ratio of 1/√3, which is chosen for stability reasons. These atoms have a Lennard-Jones (LJ) interaction. We place fillers such that their equilibrium position is at the center of these rectangles. Each filler is connected to its cage (host atoms sitting on the rectangle around it) by four identical springs with interactions of the form

\[ \phi_{ij} = \frac{1}{2} K (|\vec{r}_{ij} - \vec{r}_{eq}|^2) \]

A weak filler-filler LJ interaction was also introduced to avoid the structure from deforming. This is schematically shown in Fig. 1. Note that all the introduced interactions are anharmonic. The constructed model is one of the simplest possible cage structures. The dimensionality is not an issue here since the aim is not to look at the scaling but rather we fix the size of the sample and just change relevant parameters (mass and spring constant).

We use equilibrium molecular dynamics (MD) simulations to calculate thermal properties of the structure. The output thermal currents of the molecular dynamics are used to calculate the thermal conductivity with the Green-Kubo formalism:

\[ \kappa^{\alpha\beta} = \frac{1}{A K_B T^2} \int_0^\infty \langle j^\alpha (0) j^\beta (t) \rangle \, dt \]  

\[ j(t) = \sum_i \vec{v}_i \varepsilon_i + \frac{1}{2} \sum_{i,j,i,j \neq j} \vec{r}_{ij} (\vec{F}_{ij} - \vec{v}_i) \]  

\[ \varepsilon_i = \frac{1}{2} m_i |\vec{v}_i|^2 + \frac{1}{2} \sum_j \phi_{ij} \]

Where angular brackets denote the ensemble and time averaging.

Simulations were done for an 18 by 30 unit-cells lattice (1080 atoms). A set of arbitrary units were chosen since the aim was not to compare results with the experimental data quantitatively. In these units (length \(a_0\), mass \(m_0\) and time \(t_0\), LJ interaction strength \((\varepsilon)\) is set to \(2 \varepsilon_0 (\varepsilon_0 m_0 a_0^2 / k_B) \)) between host-host atoms and to 0.03\(\varepsilon_0\) between filler-filler atoms, temperature is set to 0.03 \(\varepsilon_0 / k_B\), neighboring interaction cutoff is 2.5\(a_0\), the MD time step is set to 0.2\(t_0\) (which is half of the maximum time step at which the structure is still stable). Before each run, the lattice is equilibrated with a Langevin thermostat. A micro-canonical MD simulation is run for 500,000 steps. These runs are repeated with 100 different initial conditions in order to simulate an ensemble averaging. Long time averaging is required to minimize the time averaging error-bar. Ensemble averaging is used to sample the phase space. With these measures, the thermal conductivity can be calculated with less than 20 percent uncertainty.

**RESULTS**

It is generally believed that the smaller and the heavier the ion in voids, the larger the reduction in the lattice thermal conductivity. Large cage sizes and small filler ions can have larger atomic displacement parameters. Recently Matsuhira et al. [12] showed that the Einstein temperature decreases linearly (with few exceptions) as the cage size increases. Fleural et al. [3] experimentally showed that the thermal conductivity decreases exponentially as the atomic displacement parameter increases [13]. Sales et al. [14] were able to connect the thermal conductivity to the atomic displacement parameter with a phenomenological approach (Debye model + Einstein oscillators).

In the current model, the atomic displacement parameter can be changed by changing the spring constant of the connecting filler-host springs. The ADP parameter is defined for each atom as the square root of the variance in the position of the atom. We then average over all atoms of the same type: \[ ADP_i = \frac{1}{n_i} \sum_{j\text{type }i} \sqrt{\langle r_j^2 \rangle - \langle r_j \rangle^2} \]

where \(r_j\) is the position of atom \(j\), the averaging is over time and the sum is over all atoms of type \(i\) in the simulated supercell.

The observed trend in Fig. 2 is very interesting since it is similar to the experimentally observed trend in filled skutterudites, despite the simplicity of our model (See Fig. 7 in Ref. 13). As the spring constant decreases, frequencies shift to lower values, resulting in lower group velocities of the acoustic bands. The atomic displacement parameter increases, since bindings are weaker and atoms can move more freely. This in turn, results in stronger phonon-phonon scatterings and
therefore shorter life times. Both reductions in group velocities and life times result in lower thermal conductivity. We analyzed the group velocities and life times and observed that while at low frequencies decrease in the group velocities is dominated, at high frequencies, the main contribution is from phonon life times. Since the main contribution to the overall thermal conductivity is from low frequencies, one can conclude that overall the main cause of thermal conductivity reduction versus ADP is the reduction of group velocities.

The mass ratio of the filler to the cage is another interesting parameter to look at. Higher filler mass corresponds to lower frequency modes and therefore is expected to reduce the thermal conductivity as it scatters lower phonon frequencies, which contribute more to the thermal conductivity. Increase of the filler frequencies by increasing the filler mass is not expected but it has been reported in some cases \cite{15, 16}, which can be attributed to the difference in the binding strength of these ions. It has also been reported that in phosphorus-based skutterudites, as one increases the cage mass, the thermal conductivity decreases \cite{17}.

We fix the host mass in our model and then scan the filler mass such that the mass ratio goes from zero to five. Figure 3 shows the resulting thermal conductivity in different directions. Note that the system is anisotropic. The thermal conductivity in the y direction is dominated by host atoms and in the x direction by fillers. Figure 3 shows that the thermal conductivity versus mass ratio has local minima. To understand where the minima come from, we analyzed group velocities and relaxation times. Let us focus on the first minimum. We choose three points on Fig. 3 corresponding to mass ratios of 0.1, 0.3 and 0.8. These points are maximum, minimum and maximum respectively. For these three points, phonon dispersions and Gruneisen parameter in the first Brillouin zone are plotted in Fig. 4 and 5 respectively. These are calculated from a lattice dynamics model. Due to symmetry, there are four equivalent parts in the FBZ. Since there are also four bands in the model, in fig. 5 we showed each band in one quarter of the FBZ.

Fillers affect both phonon velocities and relaxation times. As we introduce fillers into the lattice, two optical bands are added to the system. All bands shift to lower frequencies as the mass of the filler increases. For acoustic bands this means lower group velocities and therefore less contribution to the thermal conductivity (Fig. 4a). The optical bands are usually flat but when they come close enough to the acoustic bands of the host,
they hybridize with them. The hybridization gives some features to the optical bands. They gain a finite slope and are more populated since they have shifted to lower frequencies and so they start to contribute to the thermal conductivity (see Fig 4b).

Fillers affect relaxation times as well. Figure 5 shows the Gruneisen parameter which is inversely proportional to the lifetime squared [18]. The figure shows that in the acoustic bands Gruneisen parameter decreases resulting in increase of the relaxation times with the mass ratio. This may be understood in terms of the Fermi Golden rule, which displays a decreasing scattering rate versus mass. The competition between decreasing velocities and increasing relaxation times results in local minima in the thermal conductivity versus mass ratio.

Finally we looked at the off-center parameter. It is known that in some clathrates, the filler atom is unstable at the center of the cage and has a tendency to move to an off-center position [19]. In the simple spring model, this is equivalent to having negative spring constant. A negative spring constant will cause the filler potential to have a double-well shape. If the barrier height between the wells is high compared to the energy of the phonons, then atoms will be trapped in one side of the well randomly. The random alignment of the filler atoms causes disorder scattering for phonons. If the barrier height is small compared to the phonon energy (system temperature), then filler atoms can absorb energy from phonons and jump from one side of the well to the other. In this regime, as we increase the barrier height atoms absorb more energy to pass above the barrier and therefore the thermal conductivity is reduced as the barrier height increases. As the width of the barrier (the distance between the equivalent equilibrium positions) increases, atoms move more to the off center position and scatter more phonons due to their large vibrations and therefore reduce the thermal conductivity. Figure 5 shows the reduction in thermal conductivity in different directions as the negative spring constant is increased.

CONCLUSION

In summary, we simulated the behavior of thermal conductivity of cage-like structures versus filler mean square displacements, its mass and the off-center parameter with a simple model. It was shown that the thermal conductivity decreases as atomic displacement parameter increases, which is a consequence of weaker binding between the filler and the cage. The reduction mainly comes from the reduction in the group velocities. As we increase the filler mass, there are local minima in the thermal conductivity, which are consequences of competition between decreasing group velocities and increasing relaxation times. Furthermore we showed that one can increase the off center parameter by increasing the negative spring constant and creating double well potential. This will result in further reduction of the thermal conductivity.

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REFERENCES


